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Novel main-chain polyrotaxanes synthesized via ATRP of HEMA initiated with polypseudorotaxanes comprising BriB–PEG–iBBr and α-CDs

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ABSTRACT

A novel strategy for the preparation of main-chain polyrotaxanes with lengthily tunable PHEMA as outer bulky stoppers was described in the present study. Polypseudorotaxanes made from the self-assemblies of a distal 2-bromoisobutyryl end-capped PEG with a varying amount of α-CDs in aqueous media were used as macroinitiators *in situ* to initiate the ATRP of HEMA catalyzed by Cu(I)Br/PMDETA at room temperature. The resulting polyrotaxanes were characterized in virtue of ^{1}H NMR, GPC, FTIR, XRD and DSC analyses. It demonstrated that the target polyrotaxanes were successfully synthesized and both the in-chained number of HEMA and the threaded number of α-CDs were adjustable to some extent. As the active Br groups held at two terminals and combining the unique properties of general polyrotaxanes with that of block copolymers, these supramolecular polymers show the potential as macroinitiators used for new ATRP polymerizations.

1. Introduction

Polyrotaxanes (PRs) comprising a linear polymer as an axle and numbers of cyclodextrins (CDs) as rings stopped by bulky end-capping groups have attracted tremendous interests since their first report by Harada and colleagues in the 1990s [1], due to not only their inherent scientific importance, but also their potential applications as smart materials for hydrogels [2], slide-ring gels [3], biosensors [4], carriers for drug delivery [5], fibber spinning [6], etc. A variety of bulky groups and end-capping reactions have been exploited to prepare PRs from their precursors of polypseudorotaxanes (PPRs) to date. Besides coupling 2,4-dinitrofluorobenzene with amine-terminated PEG [7], some even intriguing end-capping strategies have been developed, e.g. the reaction of PPRs comprising permethylated α-CDs and poly(tetrahydrofuran) with electrophiles in the solid state [8], using Huisgen cyclization of azido- and alkynyl-modified precursors in the presence of Cu(I) [9] and via the radical telomerization of *N*-isopropylacrylamide to form poly(*N*-isopropylacrylamide) under UV radiation [10,11]. To our knowledge, there has not yet been a systematic study devoted to the introduction of lengthily tunable polymers into PRs as the bulky end stoppers.

As a versatile method to synthesize polymers with well-controlled molecular weight and narrow molecular weight distribution, the Atom Transfer Radical Polymerization (ATRP) has been successfully applied in a wide variety of monomers, such as (meth)acrylates, (meth)acrylamides, acrylonitrile, styrene, etc. [12,13]. The ATRP is also a competent pathway to prepare block copolymers, such as PS-*b*-PEG and PEG-*b*-PMMA copolymers [14], as well as graft copolymer [15] and star-like copolymers [16] with controlled architectures. Most of the ATRPs are carried out at relatively high temperatures (>80 °C) either in the bulk or in nonaqueous media [17,18]. Recently Armes and colleagues have reported an ambient temperature ATRP of 2-hydroxyethyl methacrylate (HEMA) in aqueous or water/methanol media [19–21].

In 2006, Ritter and Pang described a kind of side-chain polyrotaxanes synthesized via the ATRP of a methylated β-CD-based macromonomer with methyl methacrylate [22]. In the present study, PPRs were firstly prepared from the self-assemblies of a distal 2-bromoisobutyryl end-capped PEG with a varying amount of α-CDs in aqueous solution. After that these supramolecular entities were intended *in situ* to initiate the ATRP of HEMA by using Cu(I)Br/*N*,*N*,*N*′,*N*′,*N*′-pentamethyldiethylenetriamine (PMDETA) as catalyst at room temperature to give a kind of main-chain polyrotaxanes featured with lengthily tuneable poly(2-hydroxyethyl methacrylate) (PHEMA) block as bulky end stoppers. The excellent biocompatibility and good blood compatibility of PHEMA [19] would foster the resulting PRs to be used as smart biomaterials for sliding gels, biosensors, carriers for drug controlled release and scaffolds for tissue engineering. In addition, the active Br end groups offer the opportunity to further modify these supramolecular polymers.

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2. Experimental section

2.1. Materials

α-CD (TCI, Japan) was used as-received. PEG ($M_n = 4000$, PEG 4K) was imported from Japan and distributed domestically. 2-Hydroxyethyl methacrylate (HEMA) (Acros, Belgium) was vacuum distilled and stored over CaH_2 before polymerization. 2-Bromoisobutyryl bromide and 4-dimethylaminopyridine (DMAP) were purchased from Alfa-Aesar, USA, and *N*,*N*,*N*′,*N*′,*N*′-pentamethyldiethylenetriamine (PMDETA) was available from Aldrich, USA and they were used without further purification. All other reagents used were of analytical grade.

2.2. Synthesis of macroinitiator (BriB–PEG–iBBr)

For a typical synthesis, in a three-neck round-bottom flask, PEG 4K (20.0 g, 5 mmol) was dissolved in 100 ml of dry CH_2Cl_2. After triethylamine (1.01 g, 10 mmol) and DMAP (0.61 g, 5 mmol) were added, the reaction mixture was cooled to 0 °C. 2-Bromoisobutryl bromide (2.87 g, 12.5 mmol) was dissolved in 20 ml dry CH_2Cl_2, and then added to the PEG 4K solution dropwise under continuous stirring over a 1 h period using a pressure-equalizer funnel. The reaction mixture was stirred for 24 h at room temperature. After the reaction was completed, it was filtered to remove the resulting triethylamine hydrobromide. The solvent was concentrated and precipitated in *n*-hexane, filtered, and dried under vacuum. Finally, the crude polymer was dissolved in water and extracted from methylene chloride. After drying over magnesium chloride, the solvent was again precipitated in *n*-hexane, filtered, and dried under vacuum to give the product, yield 80%. FTIR/cm^{-1}: 2866 (CH_2, CH_3), 1736 (C═O), 1109 (C–O). ^{1}H NMR (400 MHz, DMSO-d_6)/ppm: δ 4.242 (4H, –CH_2–CH^*_2–O–C(═O)–), 3.636 (4H, –CH^*_2–CH_2–O–C(═O)–), 3.587–3.446 (360H, –OCH_2–CH_2–O–), 1.893 (12H, –CH_3).

2.3. Preparation of triblock copolymer (PHEMA–PEG–PHEMA)

A preparation of PHEMA–PEG–PHEMA via the ATRP was as follows. BriB–PEG–iBBr (0.10 g, 0.023 mmol), HEMA (0.13 g, 0.92 mmol) and PMDETA (5.0 mg, 0.028 mmol) were dissolved in water. After the solution was quenched into liquid nitrogen, CuBr (4 mg, 0.028 mmol) was added. The reactor was degassed by using three freeze–pump–thaw cycles and then sealed. The preparation reaction started and continued for 6 h under stirring when the mixture was warmed to 25 °C. On exposure to air, the polymerization stopped. Product was obtained by dialysis against distilled water using a cellulose membrane (MWCO 7000) for 2 days and freeze-dried.

2.4. Preparation of polypseudorotaxane (PPR)

As a typical example, 0.46 g α-CD was dissolved in 1.5 ml water to get a saturated solution, and it was then added to 0.10 g BriB–PEG–iBBr in 0.5 ml water, followed by vigorous stirring at room temperature for 2 days. After standing for 30 min, a white, physical gel was formed as a result of non-covalent interactions of the self-assemblies of α-CDs with linear PEG backbone. To get the PPR powders, the gel was washed with a small amount of distilled water and freeze-dried.

2.5. Synthesis of polyrotaxane (PR)

The PPR suspension was prepared as described above. 0.46 g α-CD was dissolved in 1.5 ml water and then added to 0.10 g BriB–PEG–iBBr in 0.5 ml water. After 2 day vigorous stirring at room temperature, HEMA (0.13 g, 0.92 mmol) and PMDETA (5.0 mg, 0.028 mmol) were added dropwise to the PPR suspension under continuously stirring. After quenching with liquid nitrogen and adding 4.0 mg CuBr, the reactor was degassed by using three freeze–pump–thaw cycles and sealed. The polymerization started and continued for 6 h under stirring at 25 °C. On exposure to air, the polymerization stopped and the crude product was washed using distilled water to remove the Cu^{2+} salts and freeze-dried. A thorough purification was carried out by incubating in an excess of DMSO for 12 h at 60 °C, followed by precipitation into acetone to remove unthreaded α-CDs and corresponding triblock copolymers. Finally the precipitate obtained was vacuum dried.

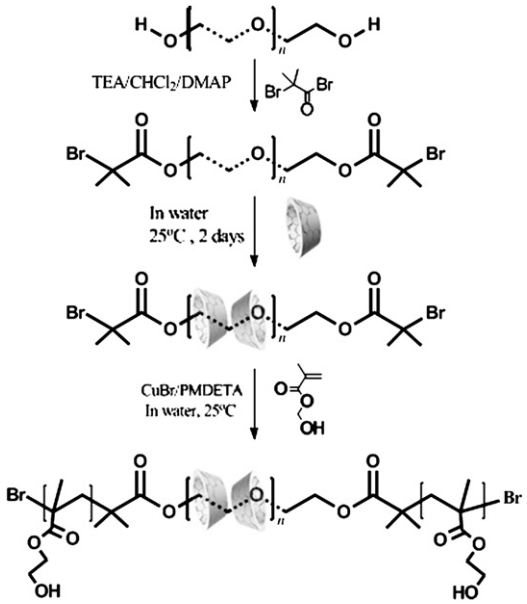
2.6. Measurements

^{1}H NMR spectra were recorded on Bruker ARX 400 NMR instrument at room temperature with DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. The molecular weight and polydispersity index of the PRs were determined at 50 °C with a gel permeation chromatography (GPC) conducted with a Waters 1515 pump, three Waters Styragel columns (HT3, HT4, HT5) and a Waters 2414 differential refractive index detector. DMF was used as eluent at a flow rate of 1.0 ml/min. Polystyrene was utilized for calibration standards. FTIR spectra were measured using Shimadzu IR Prestige-21 FTIR spectrometer at room temperature in the range of 4000–500 cm^{-1} with a resolution of 2 cm^{-1} and 20 scans. Powder samples were prepared by dispersing the samples in KBr and compressing the mixture to form disks. Wide-angle X-ray diffraction (WXRD) measurements were performed with powder samples using Shimadzu XD-D1 X-ray Diffractometer. The radiation source used was Ni-filtered, Cu Kα radiation with a wavelength of 0.154 nm. The voltage was set to be 35 kV and the current 20 mA. Samples were placed on a sample holder and scanned from 10° to 50° in 2θ at a speed of 5°/min. Differential scanning calorimetric (DSC) measurements were carried out using a Netzsch DSC 204 differential scanning calorimeter. The DSC thermograms covered a temperature range of −30 to 150 °C at a scanning rate of 10 °C/min.

3. Results and discussion

3.1. Synthesis of polyrotaxanes by ATRP

A preparation strategy of polyrotaxanes via the ATRP of HEMA is illustrated in Scheme 1. Their theoretical feed/found compositions and yields are summarized in Table 1. BriB–PEG–iBBr was prepared from the reaction of PEG 4K with 2-bromoisobutyryl bromide as reported previously [19]. To a solution of BriB–PEG–iBBr in water was added an aqueous solution of α-CDs, and polypseudorotaxane was formed as a result of the self-assembly of a linear PEG with α-CDs. Evidently, the resulting suspension became increasingly viscous along with increasing the amount of α-CDs. An opaque physical gel is usually formed after standing for around 60 min due to the non-covalent interactions of these supramolecular entities, and the gel is thixotropic and reversible [23–25]. Compared with OH–PEG–OH or HS–PEG–SH, which could form gel with α-CDs in more or less than 10 min [10,11], the threading process of α-CDs onto BriB–PEG–iBBr is apparently slower and it needs about 1 h for the bigger steric hindrance of the terminal *gem*-dimethyl groups. As the self-assembly of α-CDs with the macroinitiator was carried out in aqueous solution, a water-soluble HEMA monomer was the choice of interest. Meanwhile the ATRP proceeded at 25 °C for 6 h, not at a relatively higher temperature due to the fact that a higher temperature would severely cause the dethreading of α-CDs off the PEG backbone [26,27]. Though Cu(I)Br/2,2′-bipyridine was also successfully applied to catalyze the ATRP of HEMA in methanol or



Scheme 1. Preparation strategy of polyrotaxanes via ATRP of HEMA in aqueous solution.

methanol/water media [19], it appeared that Cu(I)Br/PMDETA works well here in aqueous media.

3.2. Characterization of polyrotaxanes

The resulting PR products were characterized by using ^{1}H NMR analysis with DMSO-d_6 as solvent. ^{1}H NMR spectra of pure α-CDs and a polyrotaxane sample PEG–20CD–40 are illustrated in Fig. 1. If α-CDs are steadily held on the axle chain, their resonance peaks would broaden and slightly different chemical shifts could be discerned because of the chemical environmental change after formation of the PRs as described previously [27]. In fact, all the resonance peaks of α-CDs in the PRs are evidently broadened, and the corresponding resonance peaks of the hydroxyl groups (O_2H, O_3H, O_6H) are also different from those of the pure α-CDs. The peaks of –OH groups of HEMA are superposed with H1 of α-CDs at δ 4.795 ppm and $-CH_2-O-$ superposed with H5 of α-CDs at δ 3.586 ppm. The peak at δ 1.891 ppm corresponds to the $-CH_3$ contiguity to the Br end group. The other resonance peaks in the PR are assigned as follows: O_2H and O_3H of α-CD at δ 5.442–5.619, O_6H at 4.440–4.496, $-CH_2-$ of PHEMA at 1.787 and CH_3- at 0.768–0.940 ppm. Multiple resonances at δ 3.586–3.768 ppm are ascribed to the chemical shifts of H_3, H_6 and H_5, while PEG protons appear at δ 3.506 ppm. It clearly indicated that α-CDs are successfully threaded onto the PEG backbone and impeded by the bulky PHEMA blocks. The average in-chain number of α-CDs was readily calculated from the integration area ratio of the proton resonance peak of α-CD (O_6H) to that of the methylene protons in the central PEG axle, while the degree of polymerization (DP) of PHEMA was easily obtained from the integration area ratio of the proton resonance peaks of methyl group of HEMA unit to that of the methylene protons in PEG. Because of the broadening of resonance peaks of α-CDs leading to the superposition of H3, H6, H5 (superposed with the $-C(=O)-O-CH_2-$ group of HEMA) of α-CDs and methylene protons of PEG, the integration area of the methylene protons of PEG should be calculated by subtracting integration of one time $-C(=O)-O-CH_2-$ group (identified as *d* in Fig. 1C) of HEMA unit and three times integration of O_6H peak in α-CD from the integration of the multiple resonances at δ 3.586–3.768 corresponding to the areas of the foregoing superposition peaks for calculating.

Table 1
Compositions and yields of polyrotaxanes

Entry	Name	Molar composition (BriB–PEG–iBBr: α-CD:HEMA)		Molecular weight and polydispersity index			Yield[d] (%)
		Feed ratio	Found ratio[a]	M_n[a]	M_n[b]	M_w/M_n[b]	
1	PEG–0CD–40	1:0:40	1:0:37	9×10^3	3.93×10^4	1.31	86
2	PEG–20CD–40	1:20:40	1:18:38	2.6×10^4	7.35×10^4	2.54	38
3	PEG–20CD–80	1:20:80	1:16:67	3.0×10^4	1.07×10^5	2.87	40
4	PEG–20CD–120	1:20:120	1:17:117	3.4×10^4	1.49×10^5	2.97	43
5	PEG–30CD–40	1:30:40	1:25:35	3.2×10^4	–[c]	–[c]	34
6	PEG–40CD–40	1:40:40	1:33:39	3.9×10^4	–[c]	–[c]	31

[a] Determined by ^{1}H NMR analysis in DMSO-d_6.
[b] Determined by GPC in DMF at 50 °C at 1.0 ml/min using PS as calibration standards.
[c] PEG–30CD–40 and PEG–40CD–40 were not soluble in DMF completely, so their GPC results were not gained.
[d] Yield based on final product after incubating in DMSO at 60 °C for 12 h, followed by precipitation into acetone.

Usually, DMSO is the only solvent to dissolve polyrotaxanes. Surprisingly, the main-chain PRs featured with adjustable PHEMA blocks as end stoppers are soluble in DMF in the cases of the threaded number of α-CDs below 20. As a result, the molecular weight and polydispersity index of these PRs can be evaluated by GPC analysis using DMF as solvent. Fig. 2 depicts the GPC traces of PEG–20CD–PHEMA with varying lengths of PHEMA blocks. All the samples exhibited a nearly symmetrical and unimodal peak and an increase trend in the molecular weight with increasing the HEMA to macroinitiator feed ratio as well. Although relatively higher polydispersity indexes of 2.50–3.00 were evidenced for these main-chain PRs compared with PEG–0CD–40, these values were considered to be reasonable for this kind of supramolecular self-assemblies. Importantly, the GPC results clearly demonstrated that the PRs are formed via the ATRP of HEMA in the aqueous media rather than a mixture of PPRs and PHEMA.

Additionally, all the molecular weights determined by GPC were substantially higher than those by ^{1}H NMR analysis. This difference was also noticed earlier for the homopolymers of HEMA prepared via the ATRP [19], likely caused by the systematic errors in the GPC analyses. Polystyrenes as calibration standards are unlikely to be reliable for analysis of methacrylic polymers because DMF is only a marginal solvent for polystyrene, which would lead to a significant over-estimation of the true molecular weight of the well-solvated HEMA homopolymers [15]. At the same time, the rigid polyrotaxane block would possess the extended polymer chain conformation with the increasing hydrodynamic volume to result in a higher GPC molecular weight than that expected by ^{1}H NMR analysis.

Regarding the DP of PHEMA, it was well in accordance with the feed ratio with or without adding α-CDs. It implied that the high initiation efficiency was achieved, and the adding α-CDs did not weaken the initiation activity of the PPR initiator to initiate HEMA to polymerize. As for the threaded number of α-CDs, it was found to change from 18 to 32 corresponding to the molar feed ratio from 20 to 40. The higher the feed ratio, the higher is the threaded number of α-CDs. It seemed that the threaded α-CD number was also adjustable to some extent. Taking into account one α-CD including two PEG repeating units, the maximum number of α-CDs threaded onto the PEG 4K backbone is around 45. Evidently, an increasing amount of α-CDs cannot ensure them to reach this maximum value. It was probably due to the fact that there is the equilibrium between the threading and dethreading of α-CDs.

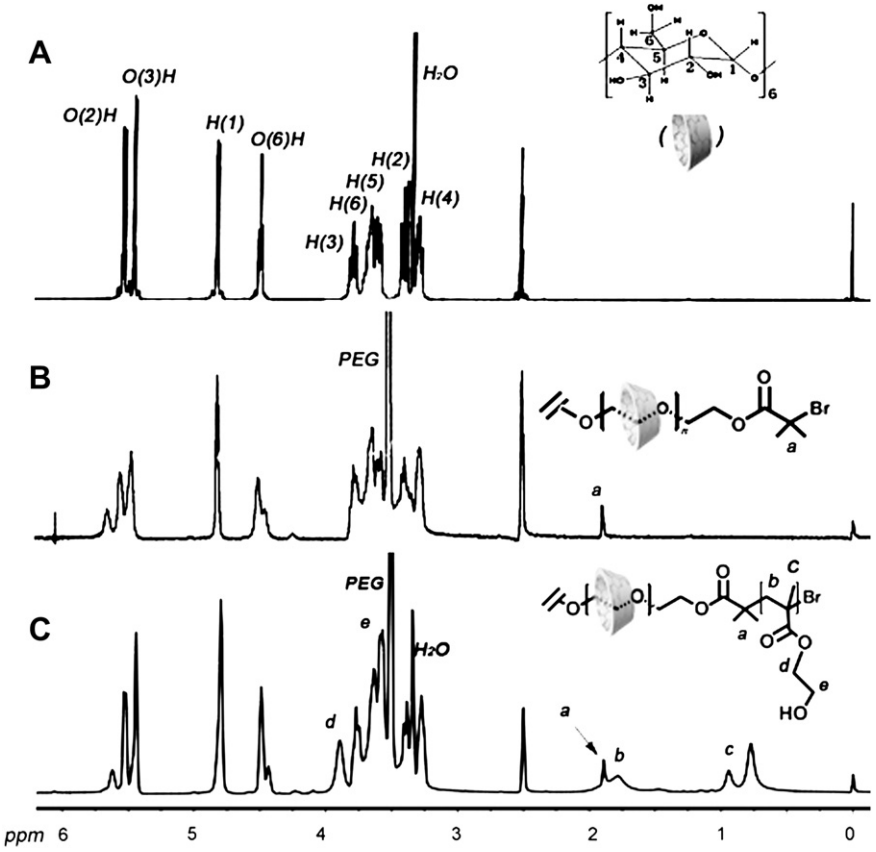


Fig. 1. ^{1}H NMR spectra of pure α-CD (A), PEG–20CD (B) and PEG–20CD–40 (C) in DMSO-d_6.

While more α-CDs are threaded onto the PEG backbone, they would show an increasing tendency to dethread off the axle chain leading to a lower threaded number than expected. However, when a smaller amount of α-CDs is added, the found feed composition would be close to the theoretical ones, just as in PEG–20CD–40.

The FTIR spectra of the PRs and their precursors are shown in Fig. 3. The peak for the carbonyl associated with the PHEMA ester appears at 1736 cm^{-1}, indicating that the HEMA monomers are in-chained because of a significant increase in the intensity of this bond stretching vibration of PEG–0CD–40 (C) and PRs (D–F) compared with their precursor BriB–PEG–iBBr (B). The C–O–C stretching vibration of carbonyl group in ester linkages appears at 1109 cm^{-1}. The PEG–0CD–40, pure α-CD and PRs showed broad bands due to hydroxyl stretching vibration at 3100–3700 cm^{-1}. C–H stretching vibration of PEG appears at 2883 cm^{-1} while that of α-CD appears at 2926 cm^{-1}. However, after adding α-CD, the C–H vibration tends to be merged,

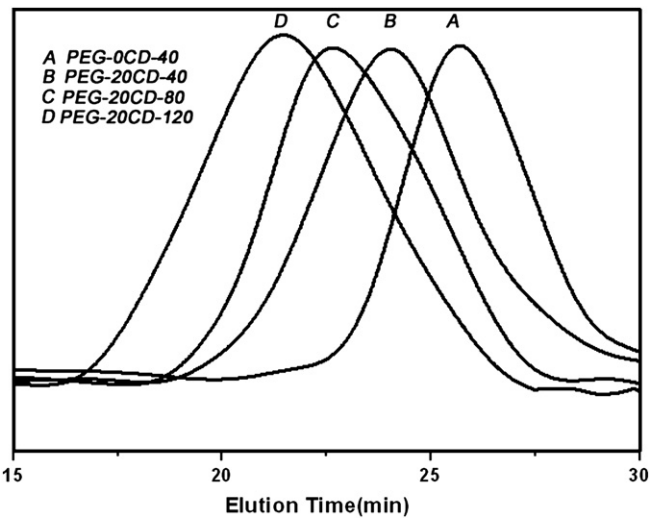


Fig. 2. GPC traces of PEG–0CD–40 (A), PEG–20CD–40 (B), PEG–20CD–80 (C) and PEG–20CD–120 (D).

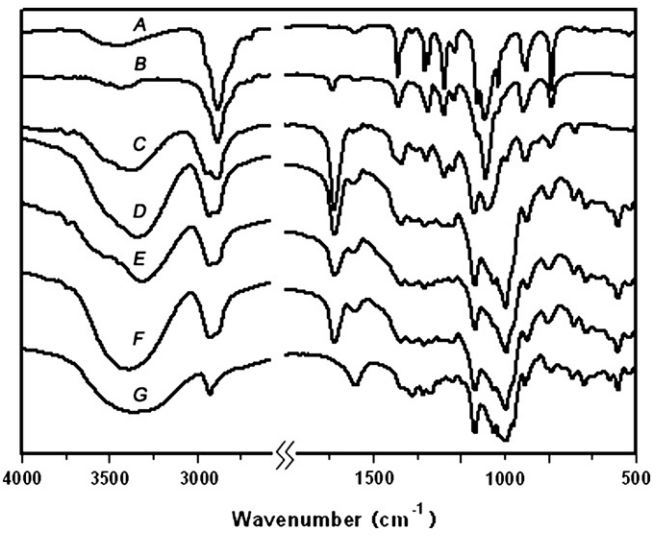


Fig. 3. FTIR spectra of PEG 4K (A), BriB–PEG–iBBr (B), PEG–0CD–40 (C), PEG–20CD–40 (D), PEG–30CD–40 (E), PEG–40CD–40 (F) and pure α-CD (G).

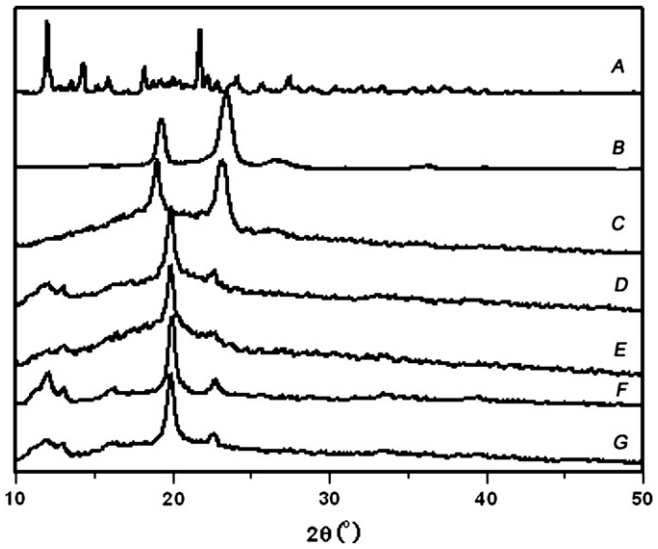


Fig. 4. X-ray diffraction patterns of pure α-CDs (A), BriB–PEG–iBBr (B), PEG–0CD–40 (C), PEG–20CD–40 (D), PEG–20CD–120 (E), PEG–30CD–40 (F) and PEG–40CD–40 (G).

especially in PEG–40CD–40, and shifts to higher frequency at 2940 cm^{-1}, likely caused by the non-covalent interaction between C–H of α-CD and the PEG backbone. All of the other peaks of the PHEMA blocks and those of α-CDs were clearly found in the spectra of the PRs. This provided the further evidence confirming that the resulting PRs are composed of α-CDs threaded onto a PEG axle flanked by PHEMA blocks as bulky stoppers and not a mixture of PPRs and PHEMA.

Though the as-synthesized PRs contain a varying amount of α-CDs, a channel-type crystalline structure for the polyrotaxanes was easily evidenced in their X-ray diffraction patterns as shown in Fig. 4. The major peaks at 12.04°, 14.36°, 18.24° and 21.76° were found for the pure α-CDs. The pattern of BriB–PEG–iBBr shows prominent peaks at 19.15° and 23.35°, and that of PEG–0CD–40 looks rather similar to it. However, the diffraction patterns of the PRs (D–G) are all quite different from that of pure α-CDs or BriB–PEG–iBBr and PEG–0CD–040. The peak appeared at $2\theta = 19.69°$ ($d = 4.32$ Å) is the characteristic diffraction peak to strongly support the channel-type crystalline structure of the obtained polyrotaxanes [1,10,11].

From the DSC curves as shown in Fig. 5, a clear endothermic peak appears at 40.8 °C corresponding to the melting point of PEG

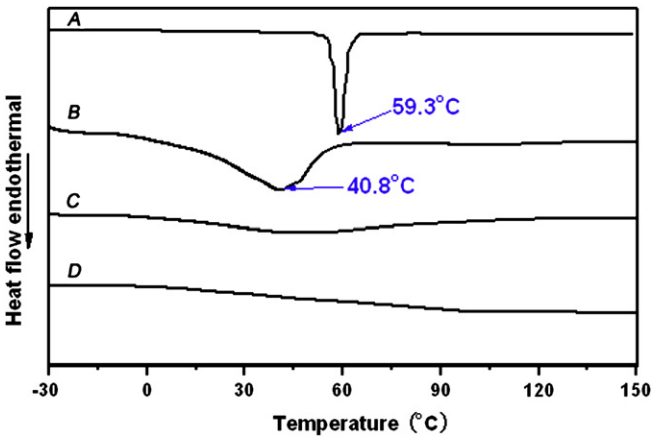


Fig. 5. DSC curves of PEG 4K (A), PEG–0CD–40 (B), PEG–20CD–40 (C) and pure α-CDs (D).

crystalline phase in the triblock copolymer PEG–0CD–40 (B) without α-CDs threading, while for PEG 4K (A) it emerges at 59.3 °C. The lower temperature of endothermic peak for the former is certainly ascribed to the interference of the PHEMA blocks attached to the two terminals of PEG axle. The corresponding endothermic peak is almost absent as evidenced in PEG–20CD–40, because the PEG chain is included into the channel of the host α-CD lattices, which restrict it from aggregating to form the crystalline phase again.

4. Conclusion

A kind of novel main-chain polyrotaxanes has been prepared via the ATRP of HEMA initiated by polypseudorotaxanes made from the self-assemblies of a distal 2-bromoisobutyryl end-capped PEG with a varying amount of α-CDs catalyzed by Cu(I)Br/PMDETA in aqueous media at room temperature. The incorporated number of HEMA is adjustable by changing its feeding ratio to the macroinitiator, while the threaded number of α-CDs is also tunable to some extent. The resulting polyrotaxanes are soluble in DMF when the threaded number of α-CDs is below 20. Their GPC traces exhibited a nearly symmetrical and unimodal peak. Holding the active Br end groups, they show the potential to be used as macroinitiator to initiate new ATRP processes. As combining the unique properties of general PRs with that of block copolymers, these polyrotaxanes are promising to be used as smart materials for the preparation of supramolecular sliding gels, biosensors, carriers for drug controlled release and scaffolds for tissue engineering.

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