Solid-State End-Capping of Pseudopolyrotaxane Possessing Hydroxy-Terminated Axle to Polyrotaxane and Its Application to the Synthesis of a Functionalized Polyrotaxane Capable of Yielding a Polyrotaxane Network

Nobuhiro Kihara,*,† Kazuma Hinoue,† and Toshikazu Takata‡

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Gakuen-cho 1-1, Sakai, Osaka 599-8531, Japan, and Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

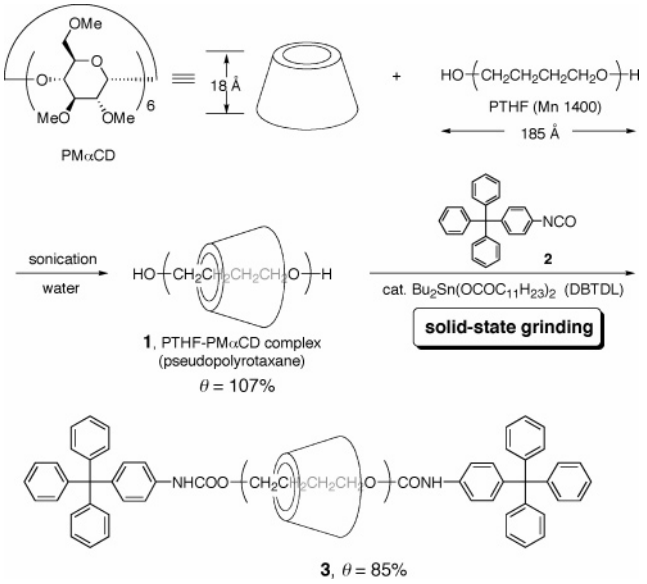
Received August 12, 2004
Revised Manuscript Received November 7, 2004

Harada et al. first reported that the complexation of linear polymers such as poly(ethylene glycol) (PEG) and poly(tetrahydrofuran) (PTHF) with cyclodextrins in water by the aid of hydrophobic interaction leads to the simple and practical entry to the synthesis of pseudopolyrotaxanes.[1−3] Because of the unique structure of the polyrotaxanes formed by the end-capping of the pseudopolyrotaxanes, a variety of sound applications such as stimuli-responding systems,[4] polyrotaxane network,[5] insulated molecular wires,[6] and antenna molecules[7] have been extensively studied. End-capping, which is necessary to fix the polyrotaxane structure prior to such applications, however, is a difficult task due to the dethreading inclination of the axle component from the wheel. Therefore, amine-terminated axle polymers have long been employed as axles of pseudopolyrotaxanes with both cyclodextrin wheels and permethylated cyclodextrin wheels, for rapid and efficient end-capping.[1−8] The use of hydroxy-terminated polymer as axle facilitates polyrotaxane synthesis because it has the dual advantage of being widely available and applicable, in contrast to amine-termined polymer.

Meanwhile, PTHF, one of the hydroxy-terminated polymers, forms the pseudopolyrotaxane complex with permethylated α-cyclodextrin (PMαCD).[9] Since PMαCD has no hydroxy group, the complex of PMαCD and PTHF may be end-capped by the usual acylation method,[10] yielding the corresponding polyrotaxane. In this communication, the authors wish to describe the successful synthesis of polyrotaxane by end-capping of the pseudopolyrotaxane comprising of PMαCD and PTHF with electrophiles *in the solid state*. The solid-state synthesis is applied to, as an example, the preparation of a wheel-functionalized polyrotaxane which can be derived to a topologically cross-linked polymer (polyrotaxane network, or so-called *topological gel*[5]).

The ^{1}H NMR spectrum of the PTHF (M_n 1400)−PMαCD complex (**1**), prepared according to the literature,[9] showed that one PTHF axle is surrounded by 11.0 PMαCD wheels, on average. The CPK model experiments demonstrated that the PTHF chain is ca. 185 Å long, while the PMαCD wheel is ca. 18 Å high. The coverage ratio (θ) of the PTHF chain by PMαCD was calculated as 107%, indicating that the axle was completely covered by PMαCD.

Scheme 1



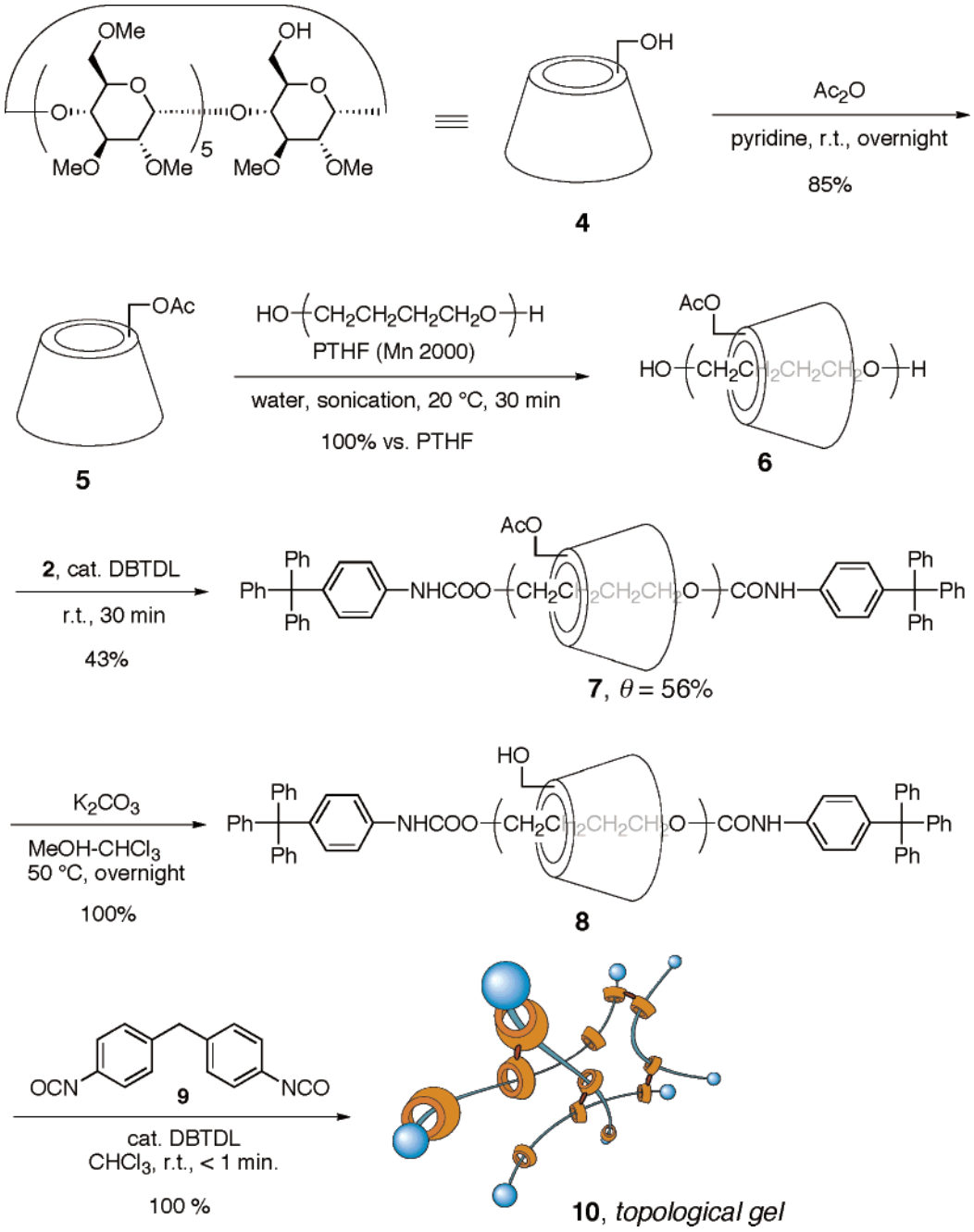
The end-capping experiment to fix complex **1** to the corresponding polyrotaxane was carried out with various electrophiles. The many acylation experiments in homogeneous systems were all in vain: in a typical case, a powder of **1** was added to a solution of large excess of 4-tritylphenyl isocyanate (**2**)[11] in the presence of a catalytic amount of dibutyltin dilaurate (DBTDL, 7 mol %) in DMAc. However, the polymer fraction obtained from the reaction mixture was just the urethane-end-capped PTHF (quantitative yield) without any PMαCD. The results clearly show that PMαCD dethreading occurs at a much faster pace than urethane formation at the axle termini when any solvent, even highly polar DMAc, is used.

We thereby subjected it to solid-state reaction. Very recently, Otera reported highly effective rotaxane synthesis in the solid state.[12] A mixture of **1**, **2**, and DBTDL was well ground in an agate mortar at room temperature. From the mixture after 30 min grinding, polyrotaxane **3** was isolated in 24% yield as the ether- and methanol-insoluble part. The ^{1}H NMR spectrum of **3** in chloroform suggests that the two terminal hydroxy groups were completely converted to urethane groups and that **3** had 8.7 PMαCD wheels on average (θ 85%). The molecular weight of **3**, which was M_n 10 200 (M_w/M_n 1.32, estimated by GPC in chloroform, based on PSt standards), corresponds well to the calculated value (10 900) by ^{1}H NMR analysis.[13] The grinding was prolonged to 90 min, but neither θ nor yield increased. Therefore, the reaction was completed within 30 min. The low yield of **3** seems to indicate that **1**, in which at least one of the terminal hydroxy groups is located in the cavity of cyclodextrin, hardly underwent solid-state reaction. This speculation is coincident with the apparent decrease of θ value during the end-capping as well as with the fact that the conversion ratio of the terminal hydroxy group to the urethane group in PTHF-based product recovered from the ether-soluble part was less than 50%. Further, when PTHF underwent a similar

† Osaka Prefecture University.
‡ Tokyo Institute of Technology.
* Corresponding author. E-mail: kihara@chem.osakafu-u.ac.jp.

10.1021/ma048337z CCC: $30.25
Published on Web 12/31/2004

Scheme 2

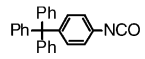
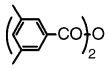
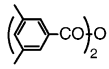


solid-state reaction with **2**, its two terminal hydroxy groups were completely converted to urethane groups. Solid-state reactions under various conditions were examined. Both pressing at 400 kg/cm^2 and sonication together with pressing afforded no polyrotaxane. When a completely heterogeneous suspension of **1** in a hexane solution of **2** and DBTDL was stirred overnight, **3** was obtained in only 1% yield (θ 54%). It was concluded that both pressing and stirring are essential to obtain densely packed polyrotaxane in good yield.

The effects of temperature and electrophile as end-capping agent were evaluated (Table 1). As the reaction temperature rose, both θ and yield increased slightly ($\theta \sim 95\%$ and yield $\sim 30\%$) (runs 1−4), suggesting that the end-capping of the terminal hydroxy groups of PTHF is accelerated at higher temperatures. Isocyanate was an effective end-capping agent, whereas acid chloride was less effective (runs 1, 5, and 6). The only trace amount of **3** was obtained when 3,5-dimethylbenzoic anhydride was used with 4-(dimethylamino)pyridine (DMAP) or tributylphosphine[2,10] as catalyst (runs 7 and 8). No polyrotaxane was obtained with triphenysilyl chloride (run 9).

The applicability of the present solid-state polyrotaxane synthesis was demonstrated by the preparation of a functionalized polyrotaxane with versatile utility that has one hydroxy group per cyclodextrin wheel. This type of functionalization may provide the fundamental structures for a wide range of polyrotaxane-related devices and materials. Monohydroxycyclodextrin **4** was prepared by the literature method with slight modification.[14] Protection of the hydroxy group by acetylation (85% yield) was followed by complexation with PTHF (M_n 2000) to produce pseudopolyrotaxane **6** (100% yield).

Table 1. Solid-State End-Capping of PTHF−PMαCD Complex 1 with Electrophile[a]

run	electrophile	catalyst	temp./ °C	polyrotaxane	yield[b] / %	θ[c] / %
1		DBTDL[d]	r.t.	**3a**	24	85
2			40	**3a**	20	90
3			60	**3a**	25	90
4			80	**3a**	30	95
5		DBTDL[d]	r.t.	**3b**	14	89
6		DMAP-Et_3N[e]	r.t.	**3c**	8	81
7		DMAP[f]	r.t.	**3c**	trace	-
8		Bu_3P[f]	r.t.	**3c**	trace	-
9	Ph_3SiCl	DMAP-Et_3N[e]	r.t.	**3d**	0	-

[a] Reaction was carried out in an agate mortar at room temperature for 30 min. 60 equiv (vs OH) of electrophile was used. [b] Ether- and methanol-insoluble part. [c] Calculated from the ^1H NMR spectrum. [d] 7 mol % vs OH group. [e] 6 mol % of DMAP and 1 equiv of Et_3N vs OH group. [f] 6 mol % vs OH group.

The solid-state end-capping of **6** with **2** gave rise to the formation of polyrotaxane **7** in which 8.2 wheels per axle on average were threaded (43% yield, θ 56%). The methanolysis of **7** quantitatively yielded polyrotaxane **8** with the hydroxy-functionalized wheels. To confirm the versatile utility of **8**, the derivation of **8** to a polyrotaxane network *topological gel*[5] was studied as an example, since **8** could be regarded as a polyhydroxy-functionalized polymer or topological cross-linker. **8** was treated with diphenylmethane diisocyanate ([NCO]/[OH] = 0.5) in the presence of DBTDL as catalyst in chloroform. The gelation immediately took place to quantitatively give gelled material (**9**); that is, the polymer cross-linked via interlocked bonding.[5] Gel **9** showed remarkable swelling property despite a fairly high cross-linking ratio: the maximal absorption of typical organic solvents was 1.80 g/g for DMF and 19.3 g/g for chloroform.

Thus, the present study successfully demonstrates that the end-capping of the pseudorotaxane with the hydroxy-terminated axle can be accomplished in a *solid-state reaction* to give the polyrotaxane with a high content of wheel component. The potential utility of this solid state synthesis was exemplified in a preparation of the wheel-functionalized polyrotaxane capable of undergoing cross-linking, leading to a novel polyrotaxane network. The gel is characterized not only by the topological cross-linking but also by the discrete cross-linked structure.

Acknowledgment. This work was partly supported by the Priority-Area-Research by the Ministry of Education, Science, Technology, Sports and Culture of Japan, and Yazaki Memorial Foundation for Science and Technology, which are greatly acknowledged.

Supporting Information Available: Experimental procedures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Harada, A. *Acta Polym.* **1998**, *49*, 3. (b) Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456.

(2) Takata, T.; Kihara, N.; Furusho, Y. In *Advances in Polymer Science*; Springer: Heidelberg, 2004; Vol. 171, p 1. (b) Takata, T. *Mirai Zairyo* (*Expected Materials for the Future*) **2002**, *2*, 1.

(3) Nepogodiev, S. A.; Stoddart, J. F. *Chem. Rev.* **1998**, *98*, 1959. (b) In *Molecular Catenanes, Rotaxanes and Knots*; Sauvage, J.-P., Dietrich-Buchecker, C. O., Eds.; Wiley: Weinheim, 1999.

(4) Fujita, H.; Ooya, T.; Yui, N. *Polym. J.* **1999**, *31*, 1099. (b) Fujita, H.; Ooya, T.; Yui, N. *Macromolecules* **1999**, *32*, 2534. (c) Fujita, H.; Ooya, T.; Yui, N. *Macromol. Chem. Phys.* **1999**, *200*, 706. (d) Ikeda, T.; Ooya, T.; Yui, N. *Polym. J.* **1999**, *31*, 658. (e) Choi, H. S.; Huh, K. M.; Ooya, T.; Yui, N. *J. Am. Chem. Soc.* **2003**, *125*, 6350. (f) Ooya, T.; Eguchi, M.; Yui, N. *J. Am. Chem. Soc.* **2003**, *125*, 13016.

(5) (a) Okumura, Y.; Ito, K. *Adv. Mater.* **2001**, *13*, 485. (b) Oku, T.; Furusho, Y.; Takata, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 966 and references therein.

(6) (a) Yoshida, K.; Shimomura, T.; Ito, K.; Hayakawa, R. *Langmuir* **1999**, *15*, 910. (b) Shimomura, T.; Yoshida, K.; Ito, K.; Hayakawa, R. *Polym. Adv. Technol.* **2000**, *11*, 837. (c) Yamaguchi, I.; Nurulla, I.; Yamamoto, T. *Kobunshi Ronbunshu* **2000**, *57*, 472. (d) Taylor, P. N.; O'Connell, M. J.; McNeill, L. A.; Hall, M. J.; Aplin, R. T.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3456.

(7) (a) Tamura, M.; Ueno, A. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 147. (b) Tamura, M.; Gao, D.; Ueno, A. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2012. (c) Tamura, M.; Gao, D.; Ueno, A. *Chem.—Eur. J.* **2001**, *7*, 1390.

(8) (a) Harada, A.; Li, J.; Kamachi, M. *Nature (London)* **1992**, *356*, 325. (b) Harada, A.; Li, J.; Kamachi, M. *Nature (London)* **1993**, *364*, 516. (c) Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1993**, *26*, 5698.

(9) Szejtli, J.; Liptak, A.; Jodai, I.; Féedi, P.; Nanasi, P.; Neszmelyi, A. *Starch* **1980**, *32*, 165. (b) Okada, M.; Kamachi, M.; Harada, A. *Macromolecules* **1999**, *32*, 7202.
(10) Takata, T.; Kihara, N. *Rev. Heteroat. Chem.* **2000**, *22*, 197. (b) Kihara, N.; Takata, T. *J. Synth. Org. Chem. Jpn.* **2001**, *59*, 206. (c) Furusho, Y.; Sasabe, H.; Natsui, D.; Murakawa, K.; Harada, T.; Takata, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 179. (d) Kihara, N.; Nakakoji, N.; Takata, T. *Chem. Lett.* **2002**, 925. (e) Watanabe, N.; Yagi, T.; Kihara, N.; Takata, T. *Chem. Commun.* **2000**, 2720. (f) Kihara, N.; Shin, J.-I.; Ohga, Y.; Takata, T. *Chem. Lett.* **2001**, 592. (g) Kawasaki, H.; Kihara, N.; Takata, T. *Chem. Lett.* **1999**, 1015.
(11) Hardy, D. V. N. *J. Chem. Soc.* **1934**, 2001.
(12) Orita, A.; Okano, J.; Tawa, Y.; Jiang, L.; Otera, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3724.
(13) Since **3** is estimated to be more rigid than PSt (standards for the calibration of GPC), the comparison of molecular weight using GPC may include an error.
(14) Melton, L. D.; Slessor, K. N. *Carbohydr. Res.* **1971**, *18*, 29. (b) Tanaka, M.; Kawaguchi, Y.; Niinae, T.; Shono, T. *J. Chromotogr.* **1984**, *314*, 193. (c) Kaneda, T.; Fujimoto, T.; Goto, J.; Asano, K.; Yasufuku, Y.; Jung, J. H.; Hosono, C.; Sakata, Y. *Chem. Lett.* **2002**, 514.

MA048337Z