Difunctional Paraquat Dications (Viologens) and Their Crown Complexes: A New Class of Rotaxane Monomers

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Received September 9, 1991
Revised Manuscript Received March 23, 1992

We envision polyrotaxanes as a new class of polymeric materials. Rotaxanes are compounds comprised of cyclic molecules penetrated by linear molecules, with no covalent bonds between the linear and cyclic components.[1-3] The name is derived from the Latin words for wheel and axle. The linear components (the axles) are usually terminated with bulky end groups to prevent loss of the cyclic species (the wheels). In macromolecular analogues this novel architecture is expected to display unusual physical and chemical properties due to the resultant independence of the cyclic and linear components.[4-11] In this paper, the synthesis of polyrotaxane precursors via host-guest complexation is reported.

We have recently shown that the production of linear macromolecules in the presence of a cyclic species does produce the polyrotaxane architecture.[4,5,8-11] The enthalpic term in the free energy expression describing the threading equilibrium (eq 1) is approximately zero in the case of essentially identical linear and cyclic species, which we refer to as homorotaxanes. However, in the case where the two components differ chemically, which we call heterorotaxanes, the ΔH term may be positive (repulsive). In our initial attempts to prepare heterorotaxanes, we pushed the equilibrium from the unthreaded state to the threaded state by using large quantities of macrocycles, as either the solvent or a cosolvent, during the preparation of linear macromolecules. That is, initially we chose to prepare polyrotaxanes by the use of the statistical threading approach,[4,5,8-11] driven primarily by entropy. We have envisioned that host-guest complexation could be used as an enthalpic driving force for the threading process. By this approach highly efficient, even quantitative, complexation allows formation of difunctional (AA) rotaxane monomers suitable for production of a wide range of interesting polyrotaxanes.

(1)

$$\ln K = -\Delta G/RT = -[\Delta H - T\Delta S]/RT$$

This work was inspired by Stoddart et al., who reported that bis(*p*-phenylene)-34-crown-10 (BPP34C10) (**1**; Scheme I) complexes with [Paraquat][PF$_6$]$_2$ (**2a**) by virtue of a combination of electrostatic and charge-transfer interactions, forming essentially quantitatively a 1:1 structure (**3a**), the guest (**2a**) residing within the cavity of the host (**1**).[12] In order to prepare AA rotaxane monomers, we examined the possibility of using difunctional viologens as guests for complexation by BPP34C10.

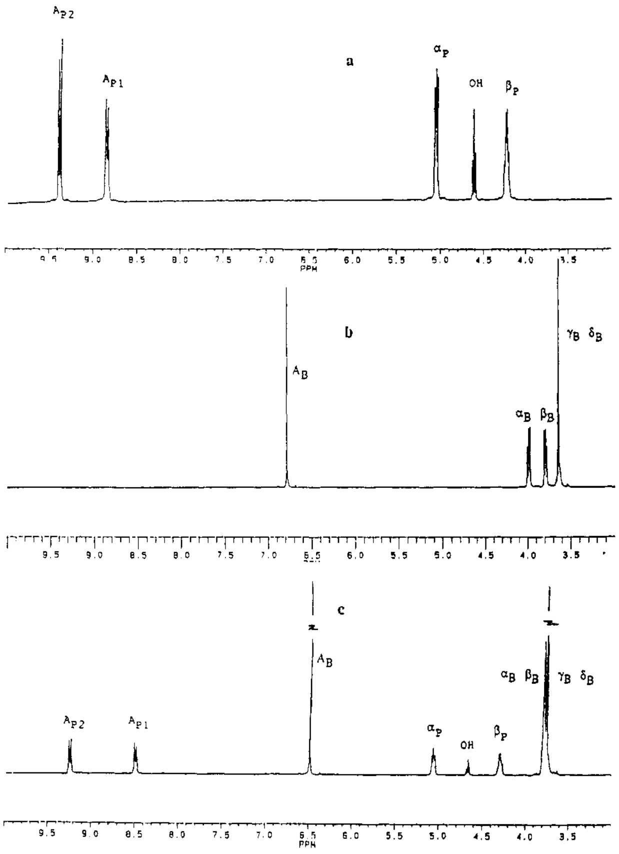

Figure 1. 270-MHz ^{1}H NMR spectra in acetone-d_6 of (a) *N,N'*-bis(2-hydroxyethyl)-4,4'-bipyridinium hexafluorophosphate (**2d**), (b) BPP34C10 (**1**), and (c) complex **3d**.

BPP34C10 was synthesized via the one-pot reaction of hydroquinone and tetrakis(ethylene glycol) ditosylate.[13] We selected 1,1'-bis[2-(carbomethoxy)ethyl]-4,4'-bipyridinium hexafluorophosphate (**2b**), 1,1'-bis(2-carboxyethyl)-4,4'-bipyridinium hexafluorophosphate (**2c**), and *N,N'*-bis(2-hydroxyethyl)-4,4'-bipyridinium hexafluorophosphate (**2d**) as difunctional viologens which could be used as polyrotaxane precursors. The procedure for **2d** is typical; it consisted of refluxing the functionalized alkyl iodide, 2-iodoethanol (27.50 g, 0.2200 mol), in the presence of 4,4'-bipyridine (16.65 g, 0.1066 mol) for 48 h. After cooling the mixture to room temperature, the resulting solid was filtered and washed with ethanol and acetone. To enhance the solubility of the dialkylated products in organic solvents, the iodide salts were converted to the bis(hexafluorophosphate) salts. For example, 1.0 g (2.1 mmol) of the crude iodide salt precursor to **2d** was dissolved in 2 mL of water and precipitated from 0.9 g (5.5 mmol) of ammonium hexafluorophosphate in 3 mL of water. The hexafluorophosphate salts were then purified by recrystallization from either water or water/alcohol mixtures.[14] Yields ranged from 40 to 90%.

Table I
^{1}H NMR Chemical Shift Changes ($\Delta\delta^a$) in Acetone-d_6 for BPP34C10 and Difunctional Paraquats in the Formation of Host-Guest Complexes[a]

complex	α_P	β_P	A_{P1}	A_{P2}	α_B	β_B	γ_B, δ_B	A_B
3b	0.09	−0.02	−0.29	−0.15	−0.20	−0.02	0.11	−0.33
3c	0.08	−0.02	−0.40	−0.19	−0.25	−0.06	0.15	−0.42
3d	0.06	0.02	−0.36	−0.13	−0.20	−0.04	0.10	−0.32

[a] $\Delta\delta = \delta(\text{complex}) - \delta(\text{free})$.

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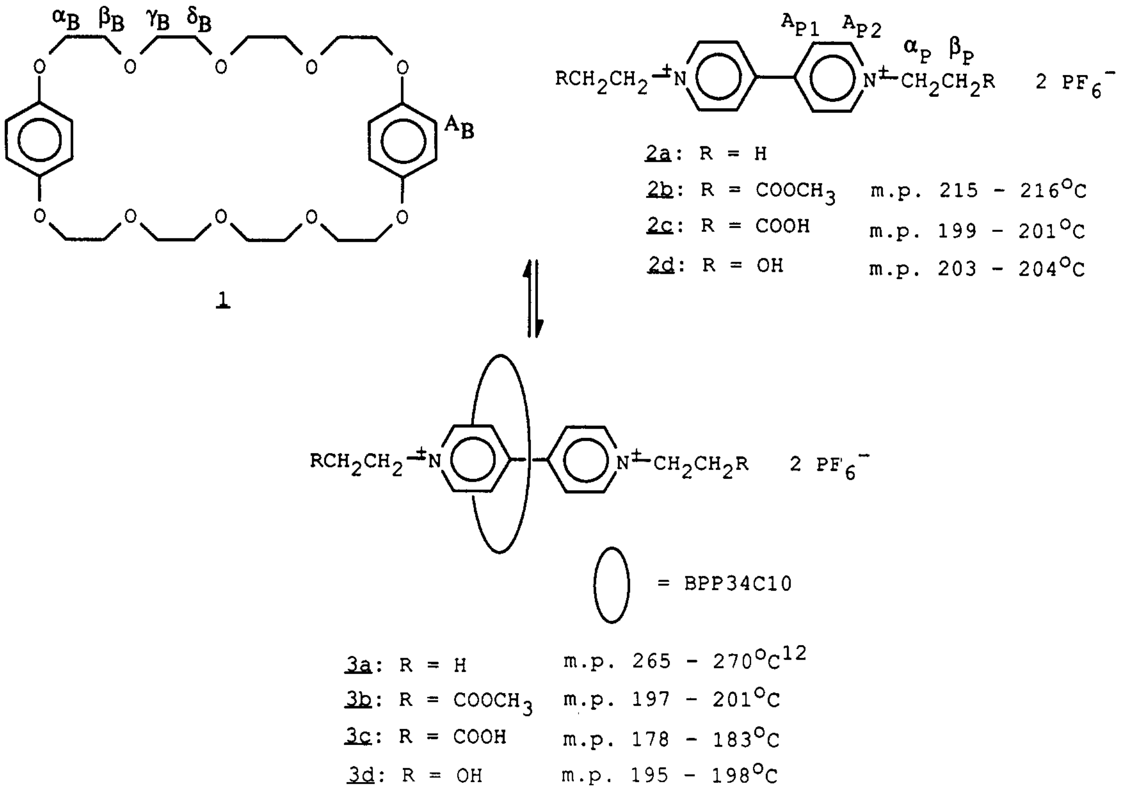
Scheme I



2a: R = H
2b: R = $COOCH_3$ m.p. 215 - 216°C
2c: R = COOH m.p. 199 - 201°C
2d: R = OH m.p. 203 - 204°C

3a: R = H m.p. 265 - 270°C[12]
3b: R = $COOCH_3$ m.p. 197 - 201°C
3c: R = COOH m.p. 178 - 183°C
3d: R = OH m.p. 195 - 198°C

Both the infrared and ^1H NMR spectra of these materials showed absorptions associated with both the macrocycle and the viologen. From comparison of the ^1H NMR spectra of **1**, **2d**, and **3d** (Figure 1), it is apparent that there are dramatic upfield shifts for the aromatic protons of the functionalized paraquat dication and the aromatic proton resonances of the macrocycle and also upfield shifts for the α and β ether protons and downfield shifts for the γ and δ protons. The chemical shift changes for all probe protons in the three complexes are listed in Table I. The sign and magnitude of these shifts indicate that an intraannular complex had been formed; the spectra are analogous to that reported by Stoddart et al. for **3a**.[12]

A typical procedure for the preparation of crystals suitable for an X-ray structure determination (**3b**) consisted of mixing BPP34C10 (0.50 g, 0.93 mmol) with 1,1′-bis[2-(carbomethoxy)ethyl]-4,4′-bipyridinium hexafluorophosphate (**2b**; 0.50 g, 0.93 mmol) in methanol (3 mL) and acetone (3 mL). The resulting intensely colored solutions were allowed to evaporate slowly in air for 3 days to yield red crystals (96–100%).[15] The X-ray diffraction results (Figure 2) confirmed that **3b** was such a 1:1 rotaxane complex. **3b** was monoclinic, belonged to the space group $C2/c$, and had unit-cell parameters of $a = 28.137$ (6) Å, $b = 11.677$ (3) Å, $c = 18.465$ (4) Å, and $\beta = 117.34$ (2)°. The X-ray crystal structure was solved by direct methods and refined by the full-matrix least-squares procedure to $R = 0.0522$ and 0.0729 for reflections with $F > 3\sigma$. X-ray crystallography of **3c** and **3d** (unrefined) revealed that these structures were similar.

However, most important of all, the picture derived from the crystal structure of this complex (**3b**) and the other complexes showed the functional groups extending outside the cavity of the crown ether, making them accessible for condensation polymerization techniques. We have successfully used **3d**, formed in situ from **1** and **2d**, as a chain extender for the prepolymer formed from poly(tetramethylene oxide) (MW = 650, 1000, and 2000) and bis(*p*-

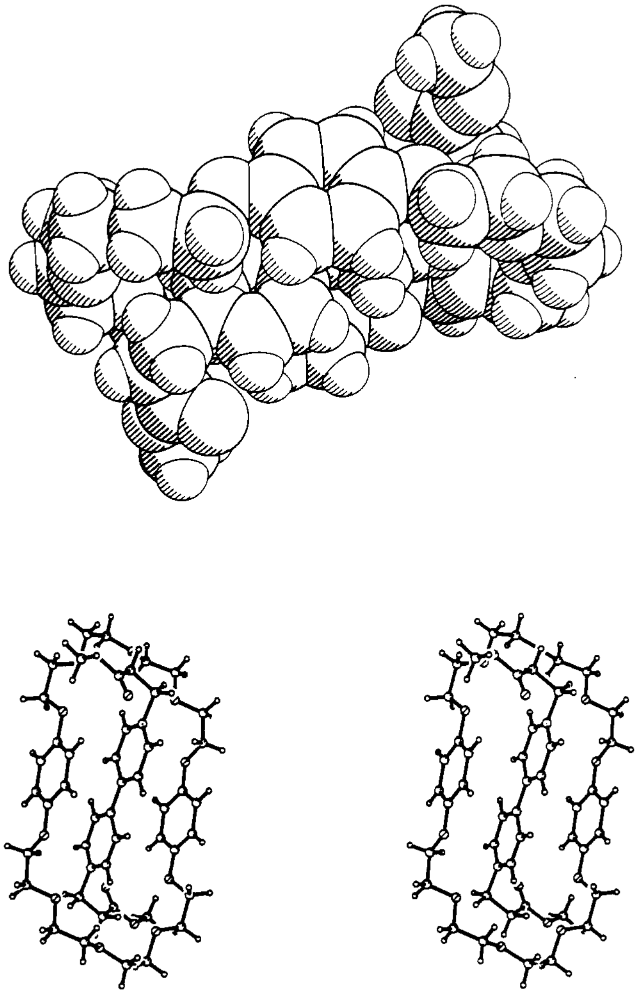


Figure 2. X-ray crystal structure of **3b** indicating the accessibility of the functional groups for polymerization.

isocyanatophenyl)methane (MDI) to prepare elastomeric polyrotaxanes and some other types of viologen-containing polyrotaxanes.[16] Similar chemical shift changes for probe protons were also observed. The ratio of BPP34C10 and **3d** incorporated in the polymers was 1:1, indicating the efficacy of this approach. Investigations are currently under way to determine how the macrocycle content effects the properties of the these ionomeric polyurethanes. The results of these investigations will be reported elsewhere.

Acknowledgment. We gratefully acknowledge financial support for this research from the National Science Foundation Polymers Program (DMR-8712428) and the NSF Science and Technology Center for High Performance Polymeric Adhesives and Composites (DMR-8809714). We are also grateful to Prof. J. F. Stoddart for sharing with us a large amount of inspiring chemistry prior to its publication.

Supplementary Material Available: Listing of structural characteristics and tables of atomic coordinates, isotropic and anisotropic displacement coefficients, and bond lengths and angles (6 pages); a table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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(14) Compounds were characterized spectroscopically (IR, NMR) and by elemental analysis, which confirmed the molecular structures. Anal. Calcd for **2b**: C, 34.85; H, 3.58; N, 4.52. Found: C, 34.76; H, 3.56; N, 4.49. Anal. Calcd for **2d**: C, 31.35; H, 3.76; N, 5.23. Found: C, 31.36; H, 3.35; N, 5.28.

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