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Polyether-based polyrotaxane synthesis with controlled β-cyclodextrin threading ratio

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Abstract

An effective one-pot polyrotaxane synthesis with control of the threading ratio is realized. 2,5-Bis(chloromethyl)-4-methoxy-1-octoxybenzene (PMOC) is condensed with a starting rotaxane consisting of a bisphenol A salt threaded into β-cyclodextrin (βCD), to lead to a βCD-threaded polyether. We demonstrate that the threading ratio of βCD on the polyether chain (ratio between the polymer repeat units and the βCD in polyrotaxane) can be varied from zero to unity depending on two parameters: the reactant concentration and the bulkiness of the counter-ion stopper in the starting rotaxane.

Keywords: β-Cyclodextrin; Polyether; Polyrotaxane

1. Introduction

In general, the driving forces in inclusion complexes between, for example, cyclodextrins (CDs) and polymeric chains are intermolecular hydrogen bonding between neighbouring CDs, steric fitting and hydrophobic interactions between the host and guest molecules [1]. Several physical and chemical parameters have been used to control the assembly of the CDs in a polyrotaxane: temperature [2], thermal treatment [3], electrical potential stimuli [4], pH [5], anionic or cationic charges in solution [6,7], and solvent effects [8].

The chemical polymerization of rotaxane units to obtain polyrotaxanes remains a real challenge, the major difficulty being the control of the threading ratio (ratio between the polymer repeat units and the βCD in the polyrotaxane) [8].

The synthesis of polyrotaxanes is not yet sufficiently developed, despite the potential interest of these products. Recently, Nishida et al. [9] showed that a polyrotaxane based on αCD, threaded onto free pre-synthesized polyethylene glycol chains with a low threading ratio, acts as both the relaxation and reinforcing reagents in Novolac-type epoxy resins, but found that the threading ratio cannot be controlled by this procedure.

Polycondensation is a rapid, high-yield, one-pot, multi-step process. It is used in the manufacture of polycarbonates, polyethers and polysulfonates from bisphenol derivatives and particularly bisphenol A [BPA: 2,2-bis(4-hydroxyphenyl)propane], the most commonly used monomer [10].

In this paper, the polycondensation of 2,5-bis(chloromethyl)-1-methoxy-4-octoxybenzene (PMOC) on a rotaxane, based on a bisphenol A salt as host and βCD as guest, is used to synthesize polyether-threaded βCD. Our aim is to prevent partially or totally dethreading of reaction intermediates when polymerization occurs. For the first time, we show that

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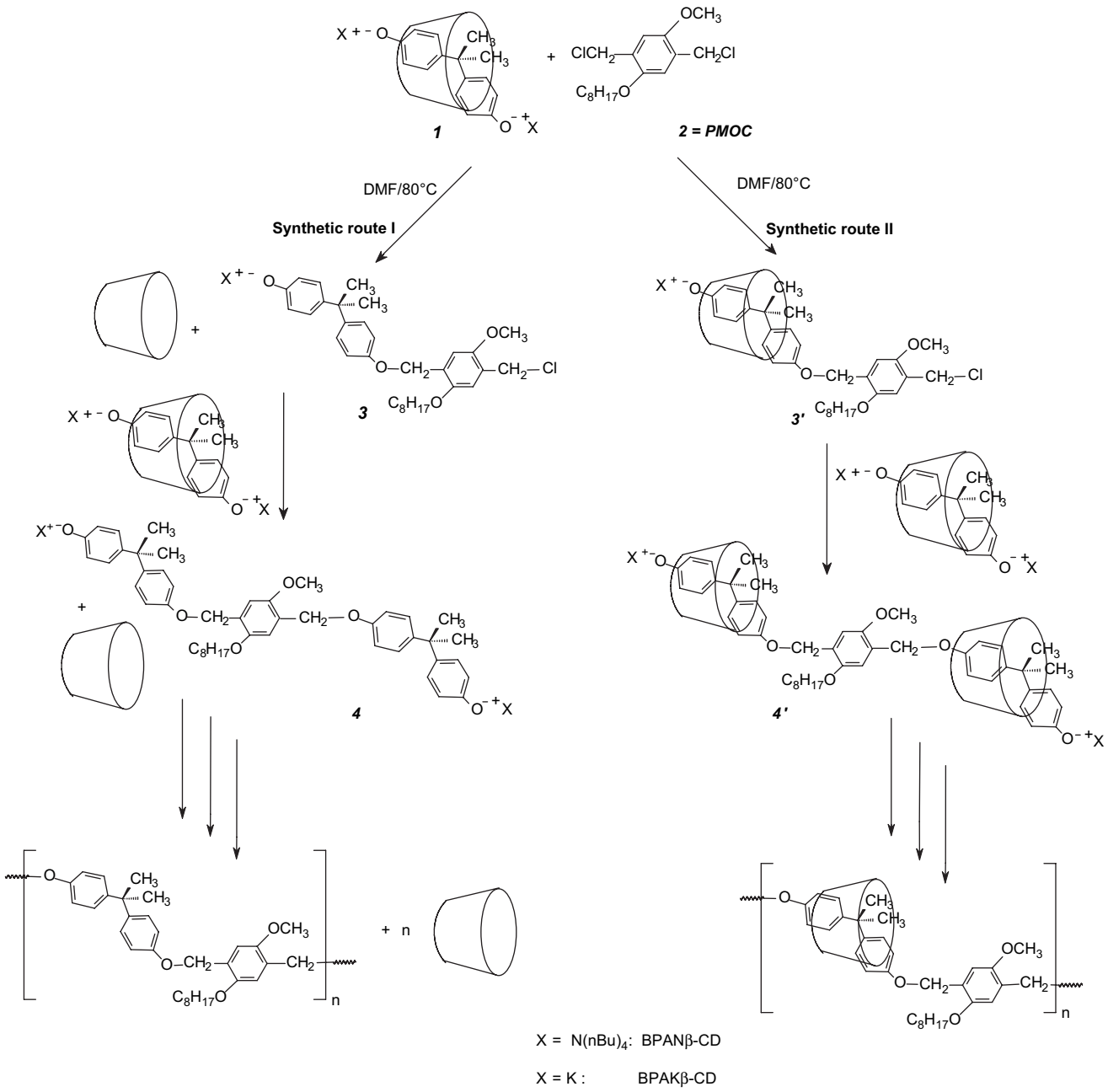
it is possible to control the threading ratio of βCD from zero (in the free polymer) to unity (in the polyrotaxane).

2. Results and discussion

Two BPA salts were used (Scheme 1): tetra-*n*-butylammonium bisphenolate (BPAN) and potassium bisphenolate (BPAK). Inclusion complexes between βCD and BPAN or BPAK were first synthesized and characterized. Stoichiometric amounts of BPA and βCD were mixed in water to obtain the 1:1 inclusion compound, then a stoichiometric amount of tetra-*n*-butylammonium hydroxide or potassium hydroxide was added to form the salts as inclusion complexes [11]; complexes (BPAN−βCD and BPAK−βCD) were isolated by lyophilization and their stoichiometries were checked by NMR measurements in D_2O [12]. Fluorescence measurements in aqueous solution show an increase in the fluorescence intensities of the inclusion complexes as compared to the free BPA salts all at the same concentration, 10^{-5} M [12].

Each complex was polycondensed with PMOC to obtain the encapsulated polyether as a polyrotaxane. The two reactions were carried out under the same experimental conditions, except for the counter-ion in the BPA salt (PMOC/inclusion complex in 1/1 ratio at 80 °C for 24 h in anhydrous DMF under argon).



Scheme 1. Polycondensation mechanism and intermediate products (free and encapsulated). The βCD orientation is arbitrary.

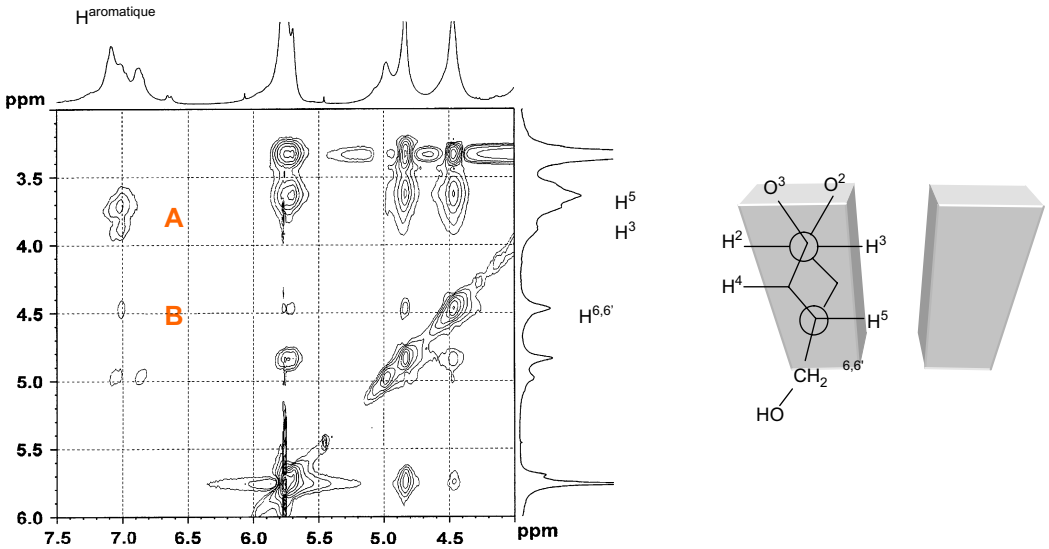


Fig. 1. 2D NMR NOESY spectrum of polyrotaxane in DMSO-d_6 at 300 MHz and numbering of a glucopyranose unit in β-cyclodextrin.

The different products were characterized by NMR spectroscopy. Surprisingly, the polycondensation of BPAN−βCD with PMOC led to a polyrotaxane with a 1:1 threading ratio [12], whereas that of BPAK−βCD with the same PMOC led to free polymer [12,13]. Fig. 1 presents the NOESY NMR spectrum of the polyrotaxane in DMSO-d_6. The H^3 and H^5 βCD protons, which are located inside the cavity, correlate with the aromatic protons of the polyether (cross-peak A); $H^{6,6'}$ protons correlate with the aromatic protons (cross-peak B), whereas the H^1, H^2 and H^4 protons, which are located outside the cavity, do not correlate with any proton of the polyether chain. These results indicate that the polyether chains are included in the βCD cavity. This result could be explained by the reaction mechanism described in Scheme 1.

Because the polycondensation reaction proceeds by successive bimolecular nucleophilic substitutions of each Cl^- ion in the dihalo derivative, PMOC, by a phenolate oxygen atom, the first step could lead to compounds **3** and **3′** (Scheme 1). Polycondensation leads to polyrotaxane when these two intermediates contain βCD. This is the case for the reaction between PMOC and BPAN−βCD, which seems to go via synthetic route II. In contrast, polycondensation leads to free polymer when the ether salt intermediate **3** leaves the βCD cavity; this seems to be the case of reaction between PMOC and BPAK−βCD, which proceeds by route I under these conditions.

To determine the origin of this difference, we explored two parameters, which are not necessarily independent.

(i) The size of the BPA salt counter-ion, which could prevent βCD dethreading when it is bulky enough and, which in this case, leads to the formation of polyrotaxanes. We have to check whether the dethreading process occurs systematically when the counter-ion is smaller than tetra-*n*-butylammonium, such as potassium.

(ii) In the reactions which proceed by a bimolecular mechanism, the rate can be enhanced by increasing the reactant concentrations. As proposed in Scheme 1, the βCD dethreading process in products **1** and **3′** occurs as a supplementary step in the condensation reaction (Scheme 1, route I). When the counter-ion is small and if there is competition between the two routes, enhancing the reactant concentrations will increase the condensation rate and result in polyrotaxane formation.

2.1. First parameter: counter-ion size

In order to study the formation of inclusion complex salts in DMF (the solvent used in the polycondensation reaction), the interaction between βCD and each BPA salt was followed by fluorescence measurements, by increasing the βCD concentration at two temperatures (25 °C and 80 °C). The ratio of BPA salt to βCD (BPA salt/βCD) was varied from 1/0 to 1/160. At room temperature, the fluorescence intensity remains constant (no evidence for complexation) up to a ratio of 1/40, where the intensity of a BPAK solution increases, indicating that BPAK and βCD start to form the inclusion complex. In contrast, for BPAN a ratio of 1/120 is necessary to achieve a fluorescence increase, indicating that tetra-*n*-butylammonium is sufficiently bulky to prevent the threading of βCD. After heating mixed BPA salt/βCD solutions of different ratios at 80 °C and cooling to room temperature, BPAK solutions show the same behaviour as before heating, whereas BPAN solutions show a fluorescence increase at a lower ratio, 1/20, than before heating. These results indicate that in BPAK solution, the βCD threading/dethreading process is possible at both temperatures; therefore polycondensation leads to free polymer under the initial experimental conditions. For BPAN the threading of βCD is more difficult at room temperature, but can be facilitated by heating. This indicates that even if the counter-cation is bulky enough to prevent the threading/dethreading process, polycondensation can be realized by the two synthetic routes.

Table 1
Variation of the polymerization yield and the threading ratio with [BPAK−βCD]/[PMOC] concentration ratio

Concentration ratio [BPAK−βCD]/[PMOC]	1/1			1/2	1/4	1/8
[PMOC] mol/L	0.1	0.2	0.3	0.2	0.4	0.8
Product	Free polymer	Polyrotaxane	Polyrotaxane	Free polymer	Oligorotaxane	Oligorotaxane
Yield	–	14	20	–	8	10
Threading ratio	–	7:1	5:1	–	3:2	1:1

2.2. Second parameter: polycondensation rate

This was checked by performing polycondensation with an excess of PMOC over the initial BPAK−βCD concentration. Several PMOC concentrations leading to different reactant concentration [PMOC]/[BPAK−βCD] ratios were tested, using the same concentration of BPAK−βCD (Table 1) and all the other parameters were not changed. Deviation from a 1/1 reactant concentration ratio will result in short polymer chains or oligomers (because of the hindrance of polycondensation propagation), but our aim was to check whether or not there is competition between dethreading and polycondensation. If there is competition this will result in encapsulated short polymer chains (oligorotaxanes).

For [PMOC]/[BPAK−βCD] ratios of 1/1 and 1/2 only free polymer was obtained, whereas ratios of 1/4 and 1/8 onwards gave short encapsulated chains [12] (Table 1). This indicates that polycondensation proceeds by both routes when a ratio of 1/4 is reached and that at this ratio, the polycondensation rate is high enough for βCD not to dethread from the encapsulated salt ethers **1** and **3′**. Note that when an excess of PMOC is used, the intermediates corresponding to the second and the later steps contain PMOC groups on both chain ends.

In order to enhance polycondensation with respect to βCD dethreading and to obtain long encapsulated polymer chains we used the same reactant ratio, 1/1, but at higher reactant concentrations (0.2 or 0.3 M) [12] than those used in the condensation of BPAN−βCD and PMOC (0.1 M). Under these conditions and for monomer concentrations of 0.3 M, we obtained polyrotaxane with a threading ratio of 5 polymer units for one βCD (5:1). This means that for the condensation of PMOC with BPAK−βCD the polyrotaxane is obtained with a threading ratio controlled to a certain extent by the reactant concentration.

In conclusion, it is possible to synthesize a polyrotaxane with controlled βCD threading ratio and we suggest the use of salts rather than neutral complexes to form encapsulated polyethers. When the counter-ion is bulky, such as tetra-*n*-butylammonium, then polyrotaxane formation with a 1:1 βCD threading ratio is very easy. When the counter-ion is small there is competition between polycondensation and dethreading, and the threading ratio can be controlled by the concentration of the reactants.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2007.04.047.

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[11] Synthesis of BPAN−βCD inclusion complex: BPA (0.228 g, 1 mmol) was dissolved in diethyl ether (5 mL), and then added to a saturated aqueous solution of βCD at 60 °C (1.15 g of βCD, 1 mmol in 100 mL of water). The mixture was stirred for 24 h at room temperature. The appearance of turbidity indicates the formation of an inclusion complex. Tetra-*n*-butylammonium hydroxide in water (0.53 M, 3.77 mL, 2 mmol) was added. The mixture was stirred for 2 h after which the solvent was removed by lyophilization and the complex obtained quantitatively as a white powder.
[12] The characterisation of rotaxane, oligorotaxane and polyrotaxanes are detailed in Supplementary data to this article.
[13] BPAN−βCD inclusion complex (1 mmol, 1.84 g) and PMOC (1 mmol, 0.33 g) were dissolved in dry DMF (10 mL). The mixture was stirred for 24 h at 80 °C under N_2, and then cooled to room temperature. Solids were precipitated by the addition of acetone (200 mL) and washed at 60 °C several times with a water/methanol (4/1) mixture to eliminate the free cyclodextrin and salts. The residue was dried under vacuum, then washed with chloroform (analytical quality). Finally the product was recovered by centrifugation (20 min, 5000 rpm) and dried under vacuum over P_2O_5. The polyrotaxane was obtained in 21% yield with a 1:1 threading ratio.