2626 *Macromolecules* **2005,** *38,* 2626−2637

Syntheses and Model Complexation Studies of Well-Defined Crown Terminated Polymers

Harry W. Gibson,[*,†] Zhongxin Ge,[†] Feihe Huang,[†] Jason W. Jones,[†,‡] Hervé Lefebvre,[†,§] Matthew J. Vergne,[||] and David M. Hercules[||]

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, and Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

Received October 22, 2004; Revised Manuscript Received January 13, 2005

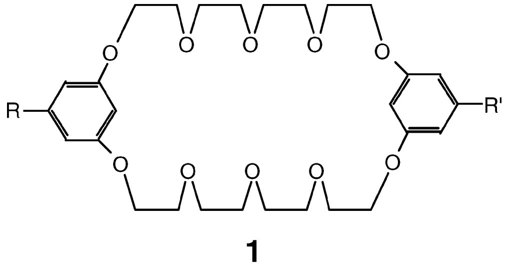
ABSTRACT: A TEMPO-based free radical initiator (**4a**) containing a dibenzo-24-crown-8 (DB24C8, **2a**) moiety was synthesized. A similar initiator (**4b**) based on bis(*m*-phenylene)-32-crown-10 (BMP32C10, **1b**) was also synthesized. The crown-based initiators were used to prepare crown ether terminated polystyrenes of narrow molecular weight distribution (PDI). The DB24C8-terminated polymer **5** was demonstrated to form a pseudorotaxane complex (**18**) with dibenzylammonium hexafluorophosphate (**17**), but because of its small cavity, **5** cannot complex bulky *N,N*′-dialkyl-4,4′-bipyridinium (paraquat or viologen) salts. On the other hand, the BMP32C10-terminated polymer **11** complexed *N,N*′-bis(*p-tert*-butylbenzyl)-4,4′-pyridinium bis(hexafluorophosphate (paraquat salt, **23**) strongly, but did not interact with dibenzylammonium hexafluorophosphate (**17**) to a detectable extent. Therefore, these new polymeric hosts are capable macromolecular building blocks for supramacromolecular chemistry using pseudorotaxane complexation, and furthermore, both show selectivity; the DB24C8 polymer is selective for secondary ammonium ion complexation, and the BMP32C20 polymer is highly selective for paraquat recognition. Future work will involve application of these new functional polymers to preparation of star, graft, and block structures by self-assembly.

Introduction

Crown ethers are an important class of compounds that undergo complexation with metal ions[1] and other species, in some cases leading to the formation of threaded structures known as pseudorotaxanes and rotaxanes.[2] Polymers containing small crown ethers, most commonly 18-membered rings, were known as early as 1970, mainly for study of cation binding.[3]

The convergence of polymer and supramolecular sciences offers great opportunity for new materials with unique properties and novel practical applications. We have utilized crown ethers to synthesize a variety of polypseudorotaxanes and polyrotaxanes (Scheme 1).[2,4−15] By carrying out step-growth polymerizations in the presence of unfunctionalized crown ethers, main chain polyester[4,5] and polyurethane[6,7] pseudorotaxanes of type A (Scheme 1) were prepared. By use of bulky monomers in step-growth polymerizations in the presence of unsubstituted crown ethers, as exemplified by the preparation of poly(ester rotaxane)s[8,9] and poly(urethane rotaxane)s,[10] polyrotaxanes of type B resulted. Poly(styrene rotaxane)s[11] and poly(acrylonitrile rotaxane)s[12] of types A and B resulted from chain-growth polymerizations. Main chain poly(acrylate rotaxane)s and poly(methyl methacrylate rotaxane)s of type A were also prepared using free radical polymerization.[13] Polymerization of suitable methacrylate monomers in the presence of unsubstituted crown ethers also yielded side chain polyrotaxanes of type D.[13] Side chain pseudorotaxane polymers of type C have been investigated in our laboratories,[14] as well as main chain pseudorotaxane polymers of type E.[15] Other investigators have also prepared such topologically interesting systems. [2,16]

Reaction of poly(methacryloyl chloride) with 5-hydroxymethyl-1,3-phenylene-1′,3′-phenylene-32-crown-10 (**1a**) resulted in highly branched or cross-linked polymers of type F, depending on the solvent and concentrations, as a result of self-association of the crown ether via hydrogen bonding and subsequent self-threading of the crown ether moieties,[17] as did other polymerizations of hydroxy- or carboxy-functionalized macrocyclic monomers.[18−20]



1

a. R = CH_2OH, R' = H
b. R = H, R' = H
c. R = R' = CH_2OH

Recently there has been increasing interest in supramolecular polymerization, the self-assembly of macromolecular species consisting of *small repeat units* bound together through noncovalent bonding. Self-complementary hydrogen bonding units have proven to be very effective.[21] And in our laboratory we have

---

[†] Virginia Polytechnic Institute and State University.

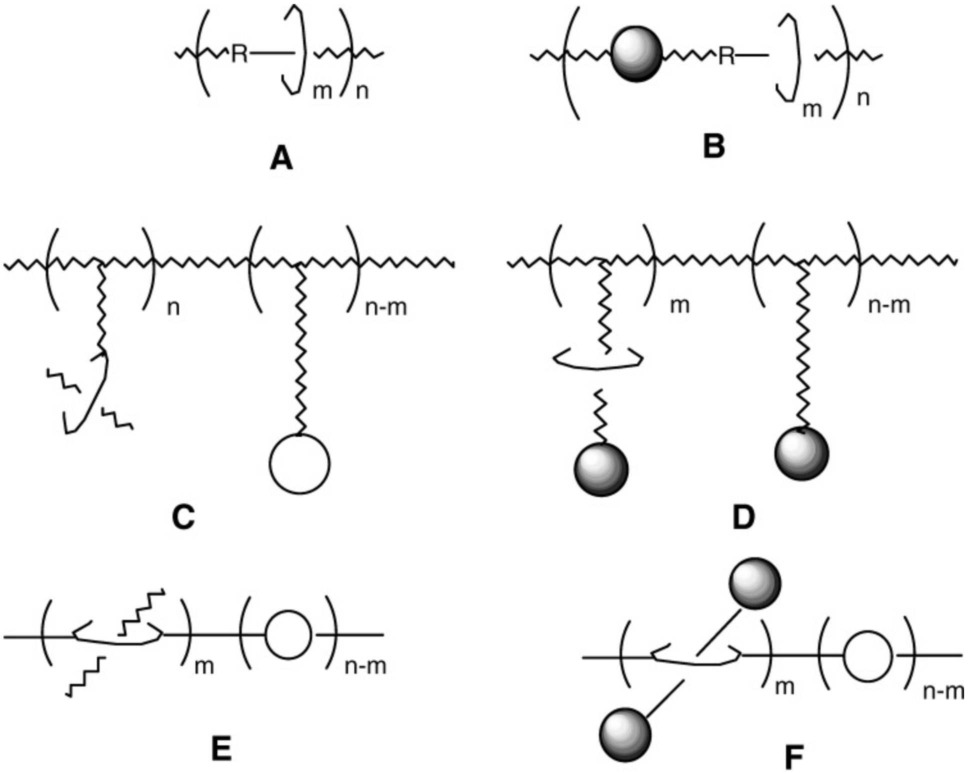
[‡] Present address: E. I. duPont de Nemours and Company, Jackson Laboratory, Deepwater, NJ 08023.

[§] Present address: Laboratoire de Synthese Macromoleculaire-UMR 7610 4, Université Pierre & Marie Curie, Place Jussieu/boite 184 75252 Paris, Cedex 05, France.

[||] Vanderbilt University.

10.1021/ma047811y CCC: $30.25

Scheme 1. Cartoon Representations of Various Types of Polypseudorotaxanes (A, C, E) and Polyrotaxanes (B, D, F)[a]



[a] A, B, E, and F are main chain systems and C and D are side chain systems. Circles and ellipses represent cyclic species; straight or wiggly lines represent linear components. Filled circles represent bulky "stoppers" that prevent dethreading of the cyclic component from the linear.

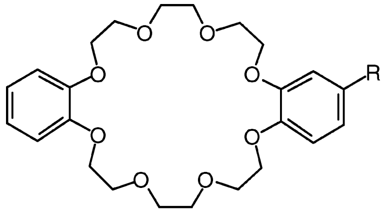
successfully produced noncovalent polymers using pseudorotaxane formation, starting from heteroditopic (AB) monomers[22] and pairs of homoditopic (AA, BB) monomers.[23] Likewise we used pseudorotaxane complexation in the self-assembly of dendrimers.[24]

The efficiency of these systems prompted us to consider application of these molecular recognition protocols to suitably *functionalized polymers* with the objective of reversibly and controllably producing large assemblies of macromolecules of designed shapes, functionalities and properties. Other efforts in this area have utilized self-complementary hydrogen bonding units,[21] hydrophilic−hydrophobic and amphiphilic interactions,[25] and metal complexation.[26] We have chosen to explore the pseudorotaxane motif because it offers the possibility of selectivity in complexation processes based on complementarity of sizes and binding site geometries of the host and guest moieties. The present article describes some of our efforts in this area.

Results and Discussion

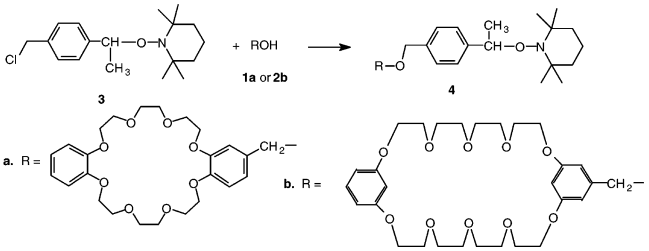
With the ultimate aim of producing noncovalent analogues of block and graft copolymers, our efforts focused on preparation of end-functionalized polymers with narrow molecular weight distributions or polydispersities. As the first examples, crown-terminated polymers were targeted. The self-assembly process to form pseudorotaxanes from dibenzo-24-crown-8 (DB24C8, **2a**) and secondary ammonium salts is a well-established paradigm[2,27] and one with which we are quite familiar.[14,23,24,28] Likewise the larger bis(*m*-phenylene)-32-crown-10 (BMP32C10, **1b**), its derivatives and para-analogues have long been known to complex both secondary ammonium salts[2,27] and 4,4′-bipyridinium salts (“paraquats” or “viologens”)[2,29] and we are experienced with these protocols as well.[6c,15,22,30−34] Thus, we chose DB24C8 and BMP32C10 as the initial hosts for these studies.

The preparation of polystyrene by stable free radical polymerization (SFRP) is well studied using tetramethylpiperidine-*N*-oxide (TEMPO) derived initiators and related systems.[35] Hence, proper incorporation of crown ether moieties into TEMPO initiators offers a means of introducing these host moieties efficiently and selectively at the chain ends, while controlling the molecular weight distributions so as ultimately to produce phase separated morphologies in the resulting self-assembled copolymers.

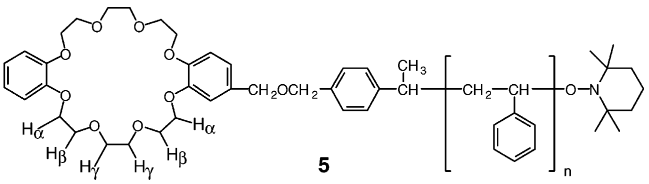


2
a. R = H
b. R = CH_2OH

A. Crown Ether—TEMPO Derivatives. The preparation of the DB24C8-TEMPO initiator **4a** from the known vinylbenzyl chloride derivative **3**[36] and crown ether alcohol **2b**[24] was straightforward via the Williamson ether synthesis. Likewise BMP32C10-TEMPO derivative **4b** was prepared from **3** and alcohol **1a**.[37]



B. Crown Ether Terminated Polystyrenes. 1. DB24C8-Terminated Polystyrene 5. Application of the DB24C8-TEMPO initiator **4a** to bulk polymerization of styrene was designed to produce relatively low molecular weight polymers whose complexation could readily be studied by NMR spectroscopy. Several runs were carried out. For example, DB24C8-terminated polymer **5** of molecular weight ~1500 was successfully prepared; it had $M_n = 1.38$ kg/mol and $M_w = 1.82$ kg/mol (polydispersity = PDI = 1.32) by GPC analysis. Another sample was targeted for a molecular weight of ca. 3 kg/mol; ^{1}H NMR indicated $M_n = 3.14$ kg/mol and GPC analysis yielded $M_n = 3.19$ $M_w = 3.27$, PDI = 1.03. Therefore, end group analysis confirmed that the polymer was ~100% terminated with DB24C8 units and molecular weight control was observed.



5

Corroborating MALDI−TOF mass spectrometric results for the sample of **5** with $M_n = 1.39$ kg/mol in 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol)/sodium iodide are shown in Figure 1. Sodium iodide ionization produced better mass spectra than ionization with silver trifluoroacetate (AgTFA), a commonly employed ionization agent for polystyrene.[38] The affinity of **5** for sodium ionization is evidenced by the fact that even in the presence of AgTFA the sodium adducts appeared at about the same intensity as the silver adducts. The average molecular weight, as judged by the maximum intensity peak at *m/z* 1658 offset by peaks in the low *m/z* region, was consistent with the GPC results.

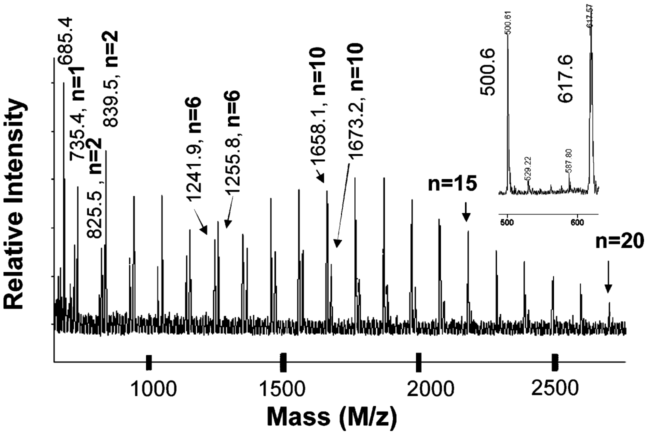
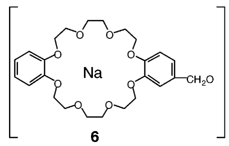
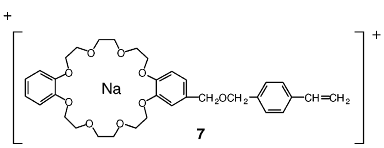


Figure 1. MALDI−TOF mass spectrum of DB24C8-terminated polystyrene **5** (GPC: $M_n = 1.39$ kg/mol and PDI = 1.32) in dithranol/NaI. In the inset at *m/z*, 500.6 and 617.6 correspond to crown end group fragments **6** and **7** as sodium adducts, as described in the text. The small *m/z* 631.5 signal corresponds to **8**. The *m/z* 685.4 peak is due to (**5**, $n = 1$ − TEMPO − CH_2)$^+$ = **9**. The rest of the spectrum consists of pairs of peaks due to (**5** − H − TEMPO + Na)$^+$ = **10a** and (**5** − TEMPO + CH_2 + Na)$^+$ = **10b**; *n* values are indicated for some of the pairs.

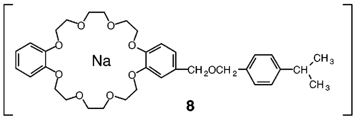
In the low molecular weight region (inset, Figure 1), the sodium adduct of the crown ether benzyloxy fragment (**6**) was observed at *m/z* 500.6. The sodium adduct of the crown ether initiator moiety (**7**) was observed at *m/z* 617.6. No other significant peaks were observed below *m/z* 500. The small *m/z* 631.5 peak corresponds to sodium adduct **8**. Also observed was a signal at *m/z* 685.4, assigned to **9**. Formation mechanisms for **7**, **8**, and **9** are proposed in Scheme 2.



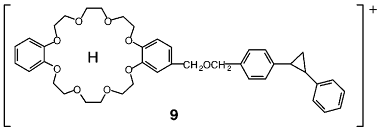
6



7

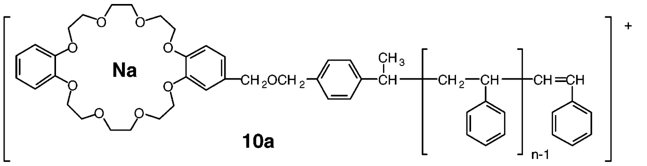


8

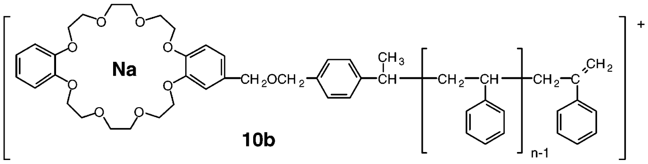


9

The higher mass region (*m/z* > 700) of the spectrum (Figure 1) contains pairs of peaks separated from each other by 14 mass units. The sequential pairs of peaks are separated by 104 mass units, corresponding to the styryl repeat unit. Two types of sodium adducts are observed: (1) the polymer after loss of a TEMPO moiety (mass 156) and a hydrogen, presumably as *N*-hydroxytetramethylpiperidine (path A, Scheme 3), for a net mass change of −134, and (2) the polymer after loss of the TEMPO group and addition of a methylene group (i.e., loss of a benzylic end group), probably via the fragmentation pathway shown in path B, Scheme 3, for a net mass change of −120. Thus, the lower mass signal in each pair corresponds to **10a**, while the higher mass signal corresponds to **10b**, for a mass difference of 14. For example, the signal at *m/z* 1449.95 is **10a**, $n = 8$ and that at *m/z* 1464.00 is **10b**, $n = 8$. It interesting that **10a** predominates for $n < 5$ and **10b** predominates for $n \geq 5$. In agreement with the report of Vairon et al.[38b] using this same matrix and a similar molecular weight polymer, the TEMPO end group was not observed.

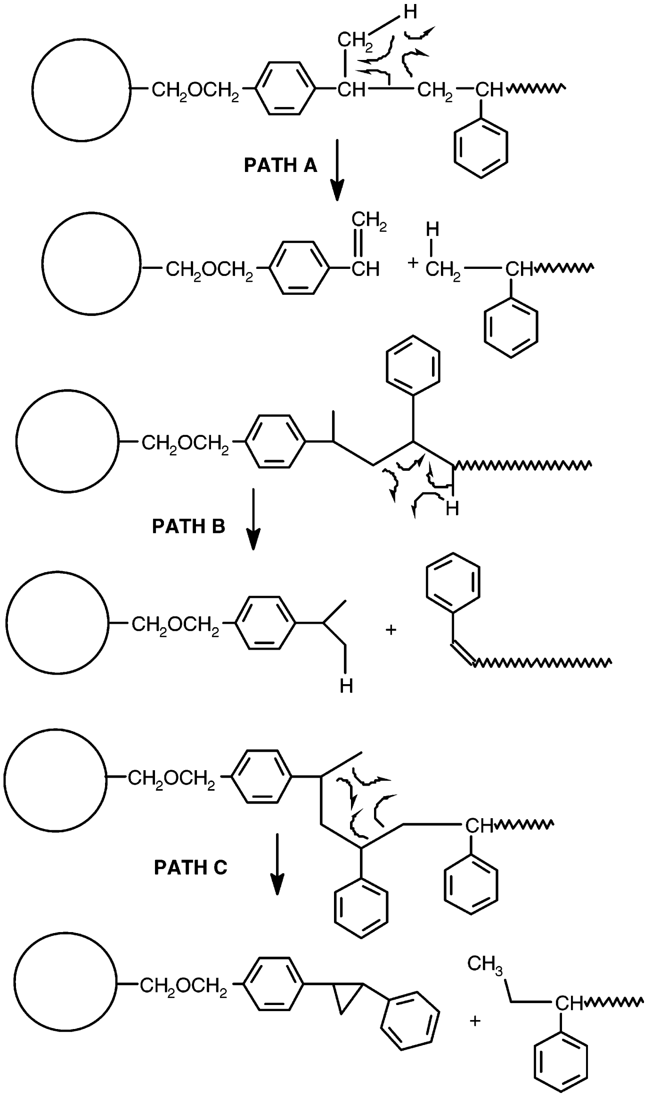


10a



10b

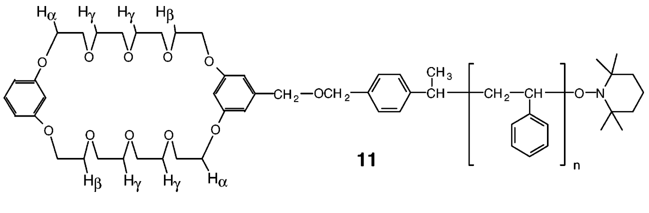
Scheme 2. Proposed Mechanisms for Formation of Crown-Based Fragements from End-Functionalized Polymers 5 and 11[a]



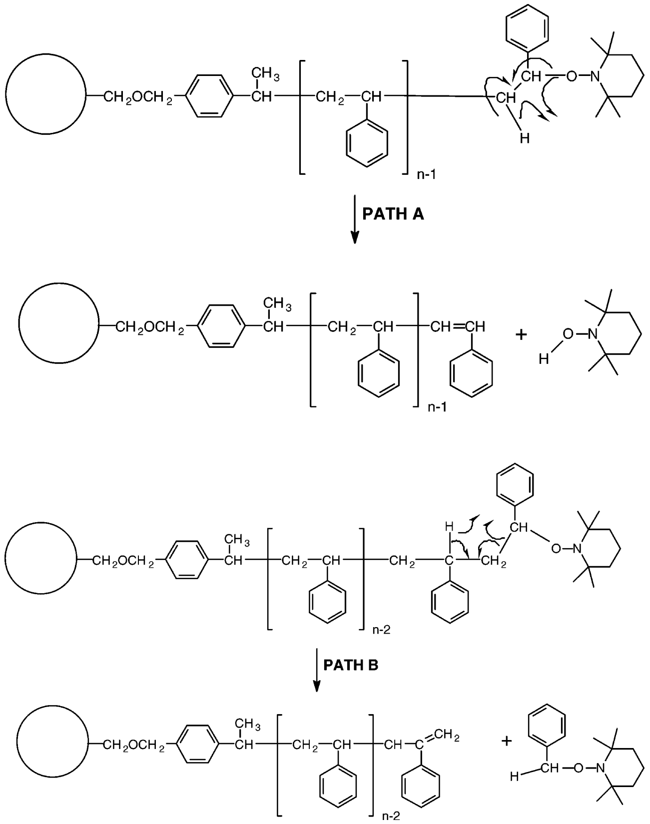
[a] From Polymers **5** and **11**, path A yields **7** and **13/14**, respectively. From polymers **5** and **11**, path B yields **8** and **15**, respectively. From polymer **5**, path C yields **9**.

However, Figure 2 contains a MALDI mass spectrum obtained from a sample resulting from evaporation of an acetone solution. Here the major signals are due to the protonated polymer, i.e., $(\mathbf{5} + H)^+$, and the minor signals are attributable to the sodium adducts $(\mathbf{5} + Na)^+$. The largest signal at *m/z* 2002, $n = 12$, corresponds reasonably well to $M_n = 2080$ determined by GPC. Here the TEMPO end groups are clearly observed.

2. BMP32C10–Terminated Polystyrene 11. Application of BMP32C10 initiator **4b** in the bulk SFRP of styrene yielded BMP32C10-terminated polystyrene **11**. The molecular weight was again controlled so the sample's ability to complex guests could be evaluated easily by ^{1}H NMR spectroscopy. For a representative sample we found $M_n = 4.52$ kg/mol and $M_w = 4.83$ kg/mol (PDI 1.07) by GPC analysis.


11

Scheme 3. Proposed Fragmentation Patterns for TEMPO End Groups of Polystyryl Crown Ethers[a]



[a] **5** yields **10a** via path A and **10b** via path B. Analogously **11** yields **16a** and **16b**.

MALDI–TOF mass spectrometric results for this sample of **11** in 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol)/sodium iodide (Figure 3) are analogous to those for analogue **5**. In the low mass region of the spectrum fragments due to the crown-initiator moiety are found (Figure 3a). Signals at *m/z* 551, 590, 686, 707, and 720 (not shown; see Supporting Information) correspond to crown end group fragments, i.e., **12a**, **12b**,

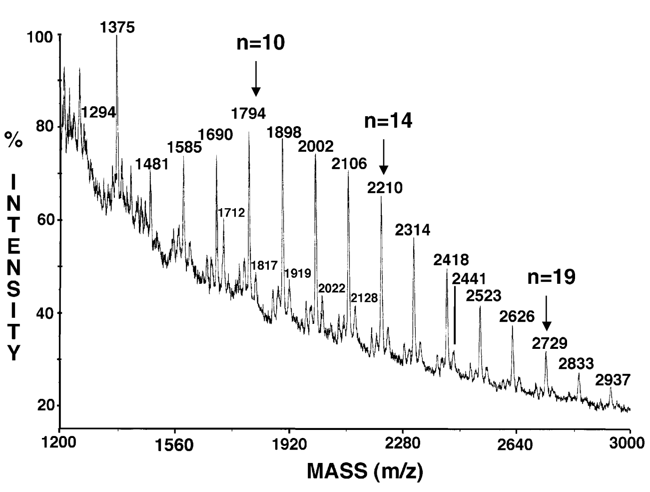


Figure 2. MALDI–TOF mass spectrum of DB24C8-terminated polystyrene **5** (GPC: $M_n = 2.08$ kg/mol and PDI = 1.23) from evaporated acetone solution. The major signals are due to $(\mathbf{5} + H)^+$ and the minor signals are due to $(\mathbf{5} + Na)^+$; *n* values are indicated for some of the pairs.

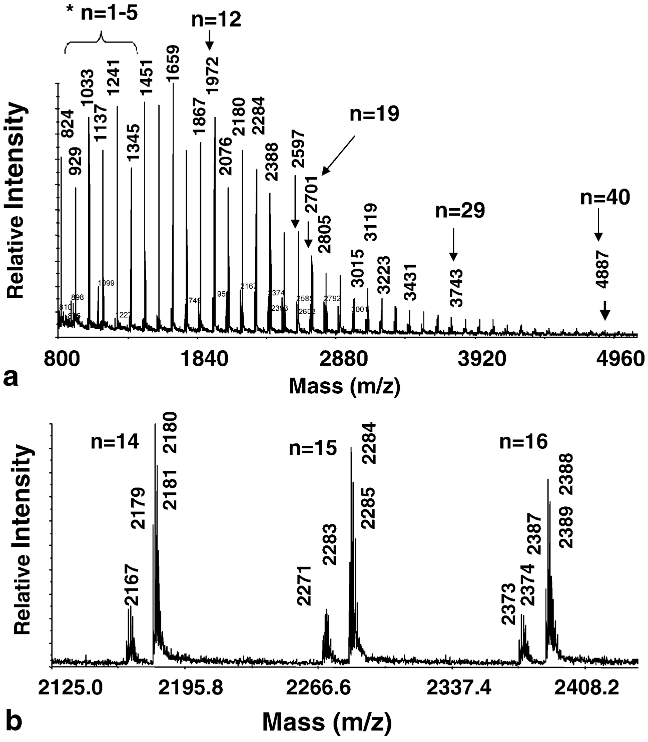
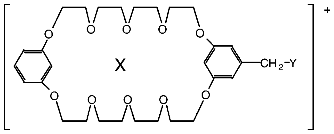
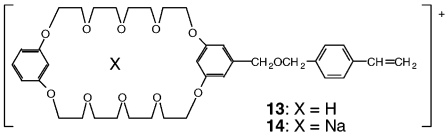


Figure 3. MALDI−TOF mass spectrum of BMP32C10-terminated polystyrene **11** (GPC: $M_n = 4.52$ kg/mol and PDI = 1.07) in dithranol/NaI. (a) *m/z* 800−5000; two distributions are observed. In the mid-mass region the signals at *m/z* 824, 929, 1033, 1137, 1241, and 1345 are attributed to the intact polymers after loss of a methyl group, $(\mathbf{11} - CH_3)^+$ for $n = 0-5$, labeled with ∗, respectively. The rest of the spectrum consists of pairs of peaks corresponding to the sodium adducts $(\mathbf{11} - \text{TEMPO} + CH_2 + Na)^+ = \mathbf{16b}$ and $(\mathbf{11} - \text{TEMPO} + Na)^+ = \mathbf{16a}$; n values are indicated for some of the pairs. The former signals dominate. (b) Expanded view of the pairs of clusters in the range $n = 14-16$. Not shown are strong signals at *m/z* 550, 686, 707 and 720, attributable to $(\text{crown-}CH_2)^+$ (**15**), $(\text{crown-initiator} + H)^+$ (**13**), $(\text{crown-initiator} + H + Na)^+$ (**14**) and $(\text{crown-initiator} + CH_2 + Na)^+$ (**12**), as described in the text; see Supporting Information.

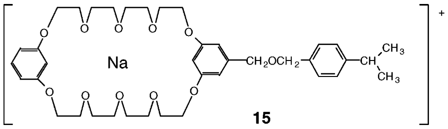
13, **14** and **15**, respectively; proposed mechanisms for formation of **13**−**15** are shown in Scheme 2.



12 **a.** X = H, Y = nil
b. X = Na, Y = O

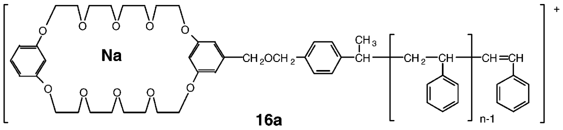


13: X = H
14: X = Na

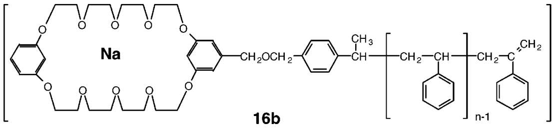


15

In the middle region the signals at *m/z* 824, 929, 1033, 1137, 1241, and 1345 are attributed to the intact oligomers after loss of a methyl group, $(\mathbf{11} - CH_3)^+$ for $n = 0-5$; this process can be attributed to α-elimination from the piperidine moiety, as observed frequently with amines.[39] In the higher mass region (*m/z* > 1345, Figure 3a) the spectrum contains two series of peaks; the pairs of peaks are separated by 104 mass units, the repeat unit of the polystyrene backbone. Within each pair of peaks the two signals are separated by *m/z* 14 as in the spectrum of polymer **5**; here, though, the major signal corresponds to the higher mass species. The lower mass species are attributed to sodium adducts of the fragments with benzylidene end groups, i.e., **16a**, and the higher mass species are due to sodium adducts of the methylene terminated fragments **16b**, presumably formed as suggested in Scheme 3. Figure 3b shows an expanded view for $n = 14$ to $n = 16$.

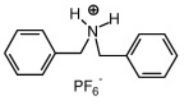


16a

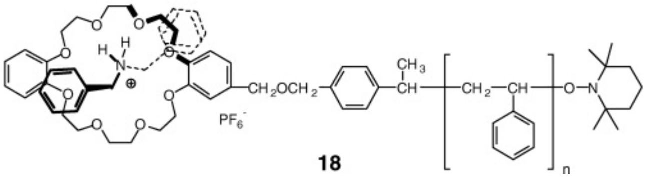


16b

Complexation of DB24C8-Terminated Polystyrene (5) with Dibenzylammonium Hexafluorophosphate (17). Interaction of 24-membered crown ether functionalized polystyrene **5** and dibenzylammonium salt **17** was expected to yield end-chain polymeric pseudorotaxane **18** as a model system. NMR spectroscopy indeed provided direct evidence for pseudorotaxane formation. A series of 1.00 mM solutions of a crown-terminated polystyrene **5** ($M_n = 3.19$ kg/mol) were prepared with varying concentrations of guest **17** ranging from 1.00 to 5.00 mM in $CDCl_3/CD_3COCD_3$ (1/1). The ^1H NMR spectra (Figure 4) indicated pseudorotaxane formation, as expected. Under these conditions exchange is slow and two sets of signals for the *N*-benzylic protons (labeled NCH) are observed, one for complex **18** and the other set for uncomplexed **17**; two sets of signals are also apparent for α-, β-, and γ-protons on the crown ether moiety of the polymer: one set for **5** and one set for **18**. These results are analogous to observations with the monomeric host−guest systems.[2,14,23,24,27,28]



17



18

The concentrations of complexed (**18**) and uncomplexed (**5**) crown ether moieties in equilibrium were determined from integration of the appropriate signals (e.g., H_γ) in the ^1H NMR spectra; the fraction p of complexed DB24C8 moieties was thus readily determined (Table 1). Likewise the concentrations of the complexed and uncomplexed ammonium species can be determined. From these integrations the stoichiometry was found to be 1:1, as anticipated. The apparent

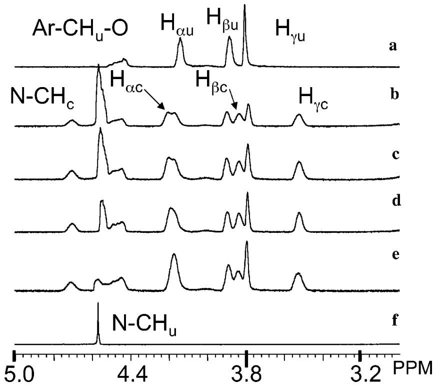


Figure 4. Partial ^{1}H NMR spectra (400 MHz, CD_3COCD_3/$CDCl_3$ (1/1), 22 °C) of (a) DB24C8-terminated polystyrene **5** (GPC: M_n = 1.39 kg/mol and PDI = 1.03) by itself; (b−e) **5** and dibenzylammonium hexafluorophosphate (**17**) [initial concentrations of crown moieties in **5** = 1.00 mM]. Key: (b) [**17**]$_0$ = 5.00 mM, (c) [**17**]$_0$ = 3.00 mM, (d) [**17**]$_0$ = 2.00 mM, (e) [**17**]$_0$ = 1.00 mM, and (f) **17** alone, 1.00 mM. u = uncomplexed; c = complexed.

Table 1. Complexation of Crown Ether Moieties of DB24C8-Terminated Polystyrene 5^a and DB24C8 (2a)^a by Dibenzylammonium Hexafluorophosphate (17) Independently in $CDCl_3/CD_3COCD_3$ (1/1) at 23 °C

[**17**]$_0$ (mM)	p of **5**^{b}	K_{aexp} of **5** (M^{-1})^c	[**17**]$_0$ (mM)	p of **2a**^{b}	K_{aexp} of **2a** (M^{-1})^d
2.00	0.491	732	4.00	0.702	907
3.00	0.493	378	6.00	0.808	960
4.00	0.496	284	8.00	0.831	776
5.00	0.499	231	10.00	0.852	694

[a] The initial concentrations of crown ether moieties in polystyrene **5** were 1.00 mM and those of monomeric crown ether **2a** were 2.00 mM. [b] p = the fraction of complexed crown ether moieties, determined by integration of the signals for H_γ. Maximum error ± 0.020. [c] K_{aexp} = [**18**]/[**5**]([**17**]$_0$ − [**18**]). [d] K_{aexp} = [complex]/[**2a**]([**17**]$_0$ − [complex]).

Scheme 4. Representation of the Complexation of Guest Salts by Crown Ethers via Formation of a Non Ion Paired Complex from an Ion Paired Salt in a Low Polarity Medium^a

$$G^+PF_6^- \overset{K_{ipd}}{\rightleftharpoons} G^+ + PF_6^-$$

$$\text{Crown} + G^+ \overset{K_a}{\rightleftharpoons} \text{Crown}{*}G^+$$

$$G^+PF_6^- + \text{Crown} \overset{K_{overall}}{\rightleftharpoons} \text{Crown}{*}G^+ + PF_6^-$$

$$K_{ipd} = [G^+][PF_6^-] / [G^+PF_6^-]$$

$$K_a = [\text{Crown}{*}G^+] / [\text{Crown}][G^+]$$

$$K_{overall} = [\text{Crown}{*}G^+][PF_6^-] / [G^+PF_6^-][\text{Crown}]$$

$$= K_{ipd} K_a$$

$$K_{aexp} = [\text{Crown}{*}G^+] / [G^+PF_6^-][\text{Crown}]$$

$$= K_{ipd} K_a / [PF_6^-]$$

$$[PF_6^-] = [G^+] + [\text{Crown}{*}G^+]$$

[a] Two equilibria are involved: (1) ion pair dissociation defined by K_{ipd} and (2) Pseudorotaxane Complex Formation Defined by K_a.

macroscopic association constants were calculated by the standard expression K_{aexp} = [complexed crown ether]/[free crown ether][free guest]; the free guest concentration is implicitly assumed to be [guest]$_0$ − [complexed crown]. The K_{aexp} values diminish as the concentration of the guest salt increases; this is analogous to the behavior of the model monomeric systems, i.e., DB24C8 (**2a**) with **17**.[28] This apparent violation of equilibrium behavior arises because although the salt is, as expected, predominantly ion paired in the low dielectric constant solvent, the complex, which forms from the free cation, is not ion paired and hence the simple single stage equilibrium implied in the equation used to calculate K_{aexp} is not valid. Complex formation generates free anion that in turn drives the ion pair dissociation equilibrium back to the salt (Scheme 4). Extensive data are normally required to determine the two true equilibrium constants: the ion pair dissociation constant, K_{ipd}, and the pseudorotaxane formation constant, K_a. The K_{aexp} values are equal to K_{ipd} K_a/[PF_6^-].[28] As the total salt concentration increases, the free anion concentration, [PF_6^-], increases and hence the relative extent of ionization of the guest salt and consequently the degree of complexation are reduced accordingly.

By comparison of the percentages of complexation of polymeric host **5** by dibenzylammonium hexafluorophosphate (**17**) with that of its monomeric analogue, dibenzo-24-crown-8 (**2a**) (Table 1), it can be seen that at comparable initial concentrations of the components the monomeric crown ether **2a** is more effective than its polymeric counterpart **5** in complexing the guest. This may be due to steric factors brought about by the polystyryl chain. We have observed similar diminished host efficiency with other polymeric systems.[14,15] However, the results demonstrate clearly that the polymeric host is effective in complexing the monomeric guest species.

A way to determine the relative K_a values for two hosts with the same guest salt is to carry out two individual experiments with the host−guest pairs in the presence of a large amount of the guest salt counterion, the latter being achieved by dissolution of an excess of the tetra(n-butyl)ammonium salt. Under these conditions the concentration of free anion, [PF_6^-], for all practical purposes, arises from ion pair dissociation of the latter very soluble salt. The tetabutylammonium cation does not interact with the crown ether. Therefore, since as noted above K_{aexp} = K_{ipd} K_a/[PF_6^-] and K_{ipd} for guest salt **17** and [PF_6^-] are essentially the same in both solutions, the ratio of the K_{aexp} values affords the ratio of K_a values.

Therefore, we examined the complexation of DB24C8-polymer **5** with dibenzylammonium hexafluorophosphate (**17**) in the presence of excess tetra(n-butyl)ammonium hexafluorophosphate in comparison to complexation of DB24C8 (**2**) itself with **17** under the same conditions (Figure 5). The K_{aexp} values were 79 and 667 M^{-1}, respectively. For **2·17** K_a = 5.1 (±0.6) × 10^2 M^{-1}.[28] From the ratio of K_{aexp} values (0.12) we estimate K_a = 61 (±7) M^{-1} for polystyryl crown complex **18**. Again the large reduction in K_a for the polymeric

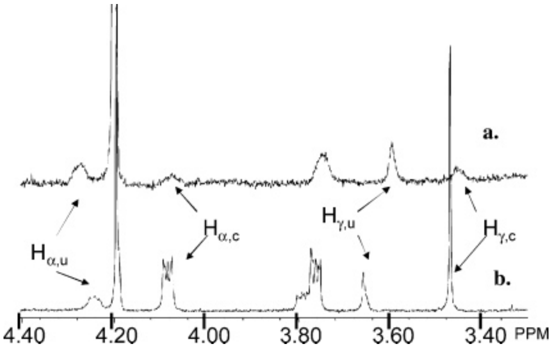
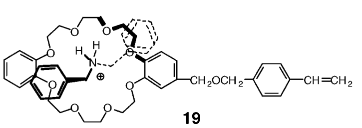


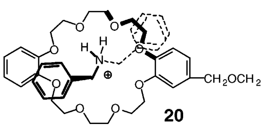
Figure 5. Partial ^{1}H NMR spectra (400 MHz, $CD_3CN/CDCl_3$ ($^2/_3$, 22 °C) in the presence of 100 mM $(n\text{-}Bu)_4NPF_6$ of (a) **5** (GPC: M_n = 1.39 kg/mol and PDI = 1.32) and dibenzylammonium hexafluorophosphate (**17**), initial concentrations of crown moieties in **5** = 2.00 mM and $[\mathbf{17}]_0$ = 6.00 mM, and (b) dibenzo-24-crown-8 (**2**) and **17,** initial concentrations $[\mathbf{2}]_0$ = 2.00 mM and $[\mathbf{17}]_0$ = 6.00 mM. u = uncomplexed, c = complexed.

host is most likely due to the adverse effects of the polystyryl chain.

The mass spectrum of a mixture of DB24C8-functionalized polystyrene **5** and guest salt **17** provides corroboration of the formation of **18**. The base peak signal at *m/z* 794 corresponds to the complex **19**. The peak at 675 corresponds to the complex **20**. These species arise presumably in the same way that the corresponding fragments **13/14** and **12**, respectively, are formed. The higher *m/z* signals in the spectrum (Figure 6a) are all attributed to polymeric complex **18** after it has lost the TEMPO end group. As can be seen in Figure 6b these signals are actually comprised of pairs of clusters. As with the parent polymer **5**, the members of the individual pairs are separated by 14 mass units. We attribute these signals to fragments **21a** and **21b** formed as shown in Scheme 3; in Figure 6b the pairs of clusters correspond to n = 5, 6, and 7. It is interesting to note that for n = 5 the higher mass fragment **21b** predominates, but for n = 7 the lower mass fragment **21a** dominates. The same behavior can be observed in Figure 1 for the parent polymer, **5**, in which the transition occurs between n = 5 and n = 6.



19



20

Interestingly when sodium iodide was added to the mixture of DB24C8-functionalized polystyrene **5** and dibenzylammonium hexafluorophosphate (**17**) the signals for the ammonium complexes were barely detectable (Figure 6c); the new pairs of signals correspond to the sodium adducts **16a** and **16b**. In the presence of NaI the pseudorotaxane is only barely observed for two reasons: 1) the sodium cation competes strongly for binding to the crown moieties[1] and 2) the iodide counterion forms a tight ion pair with the dibenzylammonium ion (decreasing K_{ipd}, Scheme 2), lowering the concentration of free cation, which is required for the complexation. This result indicates that the ammonium ion guests can be expelled by sodium ions, providing a means of switching ammonium ion pseudorotaxane formation off; such capability for switching/sensing provides exciting potential avenues for controlling macroscopic physical properties of suitably designed polymeric host−guest systems.

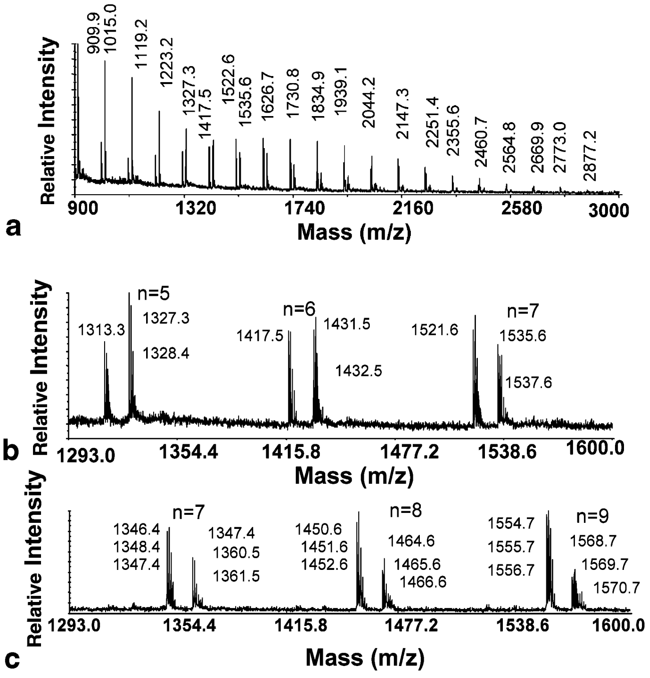
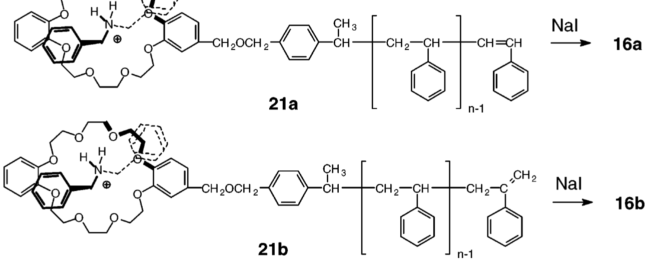


Figure 6. Partial MALDI−TOF mass spectra of a mixture of DB24C8-terminated polystyrene **5** (GPC: M_n = 1.39 kg/mol and PDI = 1.32) and dibenzylammonium hexafluorophosphate (**17**): (a) *m/z* 900−3000 spectrum in dithranol, (b) expansion of the *m/z* 1300−1600 region in dithranol, and (c) expansion of the *m/z* 1300−1600 region in dithranol with added NaI. In parts a and b, the pairs of signals correspond to the pseudorotaxane complex **18** after loss of the TEMPO end group, specifically (**5** - TEMPO + DBA)$^+$ = **21a** and (**5** − TEMPO + CH_2 + DBA)$^+$ = **21b**; n values are indicated for some of the pairs. In part c, the signals correspond to the analogous sodium complexes (**5** - TEMPO + CH_2 + Na)$^+$ = **16a** and (**5** − TEMPO + CH_2 + Na)$^+$ = **16b** as observed in Figure 3; the pseudorotaxane signals are barely observed in part c.



Complexation of BMP32C10-Terminated Polystyrene (11) with Dibenzylammonium Hexafluorophosphate (17). The model system BMP32C10 (**1b**) binds ammonium ion guest **17** in a 1:2 pseudorotaxane complex only very weakly: $K_a = 5 \pm 2$ M^{-2} in CD_3CN.[40]

To determine the possible formation of the pseudorotaxane complex **22** from dibenzylammonium salt **17** and the BMP32C10 moiety of **11**, ^{1}H NMR spectra of solutions in 1:1 $CDCl_3$:CD_3COCD_3 were examined (Figure 7). There was no evidence of complexation between the two components, either as manifest in the appearance of new signals under slow exchange or as a change in the chemical shifts under fast exchange. Since there was an excess of the guest **17** relative to the host species **11**, it appears that there is no (or perhaps very, very

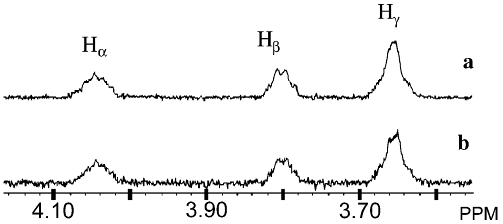


Figure 7. Partial ^{1}H NMR spectra (400 MHz, CD_3COCD_3/$CDCl_3$ (1/1), 22 °C) of (a) BMP32C10-terminated polystyrene **11** (GPC: $M_n = 4.52$ kg/mol and PDI = 1.07) (0.310 mM) and (b) **11** (0.310 mM) and dibenzylammonium hexafluorophosphate (**17**, 1.00 mM).

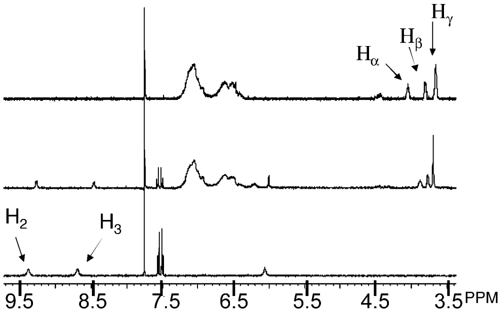
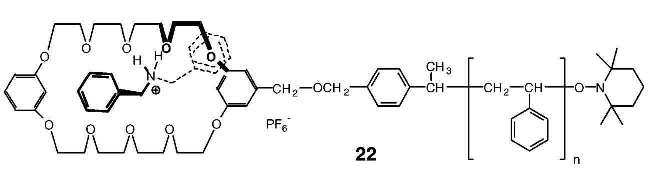
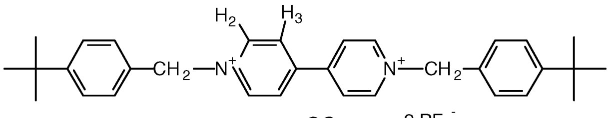


Figure 8. Partial ^{1}H NMR spectra (400 MHz, CD_3COCD_3/$CDCl_3$ (1/1), 22 °C) of (a) 1.00 mM BMP32C10-terminated polystyrene **11** (GPC: $M_n = 4.52$ kg/mol and PDI = 1.07) (top), (b) 1.00 mM **11** and *N,N′*-bis(*p-tert*-butylbenzyl)-4,4′-bipyridinium bis(hexafluorophosphate) (**23**) (middle), and 1.00 mM *N,N′*-bis(*p-tert*-butylbenzyl)-4,4′-bipyridinium bis(hexafluorophosphate) (**23**) (bottom).

weak) interaction in this system, since complex **22** is not detected.



22



23

Complexation of BMP32C10-Terminated Polystyrene (11) with *N,N′*-Bis(*p-tert*-butylbenzyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (23). In 1:1 $CDCl_3$:CD_3COCD_3 at room temperature the complexation equilibrium for polymer **11** with **23** is a fast exchange process and the observed ^{1}H NMR signals are time averaged (Figure 8). The Job plot[41] (Figure 9) demonstrates the 1:1 stoichiometry of the complex of **11** with **23**, the same as observed with the small molecule host **1b**. To establish the chemical shift of the fully complexed crown ether, the concentration of guest **23** was varied up to 10 mM while that of polymeric host **11** was maintained at 0.310 mM; the intercept of the linear plot of 1/Δ (Δ = the chemical shift change from the uncomplexed γ-protons of host **11**), vs the inverse of the concentration of guest **23** (Figure 10) yielded $\Delta_0 = 0.108$ ppm, the chemical shift change for H_γ of the fully complexed crown ether moieties in **24**; it is not known whether the crown folds around the paraquat guest to form a “taco complex” (**24b**), as we have observed with **1c**,[31,42] or a pseudorotaxane forms by threading of the paraquat moiety through the crown ether ring (**24a**).[43] The fraction of crown ether complexed, p, is equal to Δ/Δ_0.[44] In 1:1 complexes of larger crown ethers such as **1b** with paraquats such as **23** both the guest salt and the complex are ion paired in low polarity solvents and the simple expression K_a = [complex]/[host]([guest]$_0$ − [complex]) is valid.[34] Using this same expression, K_a was calculated at concentrations which yielded $p = 0.2$ to 0.9 (the Weber rule)[45] as shown in Table 2. The average value was $K_a = 751 \pm 27$ M^{-1}. This process contrasts strongly with the lack of complexation of the secondary ammonium salt **17**, reflecting the selectivity of polystyryl crown **11** for the paraquat guest over the ammonium guest.

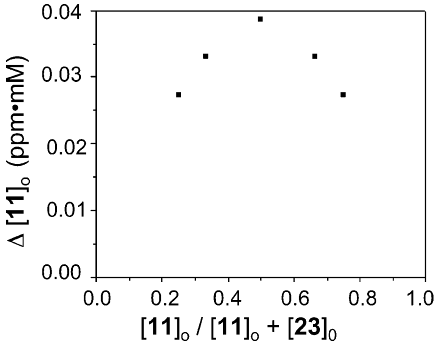
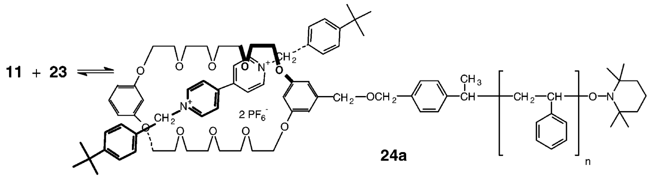
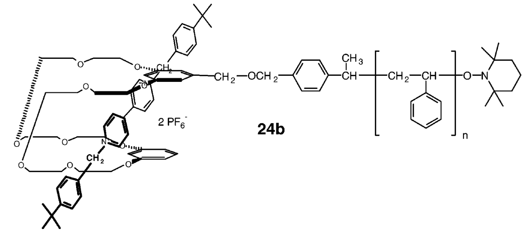


Figure 9. Job plot for complexation of BMP32C10-terminated polystyrene **11** (GPC: $M_n = 4.52$ kg/mol and PDI = 1.07) (CD_3COCD_3/$CDCl_3$, 1/1 at 22 °C) showing 1:1 stoichiometry. [**11**]$_0$ + [**23**]$_0$ = 2.00 mM. Δ = the chemical shift change of γ-ethyleneoxy protons of **11**.



11 + **23** ⇌ **24a**

and/or



24b

For comparison purposes the complexation of model crown ether **1a** and paraquat **23** was examined under the same conditions. As can be seen from Table 2 the K_a value for the polymeric host **11** is 61% of that of the monomeric host **1a**; again the reduction in binding strength is probably the result of steric effects of the polystyryl chain in the former, but the decrease is not as severe as observed with the smaller, less flexible 24-membered crown ether-containing polymer **5** with dibenzylammonium guest **17**.

The mass spectrum of a mixture of BMP32C10-terminated polystyrene **11** and paraquat **23** (Figure 11)-confirms the complexation process leading to **24**. In the low *m/z* region the spectrum contains many of the same peaks (labeled “*”) as observed with uncomplexed polymer **11** (Figure 3). However, at higher masses, the major peaks (labeled “‡”) in each set of three at intervals of 104 mass units (Figure 11b) are attributable to **25**

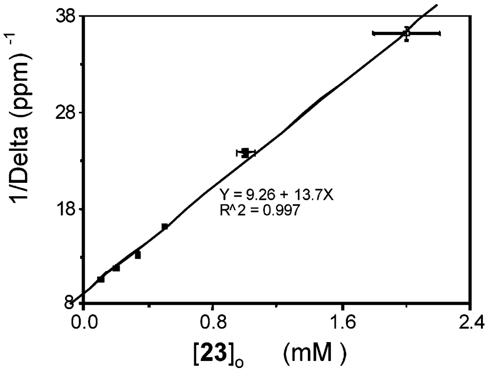


Figure 10. Inverse of chemical shift change, 1/Δ, (400 MHz, $CD_3COCD_3/CDCl_3$ (1/1), 22 °C) of γ-protons of BMP32C10-terminated polystyrene **11** (GPC: M_n = 4.52 kg/mol and PDI = 1.07) vs the inverse of the initial concentration of the paraquat guest **23**, $[\mathbf{11}]_0$ = 0.310 mM. The intercept is $1/\Delta_0$; Δ_0 is the chemical shift change that would be observed for 100% complexation of the crown ether moieties, i.e., **24**.

Table 2. Complexation of Crown Ether Moieties of BMP32C10-Terminated Polystyrene 11[a] and 5-Hydroxymethyl-1,3-phenylene-1′,3′-phenylene-32-crown-10 (1a)[a] by *N,N′*-Bis(*p-tert*-butylbenzyl)-4,4′-bipyridinium Bis(hexafluorophosphate) (23) Independently in $CDCl_3/CD_3COCD_3$ (1/1) at 23 °C

$[\mathbf{23}]_0$ (mM)	p of **11**[b]	K_a of **11** (M^{-1})[c]	p of **1a**[d]	K_a of **1a** (M^{-1})[e]
0.500	0.256	819	0.350	1.41×10^3
1.00	0.389	724	0.530	1.37×10^3
2.00	0.574	740	0.666	1.12×10^3
3.00	0.698	831	0.790	1.38×10^3
5.00	0.778	737	0.842	1.13×10^3
10.0	0.867	655	0.902	953
av (±std error)		**751 (±27)**[f]		**1.23 (±0.20) × 10^3**

[a] The initial concentrations of crown ether moieties of polymer **11** and model crown ether **1a** were maintained at 0.310 mM using M_n = 4.52 kg/mol derived by GPC. [b] p = the fraction of complexed crown ether moieties, determined by Δ/Δ_0 based on the γ-protons of the crown ether moiety; Δ_0 = 0.108 ppm. Maximum error in p: ±0.050. [c] $K_a = [\mathbf{24}]/[\mathbf{11}][\mathbf{23}]$. [d] p = the fraction of complexed crown ether moieties, determined by Δ/Δ_0 based on the γ-protons of the crown ether moiety; Δ_0 = 0.125 ppm. Maximum error in p: ±0.040. [e] K_a = [complex]/$[\mathbf{23}][\mathbf{1a}]$. [f] Using the NMR value of M_n = 4.2 kg/mol yields a concentration of crown units 0.33 mM and K_a = 7.6 (± 0.7) × 10^2 M^{-1}.

that results from the loss of two PF_6 moieties and the *t*-butylbenzyl group of the paraquat unit from complex **24**, i.e., (m/z = 104.06 n + 683.34 + 156.14 + 303.56). Losses of both PF_6 moieties are commonly observed for analogous low molar mass complexes.[22,31,42,46] Note that in the complexes the TEMPO end group is retained and with that only one cluster is seen; in other words, in the uncomplexed system, parent polymer **11**, TEMPO loss leads to the "double clusters" with m/z 14 separation (Figure 3b), consistent with the processes proposed in Scheme 3. This is not observed for complex **24**.

It is also noteworthy that with polymeric complex **24**, even though sodium iodide was used to promote ionization, the proportions of peaks labeled "diamond" and "heart" due to sodium complexes **16a** and **16b** (see Figure 10b; cf., Figure 3b) are relatively weak, in contrast to the results for complex **18**, which is relatively easily displaced by NaI. In other words, complexation of paraquat **23** by BMP32C10-functionalized polystyrene is relatively insensitive to competing sodium ion complexation. This robustness arises from several factors. First, the large 32-membered crown ether is less effective as a host for Na^+ than the 24-crown-8 system, whose cavity size is closer to that of the cation.[1] Second, the binding constant for paraquat **23** with polymeric host **11** is 10-fold greater than that of ammonium ion **17** and polymeric host **5**. Third, since BMP32C10/paraquat complexes are ion paired,[34] the I^- counterions have no effect on the binding of guest **23** by polymeric crown ether **11**.

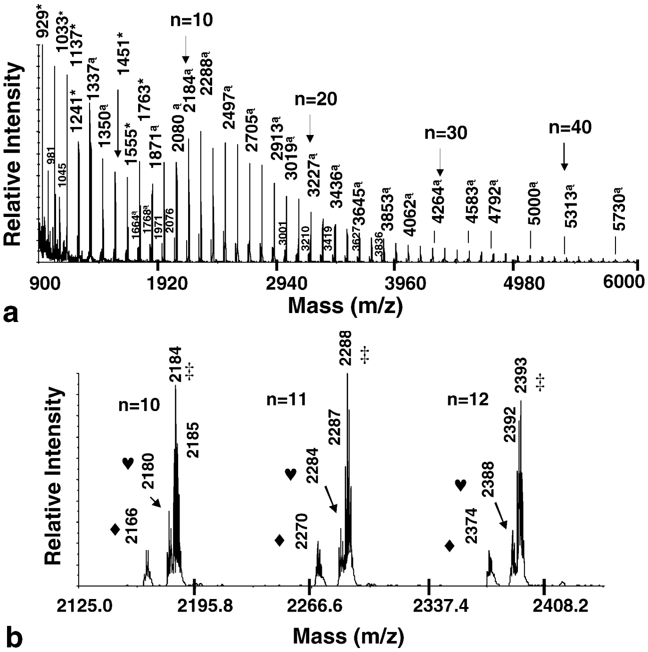
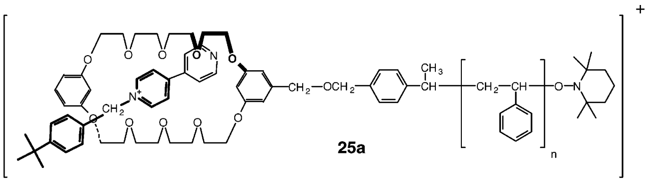
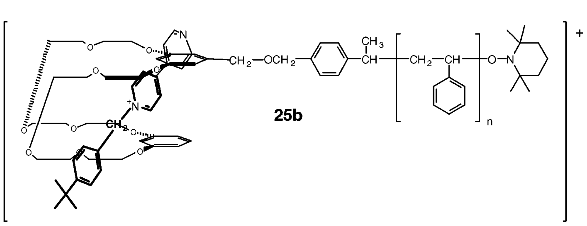


Figure 11. MALDI–TOF mass spectrum of a mixture of BMP32C10-terminated polystyrene **11** (GPC: M_n = 4.52 kg/mol and PDI = 1.07) and *N,N′*-bis(*p-tert*-butylbenzyl)-4,4′-bipyridinium bis(hexafluorophosphate) (**23**). (a) m/z 900–6000 spectrum. (b) Expanded view of m/z 2125–2408. The peaks in the lower region of the spectrum a that are marked "*" are due to $(\mathbf{11}-CH_3)^+$ as found in Figure 3. The signals marked "‡" are attributed to the pseudorotaxane complex **24** after losses of 2 PF_6 and a *p-tert*-butylbenzyl moiety, i.e., **25**; the main signals observed in part b are for **25**, n = 10–12. The two minor signals observed in part b are the same ones observed for polymer **11** by itself (Figure 3b), namely the competing sodium adducts **16a** (indicated by a "diamond") and **16b** (indicated by a "heart"). Calibration error increases at high m/z values.



25a

and/or

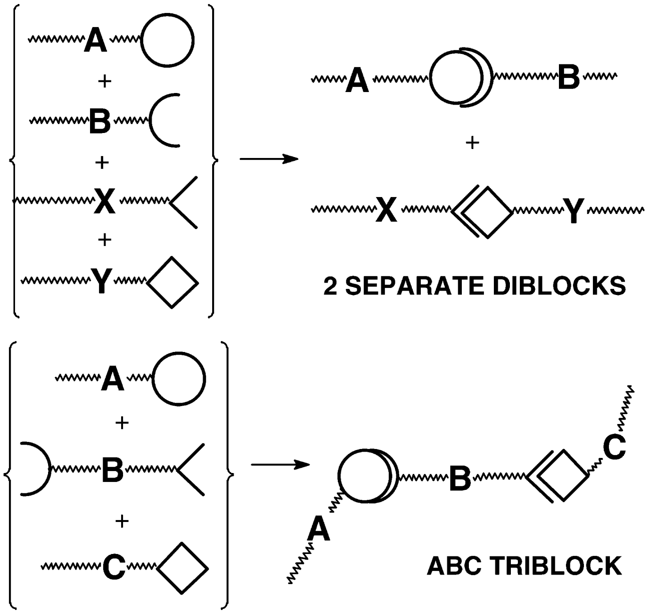


25b

Conclusions

Two TEMPO-based initiators containing different crown ethers have been shown to be suitable for SFRP of styrene, and presumably other vinyl monomers. The resultant polymers have narrow molecular weight dis-

Scheme 5. Selective Construction of a Pair of Supramolecular Diblock Copolymers from a Mixture of Four Separate Polymers with Two Pairs of Orthogonally Complementary Terminal Groups (Top) and Self-Assembly of an ABC Supramolecular Copolymer via Selective Pairwise Complexation of Complementary Terminal Host and Guest Moieties (Bottom)



tributions and a single crown ether unit at one chain end. The crown ether moieties of DB24C8-terminated polystyrene **5** have been demonstrated to be effective hosts for formation of pseudorotaxane complexes from secondary ammonium ions, e.g., **17**. The DB24C8-terminated polymer **5** is selective for secondary ammonium salts and cannot complex bulky viologen (paraquat) derivatives such as **23**, because the *tert*-butyl group is too large to penetrate the cavity of the crown ether.[47] Moreover, sodium ions are effective in displacement of the ammonium ion guests, as shown with complex **18** from dibenzo-24-crown-8-terminated polymer **5** and **17**. The bis(*m*-phenylene)-32-crown-10-terminated polystyrene **11** is highly selective for complexation of paraquats vs secondary ammonium ions; however, the paraquat guest is not easily displaced by sodium ions. The selectivity of these systems should prove useful in our future efforts to self-assemble macromolecular building blocks into switchable heierarchical structures that are sensitive to various stimuli, resulting in changes in macroscopic physical properties. Scheme 5 illustrates the use of these concepts in selective formation of two distinct supramolecular block copolymers from a mixture of four end-functionalized polymers and the formation of supramolecular triblock copolymers via selective chain end complexation. Our current efforts are focused on these objectives.

Experimental Section

Materials. Chloroform (HPLC grade, Burdick and Jackson), $CDCl_3$ (99.8% isotopic purity, with 0.05% v/v tetramethylsilane, Cambridge Isotope Laboratories), ethanol (reagent grade, denatured, Aldrich), methanol (ACS HPLC grade, Burdick and Jackson), nitrogen gas (~100%, anhydrous, from in-house liquid nitrogen source), silica gel (32−63 μm, 60 Å pore size, AdEdge) and water (deionized, purity not determined, in-house supply) were used as supplied. Styrene (99%, Aldrich) was vacuum distilled and stored over molecular sieves (5A, 4−8 mesh, Aldrich). Tetrahydrofuran (99+%, ACS reagent grade, Aldrich) was distilled from Na/benzophenone.

Instruments. A vacuum oven (Napco model 5831) was used in concert with a vacuum pump (Welch Duoseal model 1400) at ca. 1 Torr for drying samples. NMR spectra were recorded at ambient temperature on Varian 400-MHz or Bruker 500-MHz spectrometers with tetramethylsilane (TMS, $\delta = 0$) as internal standard. GPC was conducted on an ISCO model 2350 chromatograph equipped with a UV detector (Waters, model R401) at 23°C using dual Polymer Labs columns (PLgel mixed 5 μm × 300 mm) packed with cross-linked styrene-divinylbenzene; the solvent was $CHCl_3$ and toluene was used as a flow marker. The system was calibrated with polystyrene standards with molecular weights between 1.25 and 100 kg/mol. A typical solution contained ca. 2 mg/mL, of which 200 μL was injected and eluted at 1.0 mL/min. Elemental analyses were provided by Atlantic Laboratories, Norcross, GA. MALDI−TOF MS spectra were obtained at Vanderbilt University using a Voyager-DE STR (Applied Biosystems, Framingham, MA) operated in the positive ion reflector mode using an average of 200 shots with a 337 nm wavelength nitrogen laser operating at 20 Hz. For MALDI MS a 0.1 M matrix solution of 1,8,9-anthracenetriol ("dithranol") in THF salt solutions of 1 mg/mL of silver trifluoroacetate in THF or NaI in methanol, and polymer stock solutions in THF (10 mg/mL) were prepared; sample solutions were produced by mixing the polymer, matrix, and salt solutions in a 2:5:2 volume ratio, respectively, and sample plates were spotted with 1 μL aliquots. The positive ion MALDI−TOF spectrum of Figure 2 was obtained at HT Laboratories, San Diego, CA, using acetone as the solvent.

DB24C8 Initiator 4a. A mixture of TEMPO derivative **3**[36] (0.62 g, 2.0 mmol), 4-(hydroxymethyl)dibenzo-24-crown-8 (**2b**)[24] (0.957 g, 2.00 mmol) and 60% NaH (0.24 g, 6.0 mmol) in dry THF (50 mL) was stirred at room temperature for 2 h and then 24 h at reflux and cooled. A few drops of water were added to destroy the excess NaH. The solution was dried with $MgSO_4$, filtered and evaporated to dryness. The residue was purified by column chromatography, eluting with diethyl ether: 0.40 g (26%) of a colorless oil. ^{1}H NMR (400 MHz, chloroform-*d*, 22 °C): $\delta = 0.64$ (s, 3H), 1.02 (s, 3H), 1.18 (s, 3H), 1.24 (s, 3H), 1.24−1.58 (m, 6H), 1.45 (d, $J = 6.8$ Hz, 3H), 3.82 (m, 8H), 3.92 (m, 8H), 4.16 (m, 8H), 4.45 (s, 2H), 4.49 (s, 2H), 4.78 (q, $J = 6.8$ Hz, 1H), 6.80−6.92 (m, 7H), 7.25−7.35 (m, 4H). LR FAB MS (NBA), *m/z*: 774.6 $(M - H + Na)^+$, 3%; 752.4 $(M + H)^+$, 8%; 596.3 $(M - TEMPO + H)^+$, 2%; 461.3 $(M - C_{18}H_{28}NO_2)^+ = (DB24C8CH_2)^+$ (**6**), 44%; 156.1 $(TEMPO)^+$, 59%; 45.0, 100%. HR FAB MS (NBA), *m/z*: 752.4395 $(M + H)^+$, calcd 752.4374; 461.2167 $(M - C_{18}H_{28}NO_2)^+ =$ **6**, calcd 461.2175. Anal. Calcd for $C_{43}H_{61}NO_{10}$: C, 68.68; H, 8.18. Found: C, 68.39; H, 8.20.

BMP32C10 Initiator 4b. To a solution of **3** (0.619 g, 2.00 mmol) and 5-(hydroxymethyl)-1,3-phenylene-*m*-phenylene-32-crown10 (**1a**)[37] (1.133 g, 2.00 mmol) in dry THF (50 mL) was added 0.24 g of 60% NaH (6.0 mmol). The solution was stirred at 25°C for 2 h and then 24 h at reflux. The solution was cooled and few drops of water were added to destroy the excess NaH. The solution was dried with $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by flash chromatography (silica gel), eluting with diethyl ether: 1.27 g (75%) of a viscous, colorless oil. ^{1}H NMR ($CDCl_3$): 0.67, 1.02, 1.16, 1.28 (each br s, 3H), 1.24−1.58 (m, 6H), 1.46 (d, $J = 6.5$ Hz, 3H), 3.69 (m, 16H), 3.83 (m, 8H), 4.06 (m, 8H), 4.44 (s, 1H), 4.49 (s, 1H), 4.77 (q, $J = 6.5$ Hz, 1H), 6.45 (m, 6H), 7.11 (t, $J = 8.6$ Hz, 1H), 7.25−7.35 (m, 4H). ^{13}C NMR ($CDCl_3$): 16.94, 20.08, 23.31, 33.95, 34.19, 40.05, 59.34, 67.18, 67.24, 69.37, 70.54, 70.57, 71.60, 71.62, 82.57, 100.46, 101.33, 106.03, 106.79, 126.30, 127.28, 129.47, 136.31, 140.36, 144.93, 159.67, 159.70. Anal. Calcd for $C_{47}H_{69}NO_{12}$: C, 67.20; H, 8.28. Found: C, 67.02; H, 8.18.

Representative Synthesis of Dibenzo-24-crown-8-Terminated Polystyrene (5): A solution of 655 mg (0.873 mmol) of initiator **4a** and 5.0 mL (44 mmol) of styrene was heated at 130°C under nitrogen for 16 h, at which point it was quite viscous. The mixture was dissolved in chloroform and precipitated into methanol. The resultant solid was collected and reprecipitated twice. The vacuum-dried polymer weighed 1.4 g (27%). ^{1}H NMR (400 MHz, CDCl$_3$, 22 °C): $\delta = 1.40$ (bs, 2H), 1.80 (bs, 1H), 3.76 (m, 8H), 3.84 (m, 8H), 4.08 (m, 8H), 6.50 (bs, 2H), 7.02 (bs, 3H). GPC results: $M_n = 3.19$ kg/mol, $M_w = 3.27$ kg/mol, and PDI = 1.03. ^{1}H NMR end group analysis by referencing α-, β-, and γ-proton signals of the crown ether moiety to the aromatic signals (6.2−7.4 ppm, taking into account the contribution of the crown ether-based unit's aromatic protons) indicated $M_n = 3.09$ kg/mol, including the crown and TEMPO end groups.

Synthesis of Bis(*m*-phenylene)-32-crown-10-Terminated Polystyrene (11): A stirred solution of initiator **4b** (0.624 g, 0.744 mmol), styrene (4.5 mL, 39 mmol) and acetic anhydride (0.152 g, 1.49 mmol) under N$_2$ was maintained at 100 °C in an oil bath for 18 h. The reaction mixture became viscous and the magnetic stirrer stopped. The mixture was dissolved in chloroform and precipitated into methanol; the solid was reprecipitated several times and vacuum-dried to afford 1.3 g (32%) of colorless powder. ^{1}H NMR (400 MHz, chloroform-*d*, 22 °C): $\delta = 1.42$ (bs, 2H), 1.82 (bs, 1H), 3.70 (m, 16H), 3.84 (m, 8H), 4.08 (m, 8H), 6.50 (bs, 2H), 7.02 (bs, 3H). GPC results: $M_n = 4.52$ kg/mol, $M_w = 4.83$ kg/mol, and PDI = 1.07. ^{1}H NMR end group analysis by referencing α-, β-, and γ-proton signals of the crown ether moiety (3.6−4.2 ppm) to the aromatic signals (6.2−7.4 ppm, taking into account the contribution of the crown ether-based aromatic protons) indicated $M_n = 4.2$ kg/mol, including the crown and TEMPO end groups.

Complexation of Ammonium Salt 17 with Crown Ether-Functionalized Polystyrenes (Representative Procedure). Crown terminated polystyrene **5**, $M_n = 3.19$ kg/mol (38.2 mg) was dissolved in 6.00 mL of CDCl$_3$ to yield a solution 2.00 mM in crown ether moieties. Solutions of various concentrations of ammonium salt **17** were similarly prepared in CD$_3$COCD$_3$. Then a series of solutions of **5** and **17** was prepared by mixing the two solutions in a 1:1 volume ratio and studied by NMR. The fraction of crown moieties complexed was determined by subtraction of the integral of the signal for $H_{\gamma c}$ at 3.53 ppm from the total integral for $H_{\gamma u} + H_{\beta u} + H_{\beta c}$ at 3.72−3.94 ppm to determine $H_{\gamma u} + H_{\beta u}$, dividing this value by two to determine $H_{\gamma u}$, and then comparing the resulting integrals for $H_{\gamma u}$ and $H_{\gamma c}$.

***N,N′*-Bis(*p*-*tert*-butylbenzyl)-4,4′-bipyridinium Hexafluorophosphate (23).** A mixture of 0.31 g (2.0 mmol) of 4,4′-bipyridine, 2.28 g (10.0 mmol) of 4-*tert*-butylbenzyl bromide, 3.00 g (20.0 mmol) of sodium iodide, and 20 mL of acetone was heated at reflux for 48 h, cooled, and filtered. The solid was washed with chloroform and dissolved in a minimum amount of deionized water. Excess solid ammonium hexafluorophosphate was added until no further precipitation was observed. The precipitate was collected, dried and dissolved in a minimum amount of acetone. Excess deionized water was added. The precipitate was collected and dried. This process was repeated three times to afford pure **23** (1.56 g, 85%), mp 313.4−314.6. ^{1}H NMR (400 MHz, acetone-*d*$_6$, 22 °C) δ (ppm): 9.58 (4H, d, $J = 6.8$ Hz), 8.88 (4H, d, $J = 6.8$ Hz), 7.64 (4H, d, $J = 8.4$ Hz), 7.59 (4H, d, $J = 8.4$ Hz), 6.17 (4H, s), and 1.34 (18H, s). Anal. Calcd for $C_{32}H_{38}N_2P_2F_{12}$: C, 51.90; H, 5.17; N, 3.78. Found: C, 52.07; H, 5.18; N, 3.79.

Complexation of Paraquat Derivative 23 with the Bis(*m*-phenylene)-32-Crown-10-Terminated Polystyrene 11. Precisely weighed (± 0.01 mg) amounts of dried hosts and guests were added into separate screw cap vials. A mixture of acetone-*d*$_6$ and chloroform-*d* (1:1 in volume) was added with to-deliver volumetric pipets. Then specific volumes of each fresh solution were mixed to yield the desired concentrations. For example, to make three solutions: 0.310 mM **11**/3.00 mM **23**, 0.310 mM **11**/5.00 mM **23**, and 0.310 mM **11**/10.0 mM **23**, a 0.310 mM solution of **11** was made first by adding 5.00 mL solvent with a 5.00 mL to-deliver pipet into a screw cap vial containing 6.99 mg (0.00155 mmol) of **11** ($M_n = 4.52$ kg/mol, GPC). Then 0.600 mL of this solution was added with a 0.300 mL to-deliver pipet twice to three vials that contained 1.33, 2.22, and 4.44 mg (0.00180, 0.00300, and 0.00600 mmol, respectively) of **23** separately. ^{1}H NMR data were collected on a temperature controlled spectrometer. The mixture of acetone-*d*$_6$ and chloroform-*d* (1:1 in volume) was chosen because all compounds used here dissolve readily in it. The solutions of **1b** and **23** were prepared in the same way.

Acknowledgment. The authors are grateful to the National Science Foundation for generous support through Grant DMR0097126.

Supporting Information Available: Figures showing full MALDI−TOF mass spectra of polymers **5** and **11** with NaI. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. *Chem. Rev.* **1991**, *91*, 1721−2085. Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1995**, *95*, 2529−2586.

(2) For reviews of pseudorotaxanes and rotaxanes see: (a) Gibson, H. W.; Marand, H. *Adv. Mater.* **1993**, *5*, 11−21. Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, 843−945. (b) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725−2828. (c) Gibson, H. W. in: *Large Ring Molecules*, Semlyen, J. A., ed., John Wiley & Sons: New York, 1996, Chapter 6, pp 191−262. (d) Gong, C.; Gibson, H. W. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2,* 647−652. (e) *Molecular Catenanes, Rotaxanes and Knots,* Sauvage, J.-P., Dietrich-Buchecker, C. O., Eds.; Wiley-VCH: Weinheim, Germany, 1999. (f) Raymo, F. M.; Stoddart, J. F. *Chem. Rev.* **1999**, *99*, 9, 1643−1664. (g) Cantrill, S. J.; Pease, A. R.; Stoddart, J. F. *J. Chem. Soc., Daltons Trans.* **2000**, 3715−3734. (h) Hubin, T. J.; Busch, D. H. *Coord. Chem. Rev.* **2000**, *200*−*202,* 5−52. (i) Takata, T.; Kihara, N. *Rev. Heteroat. Chem.* **2000**, *22,* 197−218. (j) Mahan, E.; Gibson, H. W. Rotaxanes. In *Cyclic Polymers*, 2nd ed., Semlyen, J. A., Ed.; Kluwer Publishers: Dordrecht, The Netherlands, 2000, pp 415−560. **(k)** Panova, I. G.; Topchieva, I. N. *Russ. Chem. Rev.* **2001**, *70*, 23−44.

(3) Kopolow, S.; Hogen Esch, T. E.; Smid, J. *Macromolecules* **1971**, *4*, 359−360. Kopolow, S.; Hogen Esch, T. E.; Smid, J. *Macromolecules* **1973**, *6*, 133−142. Feigenbaum, W. M.; Michel, R. H. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 817−820.

(4) Wu, C.; Bheda, M. C.; Lim, C.; Shen, Y. X.; Sze, J.; Gibson, H. W. *Polym. Commun.,* **1991**, *32*, 204. Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.* **1995**, *117*, 852−874.

(5) Gibson, H. W.; Liu, S.; Gong, C.; Joseph, E. *Macromolecules* **1997**, *30*, 3711−3727.

(6) (a) Shen, Y. X.; Gibson, H. W. *Macromolecules*, **1992**, *25*, 2058. (b) Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.* **1994**, *116*, 537. (c) Loveday, D.; Wilkes, G. L.; Bheda, M. C.; Shen, Y. X.; Gibson, H. W. *J. Macromol. Sci., A.-Chem.* **1995**, *A32*, 1−27. (d) Mason, P. E.; Bryant, W. S.; Gibson, H. W. *Macromolecules* **1998**, *32*, 1559−1569.

(7) (a) Marand, E.; Hu, Q.; Gibson, H. W.; Veytsman, B. *Macromolecules* **1996**, *29*, 2555−2562. (b) Gong, C.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2331−2333.

(8) Gong, C.; Gibson, H. W. *Macromolecules* **1996**, *29*, 7029−7033. Gong, C.; Ji, Q.; Glass, T. E.; Gibson, H. W. *Macromolecules* **1997**, *30*, 4807−4813.

(9) Gong, C.; Gibson, H. W. *Macromolecules* **1997**, *30*, 8524−8525.

(10) Gong, C.; Gibson, H. W. *Macromolecules* **1998**, *31*, 308−313.

(11) Gibson, H. W.; Engen, P. T.; Lee, S.-H. *Polymer* **1999**, *40,* 1823−1832. Zhao, T.; Beckham, H. W.; Gibson, H. W. *Macromolecules* **2003**, *36*, 4833−4837.

(12) Gibson, H. W.; Engen, P. *New. J. Chem.*, **1993**, *17*, 723. Nagapudi, K.; Leisen, J.; Beckham, H. W.; Gibson, H. W. *Macromolecules* **1999**, *32*, 2, 3025−3033.

(13) Gibson, H. W.; Bryant, W. S.; Lee, S.-H. *J. Polym. Sci., Polym. Chem. Ed.* **2001**, *39,* 1978−1993.

(14) Yamaguchi, N.; Gibson, H. W. *Macromol. Chem. Phys.* **2000**, *201,* 815−824.

(15) Gong, C.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 310−314. Gong, C.; Balanda, P. B.; Gibson, H. W. *Macromolecules* **1998**, *31*, 1, 5278−5289.

(16) Inter alia: Buey, J.; Swager, T. M. *Angew. Chem., Int. Ed.* **2000**, *39,* 608−612. Yamaguchi, I. Osakada, K.; Yamamoto, T. *Macromolecules* **2000**, *33,* 2315−2319. Casper, P.; Glöck-

ner, P.; Ritter, H. *Macromolecules* **2000**, *33,* 4361–4364. Werts, M. P. L.; Van Den Boogaard, M.; Tsivgoulis, G. M.; Hadziioannou, G. *Macromolecules* **2000**, *36*, 7004–7013. Takata, T.; Kawasaki, H.; Kihara, N.; Furusho, Y. *Macromolecules* **2001**, *34*, 5449–5456. Yamagishi, T.-A.; Kawahara, A.; Kita, J.; Hoshima, M.; Umehara, A.; Ishida, S.-I.; Nakamoto, Y. *Macromolecules* **2001**, *34*, 6565–6570. Okumura, Y.; Ito, K. *Adv. Mater.* **2001**, *13*, 485–487. Tamura, M.; Gao, D.; Ueno, A. *Chem.—Eur. J.* **2001**, *7*, 1390–1397. Naka, K.; Uemura, T.; Chujo, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2053–2057. Kornysova, O.; Machtejevas, E.; Kudirkaite, V.; Pyell, U.; Maruska, A. *J. Biochem. Biophys. Methods* **2002**, *50*, 217–232. Michels, J. J.; O′Connell, M. J.; Taylor, P. N.; Wilson, J. S.; Cacialli, F.; Anderson, H. L. *Chem. Eur. J.* **2003**, *9*, 6167–6176. Lee, W. K.; Ichi, T.; Ooya, T.; Yamamoto, T.; Katoh, M.; Yui, N. *J. Biomed. Mater. Res., Part A* **2003**, *67A*, 1087–1092. Star, A.; Liu, Y.; Grant, K.; Ridvan, L.; Stoddart, J. F.; Steuerman, D. W.; Diehl, M. R.; Boukai, A.; Heath, J. R. *Macromolecules* **2003**, *36*, 553–560. Zhao, T.; Beckham, H. W. *Macromolecules* **2003**, *36*, 9859–9865. Loontjens, T. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3198–3205. Divisia-Blohorn, B.; Genoud, F.; Borel, C.; Bidan, G.; Kern, J.-M.; Sauvage, J.-P. *J. Phys. Chem. B* **2003**, *107*, 5126–5132. Tuncel, D.; Steinke, J. H. G. *Macromolecules* **2004**, *37*, 288–302. Okada, M.; Harada, A. *Org. Lett.* **2004**, *6*, 361–364.

(17) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 5862–5866.

(18) Gibson, H. W.; Nagvekar, D.; Powell, J.; Gong, C.; Bryant, W. *Tetrahedron* **1997**, *53,* 15197–15207.

(19) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 8585–8591.

(20) Delaviz, Y.; Gibson, H. W. *Macromolecules* **1992**, *25*, 4859–4862. Gibson, H. W.; Nagvekar, D. S.; Yamaguchi, N.; Bhattacharjee, S.; Wang, H.; Vergne, M. J.; Hercules, D. M. *Macromolecules,* **2004**, *37*, 7514–7529.

(21) *Inter alia:* Kato, T.; Mizoshita, N.; Kanie, K. *Macromol. Rapid Commun.* **2001**, *22,* 797–814. Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101,* 4071–4098. Loontjens, T.; Put, J.; Coussens, B.; Lange, R.; Palmen, J.; Sleijpen, T.; Plum, B. *Macromol. Symp.* **2001**, *174*, 357–371. Berl, V.; Schmutz, M.; Krische, M. J.; Khoury, R. G.; Lehn, J.-M. *Chem.—Eur. J.* **2002**, *8,* 1227–1244. Johnson, D. W.; Hof, F.; Palmer, L. C.; Martin, T.; Obst, U.; Rebek, J., Jr. *Chem. Comm.* **2003**, *14*, 1638–1639. Ten Cate, A. T.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2004**, *126*, 3801–3808. Simic, V.; Bouteiller, L.; Jalabert, M. *J. Am. Chem. Soc.* **2003**, *125*, 13148–13154. Li, L.; Beniash, E.; Zubarev, E. R.; Xiang, W.; Rabatic, B. M.; Zhang, G.; Stupp, S. I. *Nature Mater.* **2003**, *2*, 689–694. Lortie, F.; Boileau, S.; Bouteiller, L. *Chem.—Eur. J.* **2003**, *9*, 3008–3014. Ojelund, K.; Loontjens, T.; Steeman, P.; Palmans, A.; Maurer, F. *Macromol. Chem. Phys.* **2003**, *204*, 52–60.

(22) Yamaguchi, N.; Nagvekar, D.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1998**, *37,* 2361–2364.

(23) Yamaguchi, N.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 143–147. Gibson, H. W.; Yamaguchi, N.; Jones, J. W. *J. Am. Chem. Soc.* **2003**, *125,* 3522–3533.

(24) Gibson, H. W.; Yamaguchi, N.; Hamilton, L. M.; Jones, J. W. *J. Am. Chem. Soc.* **2002**, *124,* 4653–4665.

(25) Harada, A.; Miyauchi, M.; Hoshino, T. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3519–3523. Percec, V.; Mitchell, C. M.; Cho, W.-D.; Uchida, S.; Glodde, M.; Ungar, G.; Zeng, X.; Liu, Y.; Balagurusamy, V. S. K.; Heiney, P. A. *J. Am. Chem. Soc.* **2004**, *126,* 6078–6094.

(26) Smith, A. P.; Fraser, C. L. *Macromolecules*, **2003**, *36*, 2654–2660. Smith, A. P.; Fraser, C. L. *Macromolecules*, **2003**, *36*, 5520–5525. Beck, J. B.; Rowan, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 13922–13923. Marin, V.; Holder, E.; Meier, M. A. R.; Hoogenboom, R.; Schubert, U. S. *Macromol. Rapid Commun.* **2004**, *25*, 793–798. Schmatloch, S.; Van Den Berg, A. M. J.; Hofmeier, H.; Schubert, U. *Des. Monomers Polym.* **2004**, *7*, 191–201.

(27) Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1865. Fyfe, M. C. T.; Stoddart, J. F. *Adv. Supramol. Chem.* **1999**, *5,* 1–53. Takata, T.; Kihara, N. *Rev. Heteroat. Chem.* **2000**, *22,* 197–218.

(28) Jones, J. W.; Gibson, H. W. *J. Am. Chem. Soc.,* **2003**, *125,* 7001–7004.

(29) Allwood, B. L.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1058–1061. Allwood, B. L.; Spencer, N.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1064–1066.

(30) Gong, C.; Gibson, H. W. *Macromol. Chem. Phys.* **1998**, *199*, 1801–1806.

(31) Jones, J. W.; Zakharov, L. N.; Rheingold, A. L.; Gibson, H. W. *J. Am. Chem. Soc.* **2002**, *124,* 13378–13379. Huang, F.; Fronczek, F. R.; Gibson, H. W. *J. Chem. Soc., Chem. Commun.* **2003**, 1480–1481.

(32) Huang, F.; Zhakarov, L.; Rheingold, A. L.; Jones, J. W.; Gibson, H. W. *J. Chem. Soc., Chem. Commun.* **2003**, 2122–2123.

(33) Jones, J. W.; Bryant, W. S.; Bosman, A. W.; Janssen, R. A. J.; Meijer, E. W.; Gibson, H. W. *J. Org. Chem.* **2003**, *68*, 2385–2389.

(34) Huang, F.; Jones, J. W.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 14458–14464.

(35) Odell, P. G.; Listigovers, N. A.; Quinlan, M. H.; Georges, M. K. *ACS Symp. Series* **1998**, *713*, 80–95. Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101,* 3661–3688. Bisht, H. S.; Chatterjee, A. K. *J. Macromol. Sci., Polym. Rev.* **2001**, *C41*, 139–173. Jerome, R. *Macromol. Symp.* **2002**, *177*, 43–59.

(36) Dao, J.; Benoit, D.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2161–2167.

(37) Gibson, H. W.; Nagvekar, D. S.; Yamaguchi, N.; Wang, F.; Bryant, W. S. *J. Org. Chem.,* **1997**, *62*, 4798–4803.

(38) (a) Rashidezadeh, H.; Guo, B. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 724–730. (b) Dourges, M.-A.; Charleux, B.; Vairon, J.-P.; Blais, J.-C.; Bolbach, G.; Tabet, J.-C. *Macromolecules* **1999**, *32*, **2,** 2495–2502. (c) Shen, X.; He, X.; Chen, G.; Zhou, P.; Huang, L. *Macromol. Rapid Commun.* **2000**, *21*, 1162–1165. (d) Willemse, R. X. E.; Staal, B. B. P.; Donkers, E. H. D.; Van Herk, A. M. *Macromolecules* **2004**, *37*, 5717–5723.

(39) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds,* 5th ed., J. Wiley and Sons: New York, 1991; p 30.

(40) Bryant, W. S.; Guzei, I. A.; Rheingold, A. L.; Gibson, H. W. *J. Org. Chem.* **1998**, *63*, 7634–7639.

(41) Job, P. *Ann. Chim.* **1928**, *9,* 113–203. Tsukube, H.; Furuta, H.; Odani, A.; Takeda, Y.; Kudo, Y.; Inoue, Y.; Liu, Y.; Sakamoto, H.; Kimura, K. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Lehn, J.-M., Eds.; Elsevier, New York, 1996; Vol. 8, p 425–482.

(42) Bryant, W. S.; Jones, J. W.; Mason, P. E.; Guzei, I.; Rheingold, A. L.; Fronczek, F. R.; Nagvekar, D. S.; Gibson, H. W. *Org. Lett.* **1999**, *1,* 1001–1004.

(43) Although crystal structures of rotaxanes based on BMP32C20 and its derivatives have not been reported, catenanes have been prepared from these crown ethers and demonstrated by X-ray crystal structures and other studies: Stoddart, J. F.; Williams, D. J.; Amabilino, D. B.; Anelli, P.-L.; Ashton, P. R.; Brown, G. R.; Cordova, E.; Godinez, L. A.; Hayes, W.; Kaifer, A. E.; Philp, D.; Slawin, A. M. Z.; Spencerk, N.; Stoddart, J. F.; Tolley, M. S.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11142–11170. Thus, it is clear that pseudorotaxane structures derived from BMP32C10 do exist.

(44) Connors, K. A. *Binding Constants: The Measurement of Molecular Complex Stability*; J. Wiley and Sons: New York, 1987.

(45) Weber, G. In *Molecular Biophysics*; Pullman, B., Weissbluth, M., Eds.; Academic Press: New York, 1965; pp 369–397. Wilcox, C. S. In *Frontiers in Supramolecular Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Eds.; VCH: New York, 1991; pp 123–143.

(46) Huang, F.; Fronczek, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125,* 9272–9273.

(47) Chiu, S.-H.; Rowan, S. J.; Cantrill, S. J.; Glink, P. T.; Garrell, R. L.; Stoddart, J. F. *Org. Lett.* **2000**, *2*, 3631–3634. Rowan, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 164–165. Chiu, S.-H.; Rowan, S. J.; Cantrill, S. J.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem.—Eur. J.* **2002**, *8*, 5170–5183. Yokunaga, Y.; Kakuchi, S.; Akasaka, K.; Nishikawa, N.; Shimomura, Y.; Isa, K.; Seo, T. *Chem. Lett.* **2002**, *8*, 810–811.

MA047811Y