8524 *Macromolecules* **1997,** *30,* 8524−8525

Relative Threading Efficiencies of Different Macrocycles: A Competitive Trapping Methodology Based on Hybrid Polyrotaxanes

Caiguo Gong and Harry W. Gibson*

Department of Chemistry, Virginia Polytechnic Institute & State University Blacksburg, Virginia 24061

Received July 29, 1997
Revised Manuscript Received October 31, 1997

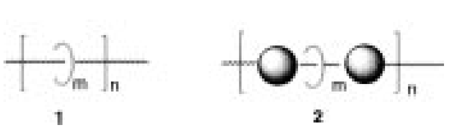
Polyrotaxanes represent a new class of macromolecular architectures.[1] As depicted in Scheme 1, in these materials macrocycles are penetrated by linear polymers and thus the two components are mechanically linked with each other either with or without blocking groups (BG) for polypseudorotaxane **1** and true polyrotaxane **2**, respectively (Scheme 1).[1−10] Since their properties are closely related to the macrocycle content (m/n value, average number of cyclics per repeat unit), the threading effiency of the cyclic species is of critical importance and a rapid, simple method to measure such values for different macrocycles would be very valuable to the field. Here, we report such a method by the preparation of hybrid polyrotaxanes.[11]

To eliminate dethreading during polymerization, we used bulky monomers, diol blocking group (BG) **3** and diacid chloride BG **4** (Scheme 2).[6] This trapping method precludes the loss of threaded cyclics during polymerization and makes it possible for us to compare the m/n values for different macrocycles in an accurate manner. In addition, since the threading process is controlled by a hydrogen bonding equilibrium (Scheme 3), the threading efficiency of crown ether-based polyrotaxanes is always related to the polymerization conditions, e.g., temperature, feed composition, and concentration.[6,7,8] Therefore, an internal standard, 30C10, was used; thus, a mixture of 30C10 and another macrocycle was used as solvent for polyrotaxane syntheses. Using this competitive threading methodology, the measured threading efficiencies of different macrocycles depend only on their true threading abilities, e.g., ring size, ring conformation, and hydrogen bonding strength with hydroxy groups. In practice, polyrotaxane **5** and hybrid polyrotaxanes **6** and **7** were prepared by polycondensation using 30-crown-10 (30C10), a mixture of 30C10 and bis(*p*-phenylene) 34-crown-10 (BPP34C10), and a mixture of 30C10 and dibenzo-24-crown-8 (DB24C8) as solvent, respectively. The unthreaded macrocycles were removed by five precipitations from THF solution into methanol.[12,13]

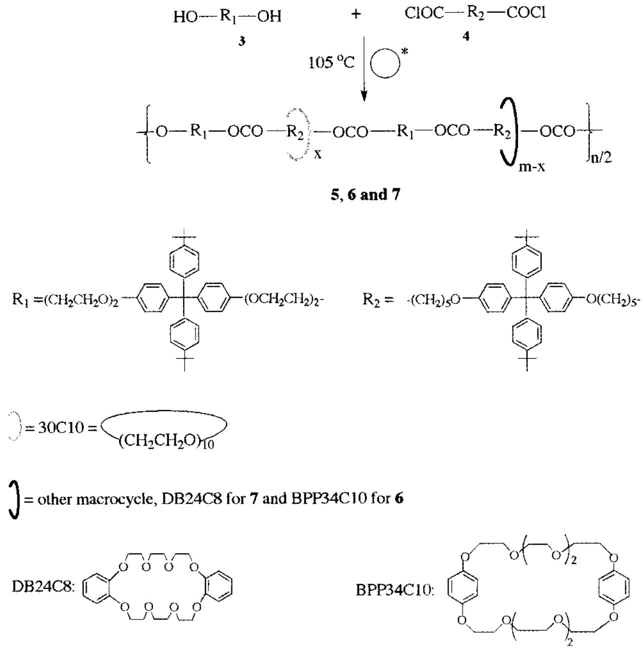
It is well understood that threaded 30C10 in polyrotaxane **5** has an upfield chemical shift compared to its free counterpart because of its through-space interaction with the electron rich aromatic rings of the BG units.[6] Interestingly, in hybrid polyrotaxane **6**, that (Figure 1b) of threaded BPP34C10 is also different from its free counterpart (Figure 1a).[5b] The ethylene protons b, c, and d are shifted upfield, surely because of the same reason as for those of 30C10.[6] The downfield shift of aromatic proton a is because of (i) the loss of free rotation of the aromatic rings upon threading[14] as observed previously for the poly(ester pesudorotaxane) of type 1[5b] or (ii) its through-space interaction with the in-chain ethyleneoxy moieties as in poly(ester rotaxane)s of type 2.[6] As expected, the same observation was made for DB24C8 in polyrotaxane **7**. Therefore, the proton NMR study directly proved the rotaxane structures of **5**, **6**, and **7**.

Scheme 1

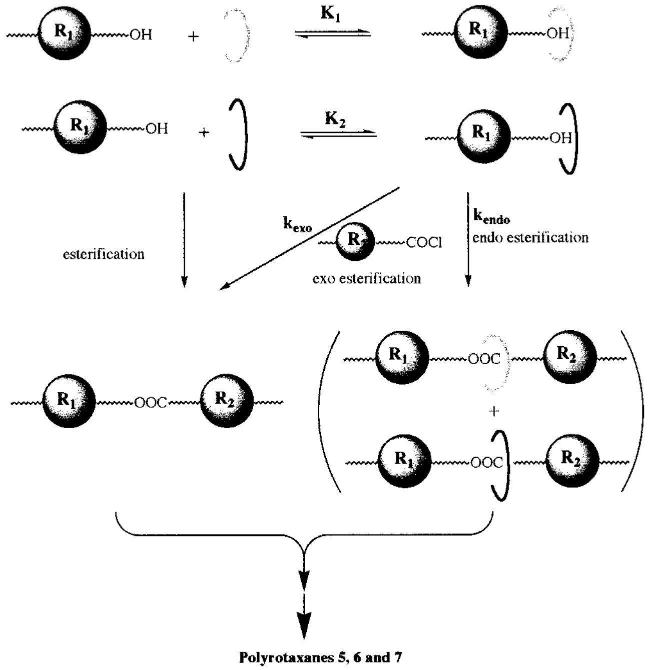
Two Types of Main Chain Polyrotaxanes



Scheme 2



Scheme 3



Capture constant = $[k_{endo}/(k_{endo}+k_{exo})]$

As the results in Table 1 show, by referring to 30C10 as the standard, BPP34C10 had a relative threading efficiency of 1.4, but the value for DB24C8, however, was only 0.84 under these conditions. The threading

S0024-9297(97)01140-6 CCC: $14.00

Table 1. Polymerization Conditions[a] and Threading Efficiencies for Polyrotaxanes 5, 6, and 7

polyrotaxane[b]	molar feed ratio of cyclic vs diol **3**	x/n, $(m - x)/n$[c]	relative threading efficiency[d]
5	30C10 (5.00)	0.11, 0	1.0
6	30C10 (2.50), BPP34C10 (2.50)	0.051, 0.069	1.4
7	30C10 (2.50), DB24C8 (2.50)	0.055, 0.046	0.84

[a] Conditions: temperature, 105 °C; time, 2 days.[12] [b] Unthreaded cyclic removed by precipitation into methanol five times.[12,13] [c] Measured by proton NMR.[12] [d] The ratio of threading efficiency of the cyclic vs that of 30C10.

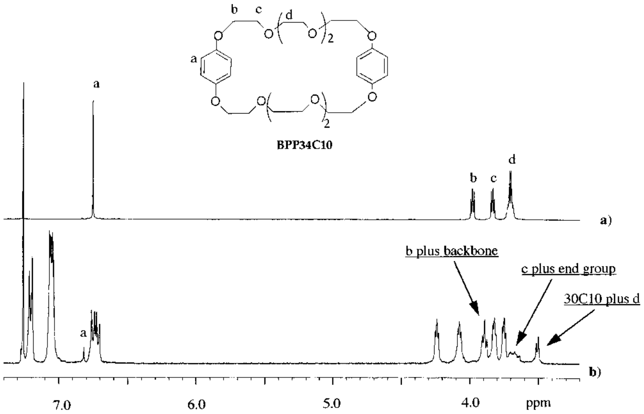


Figure 1. 400 MHz proton NMR spectra of (a) BPP34C10 and (b) hybrid polyrotaxane **6** in $CDCl_3$ at room temperature.

efficiency consists of two factors: the hydrogen-bonding association constant K and the capture constant, the fraction of hydrogen-bonded "prerotaxanes" that are threaded by endo esterification (Scheme 3). The better threading ability of BPP34C10 relative to 30C10 can be attributed to its larger ring size or possibly its higher rigidity which leads to a more open cavity, probably increasing the association and capture constants. The small ring size probably lowers both association and capture constants of DB24C8.

It is worth mentioning that the smallest macrocycle successfully used previously in polyrotaxanes was 30C10.[1,6] Therefore, this is the first time that a 24-membered macrocycle, DB24C8, has been successfully threaded onto a polymer backbone.[15] We believe the result is important to the field as well as encouraging to scientists. First, DB24C8 is commercially available and using it as the cyclic component for polyrotaxanes will save lots of precursor preparation time. In addition, since the ring movement on and/or around the backbone and the properties of polyrotaxanes are related to the ring size,[1] using such a small cyclic will probably induce interesting as well as important behaviors in these species.

In conclusion, a simple and accurate method is provided to determine the relative threading abilities of different macrocycles for polyrotaxane synthesis; this is done using 30C10 as cosolvent along with the studied macrocycle in competitive experiments. Since 30C10-based polyrotaxanes have been well studied,[6] similar systems can be explored with new macrocycles, even macrocycles as small as 24-membered rings, as demonstrated in the present work.

Acknowledgment. This work was supported by the National Science Foundation, Division of Materials Research, Grant No. DMR-93-20196 and DMR-97-06909.

References and Notes

(1) (a) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843. (b) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725. (c) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154. (d) Gibson, H. W. In *Large Ring Molecules*, Semlyen, J. A., Ed.; J. Wiley and Sons: New York, 1996; pp 191−262.

(2) (a) Wenz, G. *Macromol. Symp.* **1994**, *87*, 11. (b) Weickenmeier, M.; Wenz, G. *Macromol. Rapid. Commun.* **1996**, *17*, 731. (c) Steinbrunn, M. B.; Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2139. (d) Herrmann, W.; Keller, B.; Wenz, G. *Macromolecules* **1997**, *30*, 4966.

(3) (a) Born, M.; Ritter, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 309. (b) Born, M.; Ritter, H. *Adv. Mater.* **1996**, *8*, 149. (c) Born, M.; Ritter, H. *Macromol. Rapid Commun.* **1996**, *17*, 197.

(4) (a) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1994**, *27*, 4538. (b) Harada, A.; Okada, M.; Li, J.; Kamachi, M. *Macromolecules* **1995**, *28*, 8406.

(5) (a) Shen, Y. X.; Xie, D.; Gibson, H. W. *J. Am. Chem. Soc.* **1994**, *116*, 537. (b) Gibson, H. W.; Liu, S.; Lecavalier, P.; Wu, C.; Shen, Y. X. *J. Am. Chem. Soc.* **1995**, *117*, 852. (c) Gibson, H. W.; Liu, S.; Gong, C.; Ji, Q.; Joseph, E. *Macromolecules* **1997**, *30*, 3711. (e) Gibson, H. W.; Liu, S. *Macromol. Symp.* **1996**, *102*, 55. (f) Gong, C.; Gibson, H. W. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2331.

(6) (a) Gong, C.; Gibson, H. W. *Macromolecules* **1996**, *29*, 7029. (b) Gong, C.; Gibson, H. W. *Macromol. Chem. Phys.* **1997**, *198*, 2321. (c) Gong, C.; Ji, Q.; Glass, T. E.; Gibson, H. W. *Macromolecules* **1997**, *30*, 4087.

(7) (a) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 5862. (b) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 8585.

(8) Gong, C.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.*, in press.

(9) Mason, P. E.; Parsons, I. W.; Tolley, M. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2238.

(10) Owen, J.; Hodge, P. *J. Chem. Soc., Chem. Commun.* **1997**, 11.

(11) We define a polyrotaxane threaded with two or more different macrocycles as a hybrid polyrotaxane to distinguish it from a polyrotaxane threaded with one type of cyclic.

(12) The typical reaction scale yielded ca. 1 g of product. Due to very poor solubility of polymer backbone bearing BG moieties in methanol, the precipitation yield is higher than 90% for all polyrotaxanes **5**, **6**, and **7**, indicating a very low extent of fractionation. The m/n values for BPP32C10 and DB24C8 were measured by the integrals of the aromatic signals vs that of the backbone, e.g., proton a vs the -COOCH_2- signal at 4.25 ppm (Figure 1b) because these signals are well separated from each other. Substraction of that for proton d (calculated from the integral of proton a) from the total integral for 30C10 and proton d gave the m/n value of 30C10 (estimated relative error for m/n: ± 5%).

(13) M_w = 54K, 36K, and 42K for **5**, **6**, and **7**, respectively (PDI ~ 2.5) by GPC with PS standards.

(14) Out of phase rotation of the phenylene rings of BPP34C10 places proton a of one ring in the shielding zone of the other ring. In the polyrotaxane not only is rotation prevented but also the space between the rings is occupied and the aromatic proton a appears at nearly the same chemical shift (6.83 ppm) (Figure 1b) as those in *p*-dimethoxybenzene (6.85 ppm).

(15) DB24C8 has produced low molecular mass pesudorotaxanes: (a) Ashton, P. R.; Campbell, P. J.; Chrystal, E. S. T.; Glink, P. J.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1865. (b) Ashton, P. R.; Chrystal, E. S. T.; Glink, P. J.; Menzer, S.; Shiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1869.

MA9711405