Supplementary Material (ESI) for Chemical Communications

Thermoreversible sol-gel transition of aqueous solution of polyrotaxane composed of highly methylated α-cyclodextrin and polyethylene glycol

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ELECTRONIC SUPPLEMENTARY INFORMATION

(7 Pages)

Introduction

In this supplement, we describe the experimental procedures for the synthesis of the methylated polyrotaxane **1**-**4**, together with their characterization by means of NMR and GPC. X-ray diffraction (XRD) patterns for a 20wt% aqueous solution **1** are also shown.

Experimental Details for the Synthesis of the Methylated Polyrotaxane

General methods: Sodium hydride was purchased from Ardrich. Iodomethane and all solvents were purchased from Wako Pure Chemical Industries, Ltd.. All chemicals were obtained from commercial suppliers and were used as supplied. Polyrotaxane **5** used in this study was prepared from α-CD, poly(ethylene glycol) of average molecular weight 35000, and adamantanamine according to previously reported method.[1] The number of α-CD in the polyrotaxane was estimated at ca. 110 from the 1H-NMR signals, which corresponds to 28% coverage of PEG chain by α-CDs supposing that a α-CD molecule can perfectly cover two PEG monomer units.

Preparation of Methylated Polyrotaxane **1**. Polyrotaxane **5** (10 g) dried under vacuum at 80°C for two hours was dissolved in 100ml of DMSO dehydrated. To the solution sodium hydride (3.7g, 0.15 mol, 1.1eq to OH groups of polyrotaxane **5**) was added under argon atmosphere and rapidly stirred for 2 hours at room temperature. Then iodomethane (21.3 g, 0.15 mol) was slowly added to the suspension and stirring for 18 hours. The reaction mixture was dialyzed against water for 4 days with cellose tube (MWCO=12000) and freeze-dried to give a colourless solid. Finally, the solid was dissolved in dichloromethane, precipitated from ethanol, corrected by centrifugation and dried under vacuum at 80°C to give 5.7 g of **1** as a colourless solid. 1H NMR (400 MHz, $CDCl_3$, ppm): δ=5.2-4.8 (C(1)H of CD), 4.1-3.1 (C(2-6)H and OCH_3 of CD, and CH_2 of PEG), 3.60 (CH_2 of PEG).

Preparation of Methylated Polyrotaxane **2** and **3**. Polyrotaxane **2** and **3** were synthesised in a similar manner to preparation of **1** except for the amount of the reagent and for purification method. 0.8 and 0.6eq of sodium hydride and iodomethane were used for **2** and **3**, respectively. After dialysis the reaction mixture and freeze-dried in a similar manner to **1**, the obtained solid was washed with dichloromethane, corrected by filtration and dried under vacuum at 80°C to give 7.4 g and 8.3 g of **2** and **3** ,respectively, as a colourless solid. 1H NMR (400 MHz, DMSO-d_6, ppm): **2** δ=4.95 (C(1)H of CD), 4.76 (C(1)H of CD), 4.1-3.0 (C(2-6)H and OCH_3 of CD, and CH_2 of PEG), 3.49 (CH_2 of PEG); **3** δ=4.97 (C(1)H of CD), 4.76 (C(1)H of CD), 4.46 (O(6)H of CD), 4.1-3.0 (C(2-6)H and OCH_3 of CD, and CH_2 of PEG), 3.49 (CH_2 of PEG).

Preparation of methylated polyrotaxane **4**. **4** was prepared by using 28% sodium methoxide methanol solution instead of using sodium hydride for alkali. Polyrotaxane **5** (5 g) dried under vacuum at 80°C for two hours was dissolved in 50ml of DMSO dehydrated. To the solution 28% sodium methoxide methanol solution (2.7g, 0.014 mol, 0.2eq to OH groups of polyrotaxane **5**) was added under argon atmosphere and rapidly stirred for 2 hours at room temperature and then removed methanol under vacuum. Then iodomethane

(2.0 g, 0.014 mol) was slowly added to the solution and stirring for 18 hours. The reaction mixture was dialyzed against water for 4 days with cellulose tube (MWCO=12000) and freeze-dried to give a colourless solid. Finally, the solid was washed with dichloromethane, corrected by filtration and dried under vacuum at 80°C to give 4.5 g of **1** as a colourless solid. 1H NMR (400 MHz, DMSO-d_6, ppm): δ=5.88-5.42 (O(2)H and O(3)H of CD), 4.99 (C(1)H of CD), 4.80 (C(1)H of CD), 4.43 (O(6)H of CD), 4.1-3.0 (C(2-6)H and OCH_3 of CD, and CH_2 of PEG), 3.51 (CH_2 of PEG).

Characterisation. NMR spectra were recorded on a JEOL JNM-AL400 spectrometer. Gel permeation chromatography: (GPC) was carried out on a Shimadzu HPLC system, equipped with a refractive index detector (for **1**, Shodex K-800D and two Shodex K-806L columns, eluent: chloroform, flow rate: 1 $mLmin^{-1}$; for **2**-**5**, Shodex SB-G and two Shodex SB-806M HQ columns, eluent: DMSO/0.01M LiCl, flow rate: 0.4 $mLmin^{-1}$). Temperature dependence of transmittance of the solution was performed by Agilent 8453 UV-visible spectrophotometer equipped with temperature controller. The X-ray diffraction patterns were measured using a diffractometer (type 4037, Rigaku) with graded d-space elliptical side-by-side multilayer optics, monochromatic CuKα radiation (40 kV, 30 mA, λ = 1.542 Å), and an imaging plate (R-Axis IV) in a flat camera. The samples were sealed in quartz capillary tubes (1.5-mm diameter; 0.01-mm wall thickness) and positioned on a hot stage (Mettler FP82HT). The powders and solutions were exposed to a radiation beam for 10 and 30 minutes, respectively, with a 150-mm camera length.

Methylation ratio and purity of the products.
Figure 1 shows the 1H NMR spectra for the polyrotaxanes with different methylation ratio. The peaks at 5.61, 5.48 and 4.43 ppm for hydroxyl groups of α-CD decrease with increasing amount of the reagents. Methylation ratio of the products was estimated by comparing integrations between the regions at 6.0-4.5 ppm (OH and H1) and at 4.2-2.8 ppm (other protons). The ratio 87, 74, 52, 19% are estimated for **1**, **2**, **3** and **4**, respectively. New peak appeared at around 4.95 ppm accompanied with methylation. This peak is also assigned to H1 when OH3 is alkylated.[2] Purity of methylated polyrotaxane was examined by GPC (Fig. 2). The chromatograms for **1**-**4** show large peaks in the region of higher molecular weight comparing with PEG (Mw=35000). Slight residues are observed in the region of CDs. These results indicate that methylation of the polyrotaxane can be controlled by feeding ratio of the reagents.

XRD measurement.
Figure 3 shows XRD patterns for the 10wt% aqueous solution of **1** at 5°C (sol) and 60°C (gel) together with the powder of **1**, respectively. Two remarkable peaks, corresponding to those observed for the powder sample, are observed at 8.4° and 12.5° for the solution at 60°C, though no peaks are observed for the solution at 5°C. This result indicates that the gel has a periodical structure, such as microcrystalline, acting as physical crosslinks.[3]

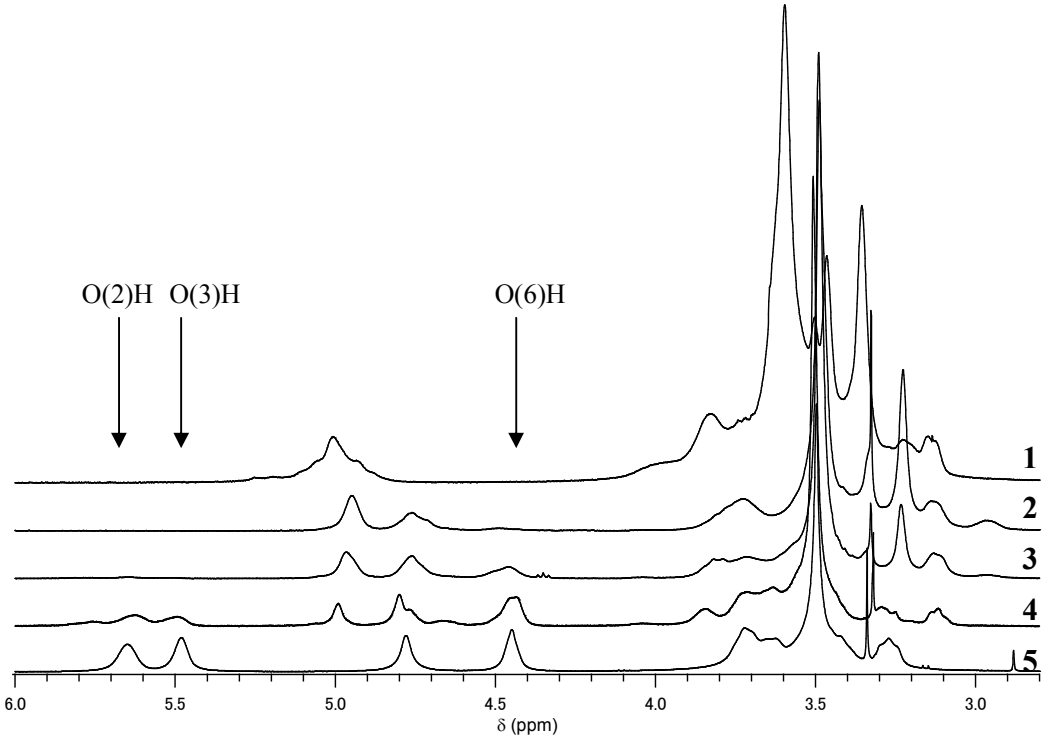

Fig. 1 1H NMR spectra for methylated polyrotaxane **1**-**5** (**1** in $CDCl_3$ and **2**-**5** in DMSO-d_6). The arrows indicate the three hydroxyl protons (O(2)H, O(3)H and O(6)H) of α-CD for unmodified polyrotaxane **5** at 5.61, 5.48 and 4.43 ppm, respectively.

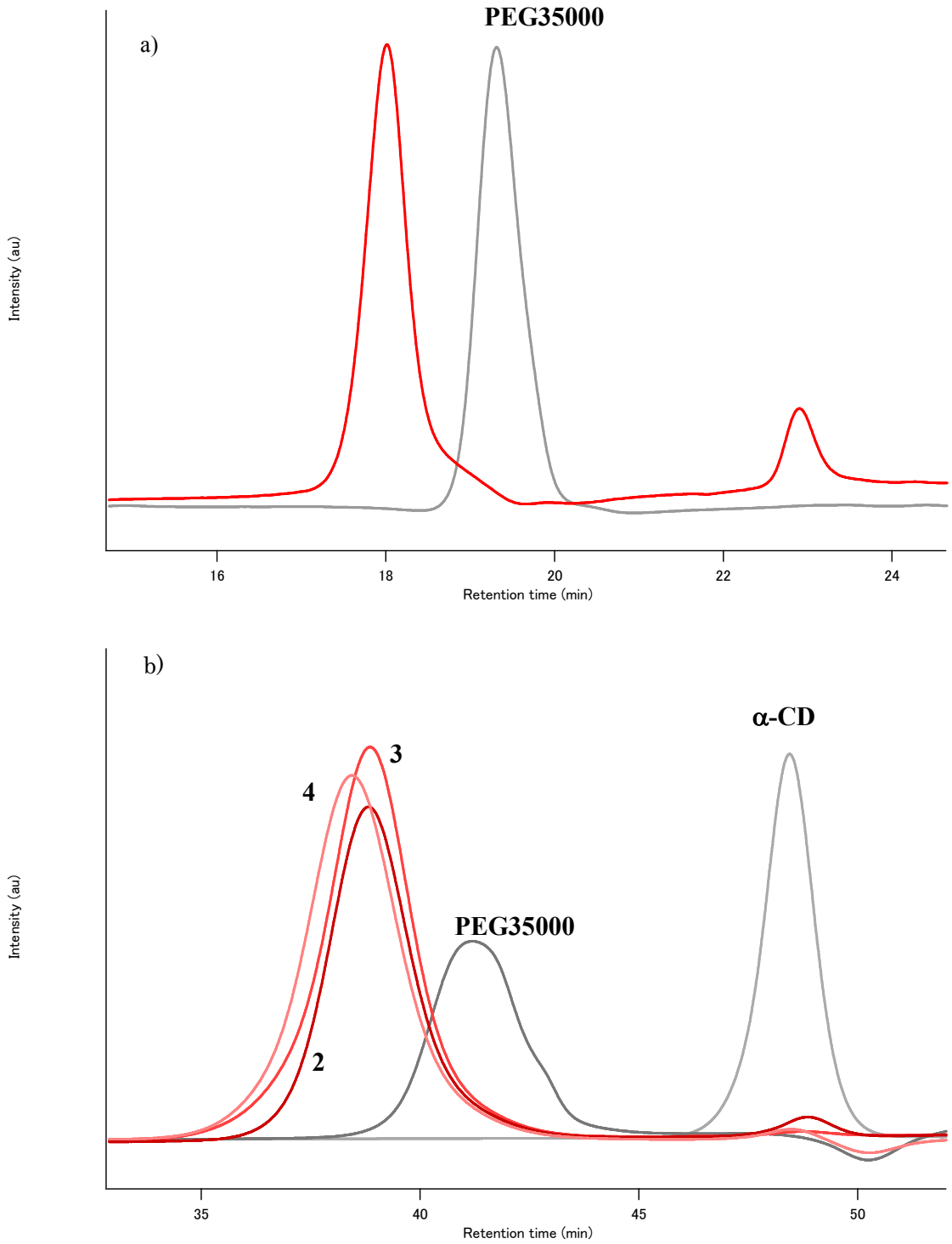

Fig. 2 Chromatograms of **1** (a) and **2**-**4** (b) with PEG35000 and α-CD.

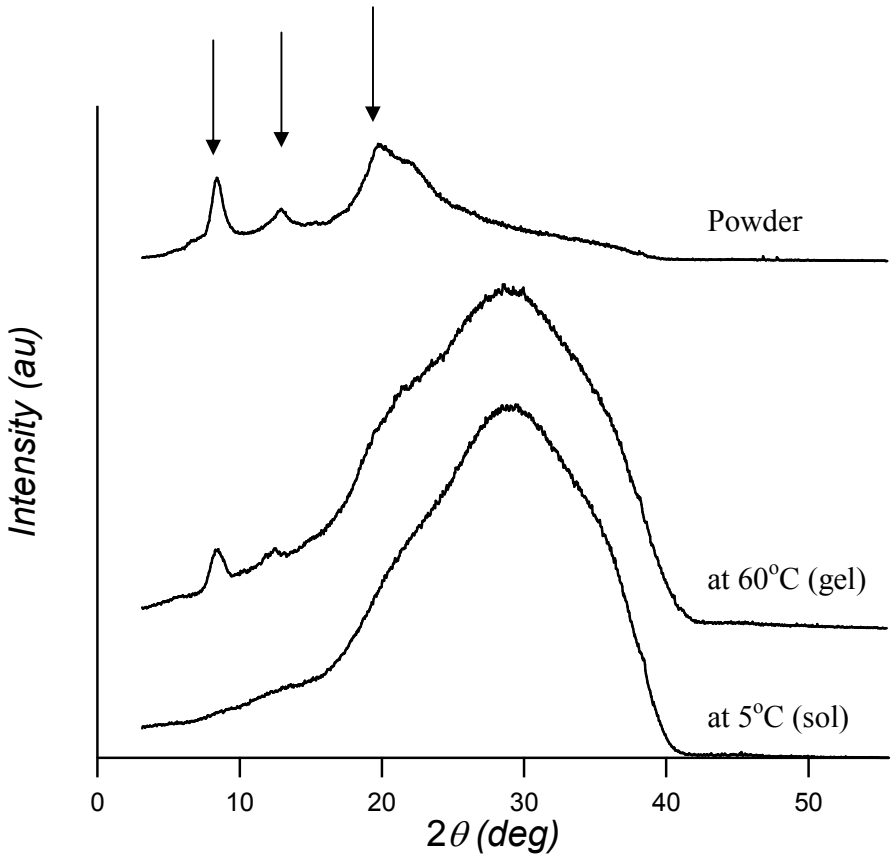

Fig. 3 XRD patterns for the 10wt% aqueous solution of **1** at 5°C (sol) and 60°C (gel) together with the powder of **1**, respectively. The arrows represent the position of typical peaks for powder of **1**.

References

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