Synthesis and Characterization of a Catenated Polystyrene−Poly(2-vinylpyridine) Block Copolymer

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ABSTRACT: The synthesis, isolation, and characterization are reported of a polystyrene−poly(2-vinylpyridine) block copolymer "catenane" with a molecular weight of about 10 000 and containing about equal masses of each of the rings. This catenane is prepared by end-to-end coupling of a P2VP dianion lithium salt with 1,4-bis(bromomethylbenzene) in THF in the presence of a PS macrocycle ($M_p = 4500$). The catenane was isolated by precipitation−extraction procedures that were optimized using a 50/50 PS-*b*-P2VP macrocycle as a model for the catenane. The catenane copolymer was characterized by SEC, ^{1}H NMR, and emission (fluorescence) spectroscopy.

Introduction

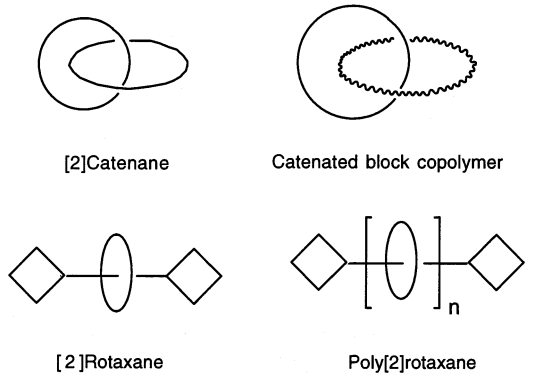
The synthesis of topologically interesting molecules has attracted considerable attention in recently years.[1−10] Structures that cannot be represented without intersecting lines such as rotaxanes,[1,2] polyrotaxanes,[5−10] and catenanes[3−7] are particularly fascinating. The synthesis and study of such compounds frequently reveals interesting information on aspects of molecular architecture and intramolecular interactions and occasionally leads to new materials with unusual properties[7] (Scheme 1).

Catenanes may be synthesized by (a) statistical threading, in which one of the macrocycles is used in large concentrations and threading of the linear precursor is predominantly entropy driven, and (b) template threading, involving an enthalpic driving force such as transition metal coordination, hydrogen bonding, $\pi-\pi$ stacking, and dipolar interactions. The synthesis of low MW (MW ≤ 1000) catenanes was studied intensively over the past few years.[3−6] Thus, Sauvage, Dietrich-Buchecker, and co-workers have developed an efficient synthesis of interlocked rings based on a transition metal mediated template that preposition the coordinating molecular threads leading to interlocked rings after cyclization.[3,4] The extensive work of Stoddart[5] and others has involved hydrogen bonding[7] and aromatic $\pi-\pi$ stacking[6] as the key driving force for the assembly of cyclic structures.

For the case of rotaxanes synthesized by the statistical threading of low MW macrocycles such as crown ethers onto linear polymers the threading efficiency is affected significantly by size and compatibility as demonstrated by Gibson and co-workers.[8−10] Earlier work by Schill et al.[11,12] and Harrison et al.[1] has shown that a ring size of at least 22 atoms is needed to thread polymethylene.

Polymeric catenanes comprised of two polymer rings and held together solely by topological constraints, i.e., lacking a chemical or physical bond between the two rings, should allow relative motions of the two rings that are not possible with linear or macrocyclic polymers. Thus, the intramolecular interactions of the two rings should be site independent so that each part of one of the rings will show the same time-averaged interaction with any part of the other ring. This "homogeneity" of polymer−polymer interactions is absent in pairs of simple linear or macrocyclic polymers. This and other properties make them a unique and fascinating topic of study.

Scheme 1. Topologically Interesting Polymers



Although polymeric [2]catenanes based on DNA have been synthesized, to our knowledge polymer [2]catenanes have not although several attempts have been reported.[13,14] For instance, catenated cycles (perhaps even multiple catenated polymers) may be formed during the synthesis of macrocyclic polymers by end-to-end coupling.[15] However, their isolation from such complicated mixtures is problematic and would involve separating isobaric dimeric macrocycles (formed by one intermolecular and one intramolecular coupling) and the catenane. Thus, the attempted synthesis of polymeric catenanes by the cyclization of polymer-supported linear polyesters in the presence of cyclic polyesters lacked convincing characterization of catenane formation due to difficulties in the separation and isolation.[13]

This is different for catenanes containing two different rings. Thus, threading a narrow MW distribution linear precursor, A, through a previously synthesized narrow distribution macrocycle, B, giving pseudorotaxane, $P_{Lin,A}-P_{cyc\ B}$, followed by end-to-end cyclization (eqs 1 and 2)

$$m\,P_{Lin,A} + n\,P_{cyc\ B} \leftrightarrows P_{Lin,A}-P_{cyc\ B} + (m-1)P_{Lin,A} + (n-1)P_{cyc\ B} \quad (1)$$

$$P_{Lin,A}\text{-cat-}P_{cyc\ B} \rightarrow P_{Cyc,A}\text{-cat-}P_{cyc\ B} \quad (2)$$

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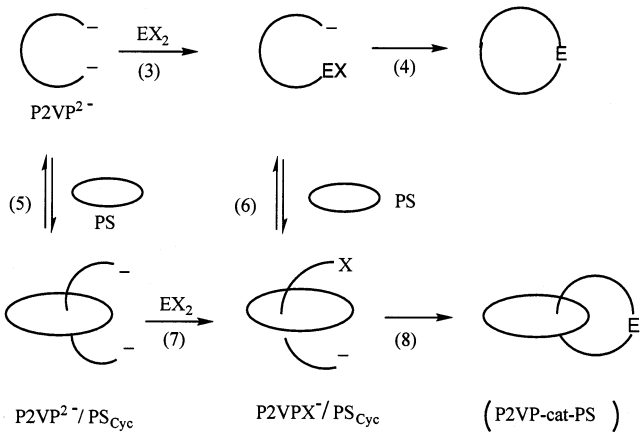
Scheme 2. Synthesis of PS-cat-P2VP by End-to-End Coupling



would give a block copolymer catenane. At least in principle, this block copolymer may be separated from each of the A and B rings and its formation is sufficient to demonstrate the formation of the $P_{Cyc,A}$-cat-$P_{Cyc,B}$ block copolymer.

The enthalpy of the threading equilibrium (eq 1) of linear precursors $P_{L,A}$ with macrocycles, $P_{C,B}$, should be positive due to the incompatibility of the coils.[3−10] Thus, although the ring closure of $P_{Lin,A}$ is carried out under high dilution conditions ($[P_{Lin,A}] = 10^{-4}-10^{-6}$ M), the equilibrium is shifted toward the "threaded state" ($P_{Lin,A}$-cat-$P_{Cyc,B}$) by keeping the concentration ($[P_{Cyc,B}]$) of the precursor macrocycle high. The catenane is then formed by covalent and thus irreversible end-to-end coupling of the $P_{Lin,A}$-cat-$P_{Cyc,B}$ (eq 2).

This approach is illustrated in Scheme 2 for the end-to-end cyclization of poly(2-vinylpyridine) dilithium in the presence of purified cyclic polystyrene.[16] Thus, the electron transfer initiated anionic polymerization of 2-vinylpyridine produces a P2 VP dianion that is relatively stable even at room temperature.[17] In the presence of a suitably sized polystyrene macrocycle this dianion precursor is trapped (Scheme 2, eqs 5 and 6) and cyclized intramolecularly with a coupling agent (EX_2) such as 1,4-bis(bromomethylbenzene) (DBX) to produce a $P_{Cyc,A}$-cat-$P_{Cyc,B}$ catenane (eq 8).

In this case, the problem of isolation of the purified catenated P2VP−PS block copolymer (P2VP-cat-PS) is reduced to finding the conditions necessary to separate it from the P2VP homopolymer cycles and higher MW cyclic and linear P2VP and uncatenated cyclic PS.[18] As living P2VP anion is unreactive toward PS,[17] the demonstration of a block copolymer with a MW that is roughly twice that of the precursors is sufficient to confirm the formation of the catenane. Although the synthesis and characterization of cyclic polymers are well-known,[19−32] the isolation and characterization of a cyclic PS-*b*-P2VP block copolymer was reported recently.[33−35]

Experimental Section

Materials. The synthesis, isolation, and characterization of macrocyclic PS homopolymers[25] and of linear and macrocyclic PS-*b*-P2VP[34] have been described. The coupling agent, 1,4-bis(bromomethylbenzene) (DBX) (TCI America, Inc., 99%), was recrystallized three times in $CHCl_3$ and dried in a vacuum oven at 45 °C for 24 h and then on a high-vacuum line (10^{-5} Torr) overnight. A macrocyclic block copolymer PS-*b*-P2VP (50/50) (MW = 13 000) prepared previously was used as a model with regard to the separation of PS-cat-P2VP from the homopolymers.[34]

Table 1. Characterization of Linear and Macrocyclic PS-*b*-P2VP and PS-cat-P2VP and Corresponding Homopolymers

sample	M_p[a]	M_w/M_n[a]	I_{em}[c]	PS (%)[d]
cyclic PS	3600[b]	1.12	200	
linear PS	4500	1.10	100	
cyclic PS-*b*-P2VP	4600[b]	1.30	16	55
cyclic PS-*b*-P2VP	9500[b]	1.32		47
linear PS-*b*-P2VP	5700	1.14	8	55
PS-cat-P2VP	10300	1.30	4	46[e]
cyclic P2VP	4400[b]	1.15	0.10	
linear P2VP	5500	1.15	0.10	

[a] Molecular weights and MW distributions determined by SEC. [b] SEC apparent peak molecular weight of the cyclic polymer which is 20−30% below that of the matching linear polymer. [c] Relative fluorescence intensity at 333 nm (excimer emission). [d] PS composition (mol %) in the block copolymers determined by NMR. [e] Calculated value is 45%.

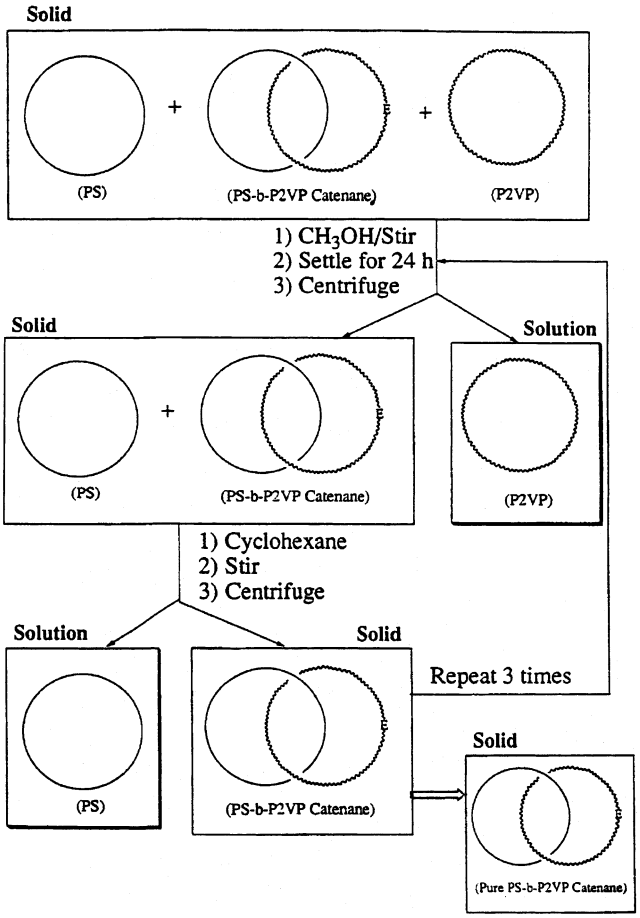
Synthesis. Fifty milliters of THF was distilled in vacuo from a diphenylmethyllithium THF solution into a 250 mL vessel. A few drops of lithium naphthalide/THF solution (0.09 M) were slowly added, and the solution turned green, indicating the absence of impurities. After introduction of an additional 0.40 mmol of lithium naphthalide, 2.0 g (1.90×10^{-2} mol) of 2-VP was distilled into the reactor over a period of about 1 h, and a small portion (5 mL) of the solution (linear precursor) was separated and reacted with methanol (0.50 mL) to give the matching P2VP precursor. The remainder of the solution was sequestered into an ampule (with a break-seal) attached to the apparatus. The cyclization of the P2VP dianion with purified DBX was carried out at room temperature (25 °C) by the simultaneous addition of the $P2VPLi_2$ (1.71×10^{-2} mol in 45 mL of THF) and 50 mg of DBX (0.19 mmol in 50 mL of THF) to 2 g of macrocyclic PS dissolved in about 50 mL of purified THF as described earlier.[24,25] The addition of equivalent amounts of living P2VP anions and DBX was carefully controlled so as to maintain a slight excess of the P2VP anion ($10^{-6}-10^{-4}$ M) as seen by a light red color. The final reaction mixture was concentrated in vacuo, precipitated in hexane, filtered, and dried in a vacuum oven overnight.

The macrocyclic and matching linear PS-*b*-P2VP block copolymers with similar degrees of polymerization as the PS-cat-P2VP were synthesized by the lithium naphthalide initiated sequential polymerization of styrene and 2-vinylpyridine followed by the end-to-end coupling with DBX as described earlier (Table 1).[34]

Isolation. To optimize conditions for the separation of the PS-cat-P2VP from the corresponding macrocyclic PS and P2VP, mixtures of 10 mg each of macrocyclic PS ($M_p = 3600$), macrocyclic P2VP ($M_p = 4400$), and a macrocyclic PS-*b*-P2VP block copolymer[34] with similar MW (apparent $M_p = 9500$; PS content of 47 wt %) and composition as the catenane dissolved in 15 mL of THF were used as model blends (Table 1). The attempted fractionation of this solution by adding of this solution (15 mL) to 200 mL cyclohexane or methanol gave stable emulsions, which could not be separated by centrifuging or prolonged settling.

An alternative separation method based on extraction was more successful (Scheme 3). Thus, methanol (90 mL) was added to the dried crude reaction product in order to remove the P2VP homopolymers. The resulting suspension was stirred and cooled to −20 °C and kept for 24 h and centrifuged. After decanting the clear supernatant solution, the solid polymer was filtered and dried overnight in vacuo, after which it was dispersed in 90 mL of cyclohexane. The resulting suspension was centrifuged and filtered, and the solid remaining after evaporation was vacuum-dried overnight and extracted six times alternately by 20 mL portions of methanol and cyclohexane, at which point the remaining solid dissolved neither in methanol nor in cyclohexane.

Scheme 3. Separation of PS-cat-P2VP from PS and P2VP Homopolymers



The SEC of the remaining solid indicated the absence of the PS or P2VP macrocycles and only showed the peak of the macrocyclic block copolymer. A similar extraction method was also previously used by Agam and co-workers during their pioneering synthetic work on oligomeric polyrotaxanes from crown ethers and oligo(ethylene glycols).[36]

Characterization. Proton NMR was performed on a Bruker model AM-250 MHz FT-NMR in deuterated chloroform. Fluorescence was carried out on a Perkin-Elmer LS-5 fluorescence spectrophotometer under an argon atmosphere. Emission spectra of 0.10 g/L in THF were recorded from 265 to 480 nm using an excitation wavelength of 258 nm. The emission intensities of all samples were measured at one time to avoid fluctuations in detector response. Each measurement was repeated 2−3 times. The wavelength reproducibility was found to be within 1 nm. SEC characterization was carried out at 35 °C on a Waters model 6000A HPLC pump and model U6K injector using THF containing 1% triethylamine at a flow rate of 1 mL/min and PS standards for calibration using both a Waters LC-75 UV detector (set at 268 nm) and a Perkin-Elmer LC-30 RI detector. Column packings were 10 μm with pore sizes of 500 and 10 000 Å, and the linear response MW range was 100−500 000.

Results and Discussion

The polystyrene (PS)-*b*-poly(2-vinylpyridine) catenane (PS-cat-P2VP) with a MW of about 10 000 was synthesized by the DBX mediated end-to-end coupling of a P2VP dianion lithium salt ($P2VPLi_2$, M_p of 55) at about 10^{-5} M in the presence of macrocyclic PS[15] having about the same mass as the P2VP cycle (Table 1, Scheme 2). The alternative approach involving the end-to-end cyclization of a PS dianion in the presence of a macrocyclic P2VP is doomed to failure because of side reactions.[17,35]

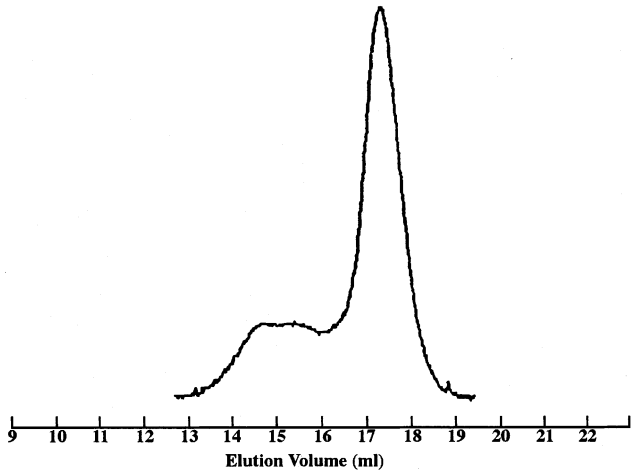


Figure 1. SEC of unfractionated reaction product of the catenation reaction of macrocyclic PS with the P2VP dianion.

The MW of the PS cycle (M_p = 4500 corresponding to a 90-carbon ring) should be large enough for the intended "threading" of the P2VP chain and relatively convenient to prepare in relatively large quantities.[25] As THF is a good solvent for PS, no extensive entanglements or knotting is anticipated.[21] Although the PS ring may be large enough to accommodate more than one threaded P2VP ring, excluded-volume considerations make such highly crowded arrangements improbable. Furthermore, the formation of such catenanes is readily detected by proton NMR of the catenane block copolymer. This process should produce a mixture of a PS-cat-P2VP, an unthreaded well-defined PS macrocycle, and the crude P2VP macrocycle consisting of a mixture of unimer, dimer, and higher MW cycles and linear P2VP, especially for the higher MW "polycondensates".[18] The anticipated low catenation yield may be increased by keeping the concentrations of the PS macrocycle and P2VP dianion as high as practical ($\sim 10^{-2}$ M).

The isolation−characterization of the PS−P2VP catenane is the key and most challenging objective of this research. This involves separating the PS-cat-P2VP from the PS and P2VP macrocycles as well as the higher MW P2VP polycondensates. The formation of low MW living $P2VPLi_2$ in the presence of a high MW polystyrene and SEC analysis of the reaction product confirmed no grafting of the P2VP onto the PS.[17,34] SEC analysis of the crude catenation mixture showed that the remaining noncatenated PS and P2VP cycles elute at about the same volume (about 17.2 mL) (Figure 1). The SEC of the PS-cat-P2VP should be similar to that of the dimeric P2VP cycle and elute around 16 mL. The higher MW P2VP multiple cycle "polycondensation" products elute at lower elution volumes.

The isolation of the 50/50 PS-cat-P2VP from its blend with PS and P2VP macrocycles is possible, at least in principle, as it is the only PS−P2VP block copolymer in the mixture. Thus, PS-cat-P2VP should be insoluble in either methanol or alkanes due to the pronounced insolubility of PS and P2VP, respectively, in these solvents. The extraction techniques needed to separate the PS-cat-P2VP from the reaction mixture were optimized by studying the separation of a more easily synthesized macrocyclic PS−P2VP block copolymer (M_p = 9500, PS% = 47%) from the corresponding PS (M_p = 3600) and P2VP (M_p = 4400) macrocycles (Experimental Section). This macrocyclic block copolymer with similar MW and composition as the catenane block copolymer

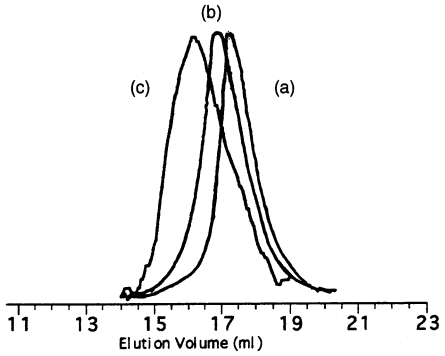


Figure 2. SEC chromatograms of (a) cyclic PS, (b) cyclic PS-*b*-P2VP (M_p = 4600), and (c) PS-cat-P2VP in THF (Table 1).

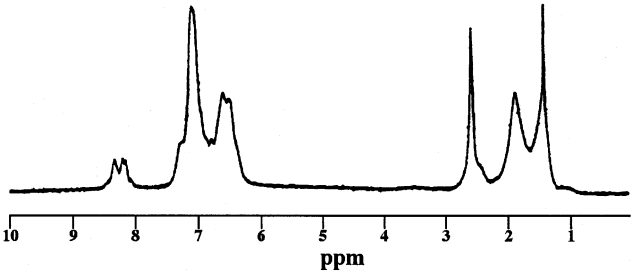


Figure 3. Proton NMR (250 MHz) of P2VP-cat-PS in deuterated chloroform.

target was synthesized by the lithium naphthalide initiated sequential block copolymerization of styrene and 2-vinylpyridine at −78 °C followed by the end-to-end coupling with DBX (Table 1).[34]

Analysis by SEC and NMR showed that the cyclohexane extracts contained only cyclic PS while the methanol extracts contained only the cyclic and higher MW P2VP "polycondensate". The mass of the remaining purified product was 20 mg, corresponding to a yield of 0.5%. Like the macrocyclic block copolymer (Experimental Section), this polymer was not soluble in either cyclohexane or methanol.

The SEC chromatogram of this solid showed a relatively narrow MW distribution polymer (M_w/M_n = 1.3), the apparent peak molecular weight (M_p = 10 000) of which approximately equals the sum of the molecular weights of the macrocyclic PS and P2VP cycles consistent with a 1:1 catenane (Figure 2). The MW distribution is a little wider than that of the precursors, and the presence of some cyclic PS or P2VP precursor contamination (<10−20%) cannot be excluded, but this contamination is probably not significant as there is no clear SEC shoulder in the low MW region. The apparent MW of the PS-cat-P2VP is a little larger than the sum of the PS and P2VP precursor cycles. It is not clear whether this is due to lower MW catenanes having been removed by extraction or to an increased spatial separation of the two rings due to their incompatiblility.

The composition of the polymer was confirmed by NMR integration of the H-6 resonance (δ = 8.25 ppm) of P2VP relative to the aromatic resonance of PS (δ = 6.3−7.3 ppm) and that of H_3-H_5 of P2VP (δ = 6.3−7.4 ppm) (Figure 3). The NMR spectra of macrocyclic PS, P2VP, and that of the low MW macrocyclic PS-*b*-P2VP block copolymer of Table 1 are shown for comparison in Figures 4 and 5 of the Supporting Information. The PS content (46%), calculated from the NMR data, agrees well with that (45%) obtained from the SEC MW data and confirms the formation of a 1:1 PS−P2VP catenane. Multiple catenation of the PS rings could not be detected. The SEC and NMR data of the PS-cat-P2VP, the linear and cyclic PS and P2VP samples, and the macrocyclic PS-*b*-P2VP are summarized in Table 1.

Fluorescence Studies. Since PS, in contrast to P2VP, exhibits strong excimer emission, a fluorescence study of linear, cyclic, and catenated PS−P2VP block copolymers was performed. Low polymer concentrations ([styrene units] = 10^{-3} M) were used, avoiding intermolecular energy transfer from PS to P2VP.[37−39] The polystyrene excimer fluorescence band at about 333 nm confirmed the presence of the PS in the PS-cat-P2VP. As expected and as shown in Table 1, its emission and that of the cyclic and matching linear PS-*b*-P2VP block copolymers are much greater than that of the cyclic P2VP as P2VP is a weak emitter.[37,40] The excimer emissions of the PS block in the linear and macrocyclic and catenated PS−P2VP block copolymer are significantly lower than that of the linear and cyclic PS homopolymers, consistent with the intramolecular quenching of PS emission by P2VP (see below). Also, the emission of the PS-*b*-P2VP macrocycle is roughly double that of linear PS-*b*-P2VP of the same MW and composition. This enhanced emission of cyclic compared to linear PS has been documented.[41]

However, the PS emission of the PS-cat-P2VP catenane is about half that of linear PS-*b*-P2VP and one-fourth of the cyclic PS-*b*-P2VP of virtually the same composition. The observations were reproducible, and the very low emission intensity of the PS-cat-P2VP would appear to be consistent with its unusual topology. Thus, in contrast to the other two block copolymers, all PS segments of the PS-cat-P2VP block copolymer have equal and conformationally unrestricted access to all segments of the PS cycle, resulting in highly efficient intramolecular quenching of PS excimer emission. This is not the case for the linear and especially for the macrocyclic block copolymer. In this case, the efficient intramolecular quenching of the styrene units is impeded by the conformational restraints inherent in these small, relatively rigid cycles that typically have glass transition temperatures that are well below that of the matching linear polymers of the same MW.[25]

In conclusion, the end-to-end cyclization of a P2VP dianion with a MW of about 5000 in the presence of a PS cycle of about the same MW yields a P2VP−PS catenane, as supported by SEC, NMR, and fluorescence measurements.

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Supporting Information Available: Proton NMR spectra of PS, P2VP, and PS-*b*-P2VP in $CDCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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