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# High yield production of high molecular weight poly(ethylene glycol)/α-cyclodextrin polyrotaxanes by aqueous one-pot approach

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ABSTRACT

An easy, one-pot, high-yield preparation of high molecular weight polyrotaxanes (PRs) from poly(-ethylene glycol) (PEG) and α-cyclodextrin (α-CD) by click chemistry is presented with novel water soluble and clickable end-capping agents containing quaternary ammonium and propargyl groups. The threading numbers of α-CD on the PEG chain were investigated by means of $^1$H NMR spectroscopy and gel permeation chromatography (GPC). When $M_n$ of the PEG axis is 35 kDa, the yield is up to 614 mg per 100 mg PEG axis and the average number of α-CDs on each PEG axis is 193. Wide-angle X-ray diffraction (WAXD) revealed that PRs form a column-type crystalline structure. The prepared PR possesses terminal alkyne groups which can connect with functional molecules to make the PR more useful. As a typical example, fluorescent rhodamine B has been successfully installed on the PR terminals.



## 1. Introduction

In the early 1990s, Harada [1–8] first reported the preparation of stable necklace-like supramolecules, polyrotaxanes (PRs), by end-capping the terminal of the pseudo-polyrotaxanes (pseudo-PRs) formed via inclusion complexation between linear polyethylene glycol (PEG) and α-cyclodextrin (α-CD) with bulky stoppers. Since then, pseudo-PRs with various topologies [9–15] and PRs capped with various bulky stoppers [16–22] were elaborated. Two-steps are generally required to prepare PRs: formation of pseudo-PRs in water and end-capping in organic solvent [23–26]. Although great progress has been made with such a two-step strategy, some big problems still remain to be addressed, such as low yield of PR and sparse threading percentage of α-CDs on PEG, due to the strong and quick dethreading inclination of the axle from the pseudo-PR during the end-capping process in an organic solvent. Consequently, it is difficult to obtain the high CD coverage ratio of PRs in large-scale, which poses an obstacle to the deep study on the property and potential application of PRs. Therefore, it is urgently calling for a novel strategy to efficiently prepare PRs.

Recently, a one-pot strategy showing great advance has been presented, which directly carries out end-capping reaction in aqueous solution of pseudo-PRs. Harada et al. prepared γ-CD-threading PR by photocyclodimerization of terminal 9-anthryl groups of the poly(propylene glycol) axis in the presence of γ-CDs [27]. Hadziioannou et al. tried to prepare α-CDs/PEG PR with sodium picrylsulfonate as capping agent in water in one pot, but the yield was much lower than that in two pots [28]. Yui et al. utilized polyethylenimine (PEI)-*b*-PEG-*b*-PEI copolymer as the axis to elaborate PR in aqueous solution capped with 9-anthraldehyde (AN) by forming Schiff base bond at lower pH 4.4 [29]. Takata et al. prepared PRs by threading diamineterminated PEG with pristine or permethylated α-CDs in water or organic solvent, respectively, and employing a bulky isocyanate as the stopper [30–32], and proved the convenience and efficiency of the one-pot strategy. Our group utilized click chemistry via the one-pot protocol to prepare "full CD" PR capped by β-CD in water at room temperature with high yield, up to 320 mg PR/100 mg PEG-4600 axis [33]. Further modification of PRs via click chemistry afforded a series of amphiphilic "sliding supramolecular polymer brushes" and novel biocompatible amino acids-functionalized PRs [34,35], showing the great potential of PR functionalization. However, so far whatever in the two pot or the one-pot strategy, both the yield and the inclusion ratio of CD threading on axis are relatively low for the high molecular weight of PEG axis.

To meet such a challenge, highly water-soluble, novel quaternary ammonium salt stoppers are synthesized in this paper, and used to facilely and efficiently prepare high molecular weight PRs by the one-pot click chemistry-based strategy. Because of the ultrahigh reactivity of the alkyl stoppers, a record high yield of PRs

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is achieved. More importantly, end-capping reaction with multi-alkynyl stoppers can install alkynyl groups on PR terminals, which can be utilized for further modification.

## 2. Experimental section

### 2.1. Materials

Poly(ethylene glycol) (PEG) (HO-PEG1-OH, $M_n$ = 35 kDa), HO-PEG2-OH ($M_n$ = 12 kDa), (t)-sodium L-ascorbate (98%), valeryl chloride (98%), and rhodamine B (RhB, 95%) were purchased from Sigma–Aldrich. 2-Azidoethanol, 4-(2-azidoethoxy)-4-oxobutanoic acid (Carboxylic azide), diazido-terminated PEG1 ($N_3$-PEG1-$N_3$), diazido-terminated PEG2 ($N_3$-PEG2-$N_3$), and azido-functionalized RhB (RhB-$N_3$) were prepared according to the Ref. [33,36] Propargyl bromide (97%), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, 98%), and N,N,N′,N′-tetramethylethylenediamine (TMEDA, 99%) were acquired from Alfa Aesar. α-Cyclodextrin (α-CD, 99%) was provided by Shanxi Liquan Chemical Co., Ltd. DMSO, $CuSO_4 \cdot 5H_2O$ and all the other materials used were obtained from Sinopharm Chemical Reagent Co., Ltd. DMF, Triethylamine (TEA) were dried over $CaH_2$ and distilled prior to use.

### 2.2. Instruments

Gel permeation chromatography (GPC) was recorded on Perkin Elmer HP 1100, using LiBr/DMF 0.01 mol/L as eluent at a flow rate of 1 mL/min, RI-WAT 150CVt + as detector and linear polystyrene as calibration at 70 °C. $^1$H NMR (300 MHz) measurements were carried out on a Varian Mercury plus 300 NMR spectrometer using $CDCl_3$ or DMSO-$d_6$ as solvent. Fourier transform infrared (FT-IR) spectra were recorded on a PE Paragon 1000 spectrometer (film or KBr disk). Wide-angle X-ray diffraction (WAXD) patterns were obtained by using Rigaku X-ray diffractometer D/max-2200/PC equipped with Cu Kα radiation (40 kV, 20 mA) at the rate of 5.0 deg/min. The samples for atomic force microscopy (AFM) measurement were prepared by spin-coating sample solutions onto freshly cleaved mica substrates at 1000 rpm, and the images were taken in the tapping mode on an NSK SPI3800. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM2010 electron microscope at 200 kV. Thermal gravitational analysis (TGA) was carried out using a Perkin–Elmer Pyris 6 TGA instrument with a heating rate of 20 °C/min under a nitrogen flow (30 mL/min). Fluorescence lifetimes were measured on Edinburgh instruments FLS 920. A flash lamp (nF900, 2.5 ns) was used to excite the samples and reconvolution fitting was utilized as the data analysis method with instrument respond function. Fourier transform infrared (FTIR) spectra were recorded on a PE Paragon 1000 spectrometer (KBr disk and film).

### 2.3. Synthesis of water-soluble mono-alkyne quaternary ammonium salt (MAS)

A 50 mL $CHCl_3$ solution of triethylamine (5.64 g, 55.7 mmol) was prepared in a 100 mL flask and cooled in an ice bath. Then, propargyl bromide (5.52 g, 46.8 mmol) was added dropwise to the solution under magnetic stirring. After being kept in darkness at room temperature for 6 h, the mixture was poured into ethyl ether (200 mL). The collected precipitate was washed twice with ethyl ether, and then dried under vacuum at 30 °C for 24 h, affording hygroscopic white powder. Yield: 9.80 g, 95.6%. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 4.29 (s, 2H, CHCC$H_2$), 3.95 (s, 1H, C$H$CC$H_2$), 3.33 (m, 6H, C$H_2$CH$_3$), 1.21 (m, 9H, CH$_2$C$H_3$). $^{13}$C NMR (75 MHz, $D_2O$): $\delta$ 81.22 (CHC$CH_2$N), 70.91 (C$H$CC$H_2$N), 53.91 (CH$_3$C$H_2$N), 48.15 (CHC$CH_2$N), 7.73 (C$H_3$CH$_2$N).

### 2.4. Synthesis of water-soluble di-alkyne quaternary ammonium salt (DAS)

TMEDA (2.92 g, 25.1 mmol) was dissolved in 20 mL DMF. The solution was cooled in an ice bath and then added dropwise with propargyl bromide (6.25 g, 52.9 mmol) under magnetic stirring. The reaction system was kept at room temperature for 10 h and followed by pouring into acetone (80 mL). The white precipitates were collected and washed twice with acetone, then dried under vacuum at 30 °C for 24 h, affording DAS as hygroscopic white powder. Yield: 8.33 g, 94.2%. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 4.59 (m, 4H, CHCC$H_2$), 4.20 (m, 2H, C$H$CC$H_2$), 4.10(m, 4H, C$H_2$C$H_2$), 3.24(m, 12H, N(C$H_3$)$_2$). $^{13}$C NMR (75 MHz, $D_2O$): $\delta$ 83.88 (CHC$CH_2$N), 70.41 (C$H$CC$H_2$N), 55.51 (CHCC$H_2$NCH$_2$C$H_2$NCH$_2$CCH), 55.35 (CH$_2$CH$_2$N′CH$_2$C$H_2$), 55.02 (CH$_2$C$H_2$N′CH$_2$CH$_2$), 52.22 (C$H_3$N′).

### 2.5. Synthesis of water-soluble tri-alkyne quaternary ammonium salt (TAS)

A mixture of DMF (70 mL) and PMDETA (7.05 g, 40.7 mmol) was charged to a 150 mL flask and kept at 0 °C. Then, propargyl bromide (14.54 g, 123,3 mmol) was added dropwise. After being stirred at room temperature for 48 h, the mixture was poured into acetone to yield white precipitate. The precipitate was collected, washed twice with acetone, and then dried under vacuum at 30 °C for 24 h. TAS was obtained as hygroscopic white powder. Yield: 19.36 g, 90.3%. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 4.75 (s, 2H, CHCC$H_2$N′), 4.67 (s, 4H, CHCC$H_2$N and CHCC$H_2$N″), 4.31(s, 1H, C$H$CC$H_2$N′), 4.28–4.24 (m, 8H, C$H_2$CH$_2$N′CH$_2$C$H_2$), 4.22 (m, 2H, C$H$CC$H_2$N and C$H$CC$H_2$N″), 3.37 (s, 3H, C$H_3$N′), 3.31 (m, 12H, N(C$H_3$)$_2$ and N″(C$H_3$)$_2$). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 82.26 (CHC$CH_2$N′), 85.04 (CHC$CH_2$N″ and CHC$CH_2$N), 72.36 (C$H$CC$H_2$N″ and C$H$CC$H_2$N), 71.54 (CHC$CH_2$N′), 55.50(N(C$H_3$)$_2$ and N″(C$H_3$)$_2$), 55.35 (C$H_2$CH$_2$N′CH$_2$C$H_2$), 55.02 (CH$_2$C$H_2$N′CH$_2$CH$_2$), 53.71 (C$H_3$N′), 51.34 (CHC$CH_2$N″ and CHC$CH_2$N), 49.94 (CHC$CH_2$N′).

### 2.6. Synthesis of PR with $N_3$-PEG1-$N_3$ via one-pot strategy (PR1A)

Typically, an aqueous solution (100 mL) of $N_3$-PEG1-$N_3$ (1.00 g, 0.028 mmol) and α-CD (12.00 g, 12.94 mmol) was ultrasonically agitated at room temperature for 5 min and then stirred overnight to form pseudo-PR1A. To this mixture, TAS (89.5 mg, 0.17 mmol, the molar ratio of alkyne to $-N_3$ was 6:1), $CuSO_4 \cdot 5H_2O$ (141.2 mg, 0.56 mmol), PMDETA (120.5 μL, 0.58 mmol) and (t)-sodium L-ascorbate (224.1 mg, 1.12 mmol) were added successively under nitrogen atmosphere. After reacting at room temperature for 10 min-24 h in darkness, the precipitate was collected by centrifugation, washed with 300 mL hot water (60 °C) for more than 5 times and then dried under vacuum at 65 °C for 24 h, affording PR1A as white powder. Yield: 357–614 mg/100 mg PEG axis. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 3.22–3.40 (br overlapped, 12H, *H*-2,4), 3.49 (m, 2H, C$H_2$ of PEG), 3.55–3.79 (br overlapped, 18H, *H*-3,5,6), 4.46 (m, 6H, O*H*-6), 4.78 (m, 6H, *H*-1), 5.41–5.51 (m, 12H, O*H*-2,3).

In other experiments, PEG2 was used instead of PEG1, and other stoppers such as TAS and DAS were used instead of MAS. In the sample code "PRnX", "*n*" represents $M_n$ of PEG axis, 35 (1) or 12 (2) kDa and "X" denotes the stoppers, MAS (A), DAS (B) or TAS (C).

The hydroxyl groups of PR can be converted to other functional moieties for the application purpose. We prepared valeryl chloride modified PR (PR-VC) according to the protocols reported in Ref. [37], as shown in Supporting information.

### 2.7. Synthesis of RhB-modified polyrotaxane (RhB-PR)

PR1C (100.1 mg) was dissolved in 5 mL of dry DMAc containing 8wt% LiCl under $N_2$. Then, the mixture was heated at 60 °C. To the mixture, CuBr (26.3 mg), PMDETA (32.3 mg), RhB-$N_3$ (100.2 mg) were added successively. After stirring overnight in darkness, the reaction system was poured into acetone. The collected red precipitate was dissolved in DMAc and poured into acetone repeatedly until RhB-$N_3$ could not be detected by UV–Vis spectrometer in the concentrated washing solution. The precipitate (RhB-PR1C) was dried under vacuum at 35 °C for 24 h to afford red powder. Yield: 95.8 mg.

## 3. Results and discussion

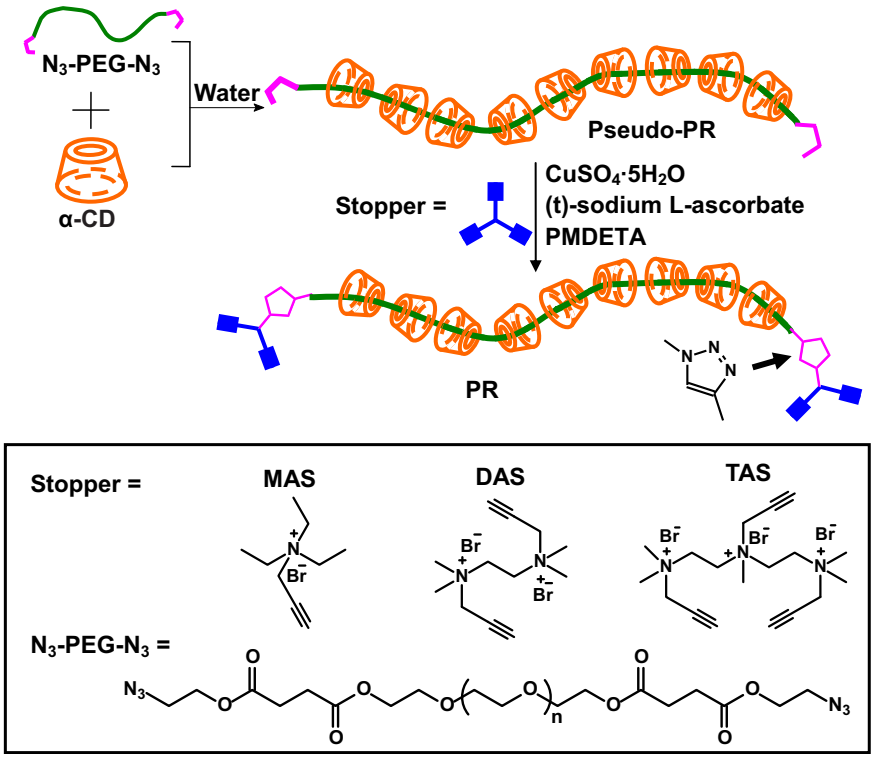
### 3.1. Design and synthesis of alkyl end-capping reagents

It has been recognized that end-capping reagents play a crucial role in the synthesis of PRs. All of the reported stoppers are almost aryl molecules, except few ones such as cage-like molecules of adamantine and cyclodextrin derivatives. Their molecular sizes are big enough to prevent the threaded CDs from dethreading. However, those bulky molecules are generally less reactive, resulting in slow end-capping and thus low yield during the PR synthesis. For instance, alkyne-functionalized rhodamine B can be used as the stopper to prepare PR via click chemistry, but the yield is only 4.47 mg per 100 mg PEG-4600 [38]; when the β-CD was used as the stopper, high yield was achieved up to 320 mg PR per 100 mg PEG-4600 via click-end capping, but the yield is quite low for the higher molecular weight axis PEG 12 kDa [33]. Accordingly, we shift our attention to alkyl stoppers. Because the end-capping is carried out in water in the one-pot click chemistry approach, the stoppers should be water soluble. So we designed alkyl ammonium alkynes as stoppers for the preparation of high molecular weight PRs. Their molecular structures are shown in Scheme 1.

The stoppers can be easily prepared by dropwise adding propargyl bromide into the DMF solution of tertiary amines. This efficient one-step process from commercial and inexpensive starting materials makes large-scale production of the quaternary ammonium salts readily accessible. The stopper structures were confirmed by $^1$H and $^{13}$C NMR spectroscopy. In the $^1$H NMR spectrum of MAS (Figure S1), the protons of the propargyl group locate at 3.95 and 4.29 ppm, and the ethyl protons appear at 1.21 and 3.33 ppm. In the $^1$H NMR spectrum of DAS (Figure S2), the protons of alkynyl group and methyl appears at 4.20 and 3.24 ppm, respectively. In the $^1$H NMR spectrum of TAS (Fig. 1(A)), the propargyl group connected to the middle nitrogen atom (N′) exhibits its methylene and alkyne proton signals at 4.75 (signal F) and 4.31 (signal G) ppm, respectively, the other two propargyl groups at the two end nitrogen atoms (N and N″) show the methylene and alkyne proton signals at 4.67 (signal C) and 4.22 (signal B) ppm, respectively, and the integration ratio of signal F to signal C is 1:2, indicating all the three tertiary amino groups are quaternized. In the $^{13}$C NMR spectrum of TAS (Fig. 1(B)), the carbon signals of alkynyl group at N′ locate at 82.26 (signal D) and 71.54 (signal B) ppm, the carbon signals of alkynyl group at N and N″ appear at 85.04 (signal C) and 72.36 (signal A) ppm, and the carbon atoms labeled as “G, H, I, J” which originally belong to PMDETA still can be observed.

### 3.2. Synthesis and characterization of PRs

The one-pot preparation of PRs was carried out in water via a two-step procedure: 1) formation of pseudo-PR from α-CD and diazide-terminated PEG; 2) end-capping of pseudo-PR with bulky quaternary ammonium salt reagents via Cu(I)-catalyzed azide-alkyne click reaction (Scheme 1). Typically, an aqueous solution of




**Scheme 1.** Synthetic protocol of quaternary ammonium salt-capped PR via chick chemistry.

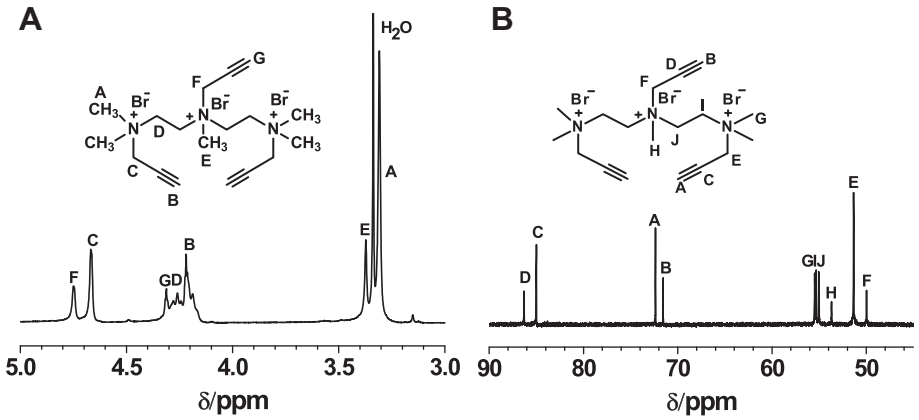



**Fig. 1.** (A) $^{1}$H NMR spectrum of tri-alkyne quaternary ammonium salt in DMSO-$d_6$, (B) $^{13}$C NMR spectrum of tri-alkyne quaternary ammonium salt in DMSO-$d_6$.

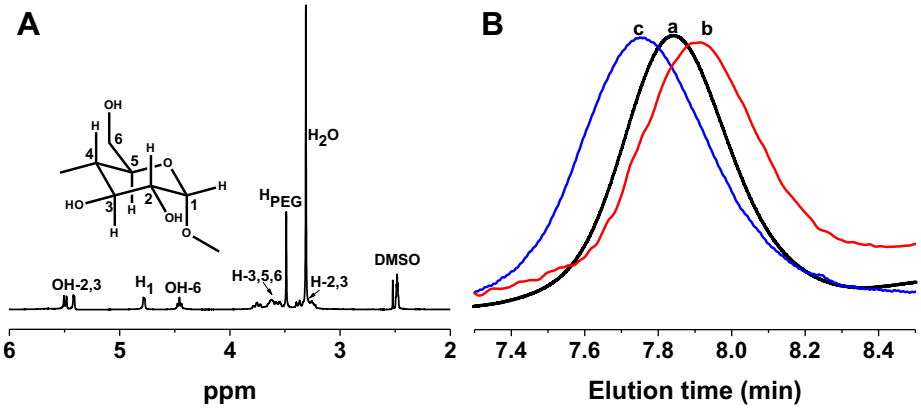



**Fig. 2.** (A) $^{1}$H NMR spectrum of the polyrotaxane prepared from PEG 35 kDa, mono-alkyne quaternary ammonium salt and α-CD in DMSO. (B) Typical GPC curves of (a) PR1A-VC, (b) PR1B-VC, and (c) PR1C-VC.

α-CD and $N_3$-PEG-$N_3$ was sonicated for 5 min and then stirred overnight at room temperature to generate pseudo-PR. To this mixture, bulky quaternary ammonium salt reagents and catalyst for click coupling were added successively under $N_2$. After 10 min-24 h, the precipitates were collected by centrifugation and washed with hot water repeatly to remove free α-CD, $N_3$-PEG-$N_3$ and unreacted stopper to yield pure PR.

The structure of PR was characterized by $^{1}$H NMR and WAXD. The $^{1}$H NMR spectrum of the present PR (Fig. 2(A)) was very similar with those of the samples previously reported [33,38]. The integration ratio of the proton signal at 3.49 ppm (hydrogen atom in the repeat unit of PEG) to that at 4.78 ppm ($H_1$ of α-CD) can be utilized to calculate the average number of α-CD in each PR ($N_{CD}$), which is a very important parameter for PRs. $N_{CD}$ was calculated according to the Eq. (1) and the values are listed in Table 1.

$$N_{CD} = \frac{M_{HO-PEG-OH} \times I_{H1}}{66 \times I_{PEG}} \quad (1)$$

Herein, $I_{H1}$ is the integration of $H_1$ peak of α-CD, $I_{PEG}$ is that of proton signal of PEG repeat unit, and $M_{PEG}$ is the molecular weight of PEG axis. For the sample, PR1C (entry 4 of Table 1), the value of $N_{CD}$ is ca. 193 and the corresponding coverage ratio, which is the ratio of $N_{CD}$ to the theoretical maximum amount of α-CDs threaded by the axis, equals ca. 48%. For other samples, use of MAS (entry 1) and DAS (entry 2) stoppers and the reaction with a varied molar ratio of the stopper and the azide groups (entry 1–4 in Table 1) all resulted in relatively high yields and big $N_{CD}$s, implying that the prepared quaternary ammonium salts were excellent end-capping reagents with seemly bulkiness, solubility and reactivity. As far as we know, the achieved yield is the record ever reported for the preparation of PRs [39–41], since the highest yield of PRs prepared from PEG 35 kDa in previous reports is ~343 mg/100 mg PEG axis and the corresponding $N_{CD}$ is 100 [23]. In addition, the yields for PRs made from PEG 12 kDa and α-CD are also quite high (Table 1), indicating the comparability of our method.

**Table 1**
Selected reaction conditions and results for the preparation of quaternary ammonium stopper capped PRs.

| Run | Sample[a] | $R$[b] | Yield (mg/100 mg PEG axis) | $N_{CD}$ (NMR)[c] | Coverage ratio (%)[d] | $N_{CD}$ (GPC)[e] |
|---|---|---|---|---|---|---|
| 1 | PR1A | 10 | 556 | 143 | 35.9 | 82 |
| 2 | PR1B | 10 | 541 | 128 | 32.2 | 56 |
| 3 | PR1C | 1 | 591 | 169 | 42.6 | 102 |
| 4 | PR1C | 2 | 614 | 193 | 48.5 | / |
| 5 | PR2A | 10 | 620 | 75 | 55.0 | / |
| 6 | PR2C | 2 | 490 | 69 | 50.4 | / |

[a] In sample code "PR*n*X", "*n*" represents $M_n$ of PEG axis, 35 kDa (1) or 12 kDa (2) and "X" denotes the stoppers, mono-alkyne quaternary ammonium salt (A), di-alkyne quaternary ammonium salt (B) or tri-alkyne quaternary ammonium salt (C).
[b] The molar feed ratio of stoppers to azide unit.
[c] The number of the threaded α-CDs per axis calculated from $^{1}$H NMR method.
[d] The ratio of $N_{CD}$ to the theoretical maximum amount of α-CDs threaded by the axis.
[e] $N_{CD}$ was calculated according to $M_n$ of corresponding valeryl chloride-modified PR obtained from GPC.

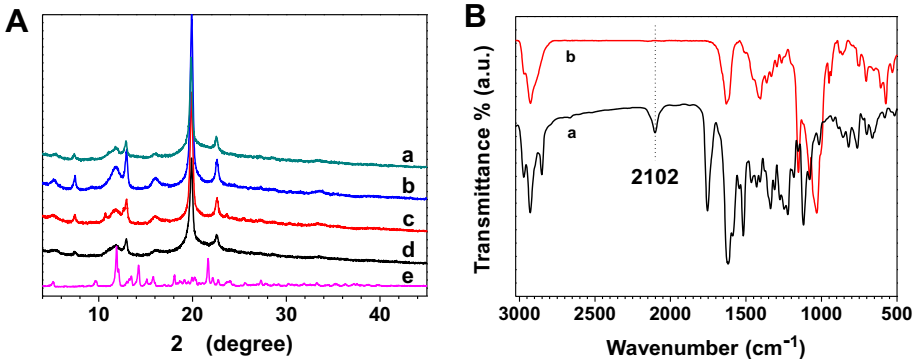
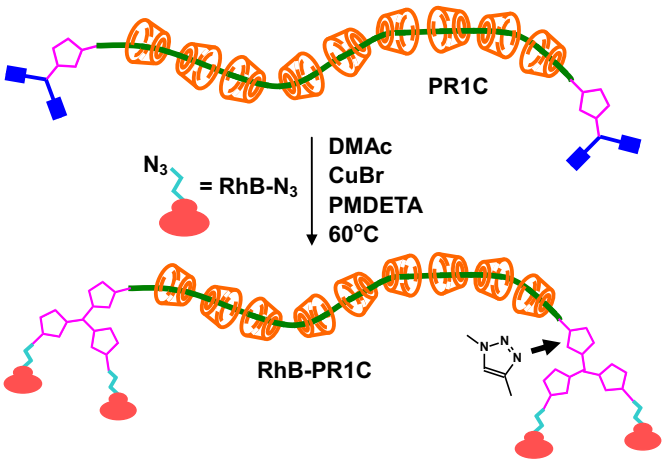



**Fig. 3.** (A) WAXD patterns of a) PR1C, b) PR1B, c) PR1A, d) PR2C, e) native α-CD. (B) FT-IR spectra of (a) RhB-$N_3$ and (b) RhB-PR1C.




**Scheme 2.** Synthetic protocol of RhB modified-PR via click chemistry.

In order to characterize the molecular weight of PR by means of gel permeation chromatography (GPC), PR1A, PR1B and PR1C with PEG axis of 35 kDa were treated with valeryl chloride to improve their solubility in DMF, according to the Ref. [33] It is interesting to note that GPC analysis of all the samples against linear polystyrene standards resulted in typical symmetric Gaussian distribution curves (Fig. 2(B)) with narrow polydispersities (polydispersity index, PDI, 1.18–1.61), indicating that we successfully synthesized host-guest supramolecular polyrotaxanes. Additionally, $N_{CD}$ can also be calculated according to Eq. (2) based on the GPC result.

$$N_{CD} = \frac{M_n - 2M_A - M_{N3-PEG-N3}}{M'_{\alpha-CD}} \quad (2)$$

where $M_n$, $M_A$, $M_{N3\text{-}PEG\text{-}N3}$, and $M'_{\alpha-CD}$ (2486.10 g/mol) denote the molecular weights of PR-VC, the stopper, the axis $N_3$-PEG-$N_3$ and valeryl chloride modified α-CD bead, respectively. The resulted $N_{CD}$s are generally smaller than those calculated from $^1$H NMR method. For instance, in entry 3 (Table 1), the $N_{CD}$ obtained through GPC method is 102, which is smaller than that calculated from $^1$H NMR result, 169. The difference may be attributed to, (1) incomplete modification of PRs, namely, the molecular weight of valeryl chloride modified α-CD bead in the practical reaction system is smaller than that used in the eq (2) ($M'_{\alpha-CD}$ = 2486.10 g/mol), (2) the interaction between PR and GPC column, (3) the different conformation between linear PS standard and PR.

WAXD is utilized to elucidate the structure of inclusion complexes in the solid state and explore the existence of pseudo-PRs and PRs [42,43]. As shown in Fig. 3(A), the WAXD patterns of pseudo-PR1A and PR1A show strong and sharp diffraction peaks at $2\theta = 20°$, demonstrating that α-CDs are stacked along the PEG chain axis to form the necklace structure and in other words, PRs possess a column crystalline structure. Thermal properties of PRs were studied by TGA (Figure S3). The initial decomposition temperature of PRs is higher than that of α-CD (ca. 300 °C), implying that the thermal stability of PRs has little difference comparing to the starting materials.

It should be highlighted that the PRs with multi-alkynyl stoppers can be further functionalized, which will extensively facilitate the application of PRs. Azido-functionalized rhodamine B (RhB-$N_3$) was used to functionalize the PRs by click coupling the azide group

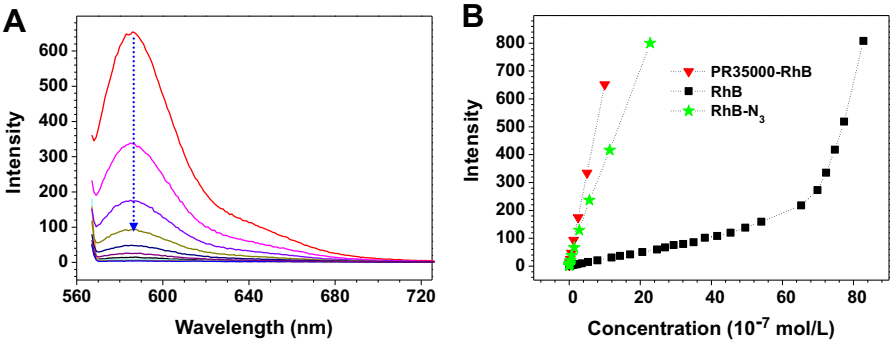



**Fig. 4.** (A) Fluorescence emission spectra of RhB-PR1C in DMSO solution with gradient concentrations from 0.05 mg/mL to 9.8 × $10^{-5}$ mg/mL (along the arrow) by step-wise dilution. (B) Fluorophores concentration versus fluorescence emission intensity of RhB, RhB-$N_3$, RhB-PR1C in DMSO solution. All the fluorescence emission spectra were excited at 564 nm and the emission peak points were at 587 nm. The emission slit was 3 nm.

with the terminal alkyne groups of PRs (Scheme 2). In the FT-IR spectrum of the RhB-PR1C (Fig. 3B-b), the characteristic absorption peak of azido group of RhB-$N_3$ at 2102 $cm^{-1}$ (Fig. 3B-a) cannot be observed, implying the occurrence of the click reaction. The presence of RhB fluorophores was confirmed by the fluorescent measurements (Fig. 4(A)). All of the samples were excited at 564 nm in DMSO solution and the emission peaks appeared at 587 nm. The plots of emission intensities as a function of fluorophores concentration are presented in Fig. 4(B). The slope of the fit line of RhB-$N_3$ was smaller than that of the fit line of RhB-PR1C, and the calculated emission coefficients were $3.53 \times 10^8$ and $6.50 \times 10^8$ L $mol^{-1}$ $cm^{-1}$, respectively. Similar to our previous report [38], even in the low concentration range, the emission intensity increases fast and almost linearly with the increase of fluorophores concentration for the RhB-$N_3$ and RhB-PR1C. In contrast, the emission intensity of neat RhB in DMSO solution is around zero in the same concentration range. This result confirmed that the PR can amplify the fluorescence emission intensity.

## 4. Conclusion

Synthesis of novel water-soluble end-capping reagents quaternary ammonium salt with multi-functional groups and an easy, one-step, high-yield preparation of high molecular weight polyrotaxanes (PRs) from poly(ethylene glycol) (PEG) and α-cyclodextrin (α-CD) by click chemistry were presented and demonstrated. We showed that these novel alkyl stoppers are of high end-capping efficiency and could result in high yield and coverage ratio of the PRs, up to 614 mg/100 mg PEG axis and 48.5%, respectively. $^1$H NMR and WAXD characterization confirmed that the PRs have column structure. The unique feature of the prepared PR is the possession of terminal alkyne groups which can connect with functional molecules to make the PRs more useful. As a typical example, the fluorescent molecule RhB-$N_3$ was successfully installed on the PR terminals.

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## Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2012.04.038.

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