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Dual-responsive polypseudorotaxanes based on block-selected inclusion between polyethylene-block-poly(ethylene glycol) diblock copolymers and 1,4-diethoxypillar[5]arene

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Based on the selective recognition of the polyethylene (PE) block of polyethylene-block-poly(ethylene glycol) (PE-b-PEG) by 1,4-diethoxypillar[5]arene (DEP5A), two novel thermo and competitive guest (1,4-dibromobutane or hexanedinitrile) responsive polypseudorotaxanes (PPRs) have been successfully constructed. The formations of PPRs both in solution and in the solid state were demonstrated by $^1$H NMR, 2D NOESY, and WAXD analyses. TGA data illustrate that PPRs exhibit higher thermal stability than their precursor diblock copolymers. Moreover, intriguing porous disk-like aggregates are produced by electrospraying of PPRs in CHCl$_3$ and the self-assembled structures of PPRs are totally changed by the addition of 1,4-dibromobutane or hexanedinitrile, demonstrating its competitive guest stimulioresponsive.

Experimental section

Materials

Monohydroxy-terminated PE-b-PEG$_{1400}$ ($M_n$ $\sim$ 1400 g/mol, 50 wt% of ethylene oxide, calculated molecular component is PE$_{145}$-b-PEG$_{1350}$ from GPC and $^1$H NMR data, see supporting information) and PE-b-PEG$_{2250}$ ($M_n$ $\sim$ 2250 g/mol, 80 wt% of ethylene oxide, calculated molecular component is PE$_{137}$-b-PEG$_{1683}$ from GPC and $^1$H NMR data, see supporting information) were purchased from Sigma Aldrich Corporation (St. Louis, MO). DEP5A was synthesized according to...
the published procedure. Chloroform (CHCl₃) was purchased from Sinopharm chemical reagent Co., Ltd (SCRC). All reagents were commercially available and used as supplied without further purification.

Analysis

$^1$H NMR spectra were collected on a temperature-controlled 500 MHz spectrometer with CDCl₃ as the solvent. GPC measurements of polymers were run at 35 °C using THF as eluent with a flow rate of 1.0 mL/min and linear polystyrene as standards. FESEM analysis was conducted on a Hitachi S-4800 electron microscope. The TEM images were obtained by a JEM-1400 Transmission Electron Microscope (JEOL Ltd, Tokyo, Japan) operated at 100 kV. WAXD measurements were carried out at room temperature using a Rigaku D/Max-2200PC X-ray diffractometer with a Cu target (40 KV, 40 mA). Powder samples for WAXD and TGA analyses were prepared from precipitated PPRs in cold precipitant (methanol or diethyl ether) and dried in a vacuum oven at room temperature for 24 h. The physical blend mixtures of PE-b-PEGs and DEP5A in the same molar ratio of corresponding PPRs were prepared by mixing PE-b-PEGs and DEP5A in a mortar and pestle for 3 min.

Results and discussion

The formation of PPRs

The preparation of PPR derived from the self-assembly of PE-b-PEG and DEP5A in CHCl₃ and its dual responsive processes are presented in Scheme 1. Partial $^1$H NMR spectra of PE-b-PEG₁₄₀₀ upon the addition of DEP5A showed that the signals of the methylene protons at δ = 1.25 ppm (H₆) in the PE block of PE-b-PEG₁₄₀₀ shifted upfield (δ = 1.23, 1.21, 1.18, 1.14, 1.09, 1.06) and splitted (δ = 1.04, 1.02, 0.98, 0.96 ppm) to H₆ (accompanied with line broadening), due to the shielding of methylene moiety by DEP5A (Fig. 1, the molar ratio of DEP5A to PE-b-PEG and the GPC data of PE-b-PEG were used to calculate). However, no shift changes were detected for the methylene protons (δ = 3.64 ppm, H₅) in the PEG block. Partial $^1$H NMR spectra of PE-b-PEG₂₂₅₀ upon the addition of DEP5A displayed similar chemical shift changes (Fig. S5) as those of PPR1. These phenomena indicated that only the PE chains were closely encircled by the macrocyclic cavities of DEP5A, forming PPRs, whereas the PEG blocks were uncovered. From 2D NOESY NMR analysis, NOE correlation signals were observed between the methylene protons (H₇) of PE chains and the methyl (H₄) and methylene protons (H₂ and H₃) of DEP5A (Fig. S7). These observations verified that the PE segments were successfully encapsulated in the cavity of DEP5A.

Fig. 1 Partial $^1$H NMR spectra (500 MHz, CDCl₃, 20 °C) of PE-b-PEG₁₄₀₀ upon the addition of DEP5A.

Dual-responsive processes of PPRs

Fig. 2 exhibited that the solution of PE-b-PEG₁₄₀₀ (10.0 mg/mL) in CDCl₃ became transparent and turbid upon heating and cooling, respectively, showing that PE-b-PEG₁₄₀₀ didn’t dissolve well enough in CDCl₃ at 20 °C. With the addition of DEP5A (44.0 eq), the mixture gradually became transparent, indicating the formation of PPR1 and its higher solubility than PE-b-PEG₁₄₀₀. With the addition of 1,4-dibromobutane (DBrBu) or hexanedinitrile (44.0 eq) to the solution, it became turbid again. These revealed that the formation and deformation of PPRs could be finely tuned by adding DEP5A and DBrBu or hexanedinitrile.

Fig. 2 PE-b-PEG₁₄₀₀ in CDCl₃ (10.0 mg/mL) and its tuning processes by heating and adding DEP5A or competitive guest molecule of DBrBu or hexanedinitrile.
Partial $^1$H NMR spectra of PPRs at different temperatures are recorded and shown in Fig. 3 and S8. At elevated temperatures, intensities of the signals at $\delta = 0.90$–0.88 ppm shifted downfield and became slightly stronger, indicating the reversible molecular recognition between DEP5A and PE segments of PE-b-PEG. All these phenomena suggested that the structure of PPRs could be reversibly tuned via heating or cooling, exhibiting thermo stimuli-responsive.

Partial $^1$H NMR spectra of PPR1 upon the addition of DBrBu are shown in Fig. 4. The signals of the methylene protons ($\delta = 1.00$ ppm, H$_b$) in PE blocks of PE-b-PEG$_{1400}$ shifted downfield ($\delta = 1.02, 1.04, 1.07, 1.10, 1.13, 1.18, 1.22, 1.24$ ppm) to H$_b$ (accompanied with line narrowing). DEP5A could form much stronger complex with DBrBu than with PE segments, so that the disassembly of PPR1 occurred.

As the methylene moiety of PE segments was unshielded by DEP5A, no shifts were detected for the signals of the methylene protons ($\delta = 3.64$ ppm, H$_c$) in PEG blocks of PE-b-PEG$_{1400}$. In addition, as a competitive guest, the effect of hexanedinitrile on the $^1$H NMR spectrum of PPRs was also investigated. As shown in Fig. 5, the signals of methylene protons (H$_b$) in PE blocks of PE-b-PEG$_{1400}$ shifted to H$_b$ upon the addition of hexanedinitrile. It can be attributed to the more stable complexation between hexanedinitrile and DEP5A, making the disassembly of PPR1 occurring.

There was no signal shifts detected of the methylene protons (H$_b$) in PEG blocks of PE-b-PEG$_{1400}$ for the methylene moiety of PEG blocks was unshielded by DEP5A. Similarly, upon the addition of DBrBu or hexanedinitrile, partial $^1$H NMR spectra of PPR2 displayed similar chemical shift changes (Fig. S12 and S16) with those of PPR1. These illustrate that the structure of PPRs could be disassembled by adding DBrBu or hexanedinitrile, exhibiting a competitive guest stimuli-responsive (Scheme 1). It can be concluded that the competitive guest which could form stable host–guest complexes with DEP5A than long alkyl chain can trigger the competitive guest stimuli-responsiveness of PPRs.

Partial $^1$H NMR spectra of PPR1 upon the addition of hexanedinitrile are shown in Fig. 5. The signals of the methylene protons (H$_b$) in PE blocks of PE-b-PEG$_{1400}$ shifted downfield ($\delta = 1.02, 1.04, 1.07, 1.10, 1.13, 1.18, 1.22, 1.24$ ppm) to H$_b$ (accompanied with line narrowing). DEP5A could form much stronger complex with DBrBu than with PE segments, so that the disassembly of PPR1 occurred.

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WAXD patterns of PPRs

WAXD patterns of DEP5A, PE-b-PEG, their physical blend mixtures, and PPRs are shown in Fig. 6. It can be seen that PE-b-PEG$_{1400}$ exhibits three prominent peaks at 19.2° for crystalline PEG
segments, at 21.4° for crystalline PE segments, and at 23.8° for both PE and PEG, respectively (Fig. 6a). For PPR1, a number of reflection peaks are presented which are different from that of DEP5A, PE-b-PEG1400, and their physical blends (Fig. 6a,1,2). The same situation is obtained for PPR2 (Fig. 6b). These indicate that PPRs formed different crystal structures, reflecting the formation of PPRs in the solid states.

**TGA of PPRs**

![TGA scans of DEP5A (1), physical blend mixtures of PE-b-PEG1250 and DEP5A (2), PPR1 (DEP5A 40.0 eq) (3), and PE-b-PEG1400 (4) a); DEP5A (1), physical blend mixtures of PE-b-PEG2250 and DEP5A (2), PPR2 (DEP5A 40.0 eq) (3), and PE-b-PEG2250 (4) b).](image)

The thermal stabilities of PPRs were investigated by TGA (Fig. 7). The decomposition temperature (T_d, a temperature at which 10% of mass loss has occurred) is used to evaluate the thermal stability [19b] and the results for the two PPRs are listed in Table 1. The T_d value for PPR1 is found to increase by 12 °C, and it increases by 5 °C for PPR2, as compared with their respective physical blend mixtures of PE-b-PEGs and DEP5A. Therefore, it is concluded that the diblock copolymers are stabilized by the formation of the PPRs, which might be attributed to the host–guest inclusion complexation between PE block of PE-b-PEG and DEP5A.

<table>
<thead>
<tr>
<th>PPRs</th>
<th>T_d(PPRs) [°C]</th>
<th>T_d(PE-b-PEG) [°C]</th>
<th>T_d(DEP5A/PE-b-PEG) [°C]</th>
<th>T_d(PPE) [°C]</th>
</tr>
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<tbody>
<tr>
<td>PPR1 402</td>
<td>391</td>
<td>380</td>
<td>392</td>
<td></td>
</tr>
<tr>
<td>PPR2 386</td>
<td>384</td>
<td>389</td>
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(T_d for free mixtures of DEP5A, DEP5A and PEG, and their solid mixtures; T_d for PPRs).

**Self-assembly of PPRs**

The size distribution curves of PPRs in CHCl_3 at various temperatures are shown in Fig S9 and S10. As can be seen, the particle size of either PPR1 or PPR2 increases with the temperature. It changes from 511.3 nm to 640.5 nm for PPR1 or 112.0 nm to 216.5 nm for PPR2 when the temperature was increased from 20 °C to 40 °C. This is probably due to the escaping of DEP5A from PE chain at higher temperatures, resulting in longer chain of the naked hydrophobic PE and thus the formation of large aggregate particles. Besides, it is found that the particle size of PPR2 is always smaller than that of PPR1 at the same temperatures, as the hydrophobic PE chain of PE-b-PEG2250 is shorter than that of PE-b-PEG1400.

The SEM and TEM images of the aggregates of PE-b-PEGs, PPRs and disassembled PPRs are shown in Fig. 8. Irregular particles are observed for PE-b-PEG1400 (Fig. 8a,b) and its corresponding PPR1 could self-assemble into network structures (Fig. 8b,c). When DBrBu was added to PPR1 solution, the threaded structures of PPR1 were destroyed and the square plate aggregates which may be formed by the self-assembly of the complex of DEP5A and DBrBu were visualized (Fig. 8c,d). Island shape aggregates are observed for PE-b-PEG2250 (Fig. 8d,e). Its corresponding PPR2 could self-assemble into network structures which is more regular than that of PPR1 (Fig. 8e,f). This can be ascribed to the fact that PPR2 has longer soft unthreaded PEG chain and shorter rigid threaded PE chain than PPR1, making it easier to form adaptive self-assembled structures. When DBrBu was added to PPR2 solution, the square plate aggregates were also got (Fig. 8f). The other irregular particles beside square plate aggregates may formed by the unthreaded PE-b-PEG chain and shorter rigid threaded PE chain than PPR1, making it easier to form adaptive self-assembled structures. All these phenomena illustrated that the self-assembled structures of PPRs can be adjusted by adding competitive guests.

**Fig. 8 SEM images of self-assembled structures in CHCl_3 at 20 °C: a) PE-b-PEG1400 (1.0 mg/mL), b) PPR1 (DEP5A, 40.0 eq), c) 40.0 eq DBrBu was added to b), d) PE-b-PEG2250 (1.0 mg/mL), e) PPR2 (DEP5A, 40.0 eq), f) 40.0 eq DBrBu was added to e).** The scale bar of a,b,c,d,e,f) is 2 μm; The scale bar of c) and f) is 10 μm; The scale bar of a,b,c,d,e,f) is 1 μm.

Electrospraying is a promising technology to prepare various polymer structures from solutions based on high-voltage electrostatic
particles (average diameter, 2.60 µm) are produced from PEx precursor diblock copolymers. The self-assembled structures of produced from PPRs are also porous (Fig. 9c,f). Near-spherical pores than these of PPRs (Fig. S22c,f). The reasons of the pores further confirming the successful formation of PPRs. Different from those of the individual PEG-b-PEGs and DEP5A, further confirming the successful formation of PPRs.

Those intriguing electrospayed porous dish-like aggregates encouraged us to explore what it was change to for disassembled PPRs. So, DBrBu was added to PPRs solution to destroy the threaded structures of PPRs. Spherical geometry particles and hemispherical aggregates with some pores on their surface were produced from disassembled PPR1 and PPR2, respectively (Fig. S22a,d). The TEM results suggested that those aggregates had less pores than these of PPRs (Fig. S22c,f). The reasons of the pores formation and the application of those tailorable aggregates of PPRs as advanced functional materials with high performance^{21} are under investigation.

**Conclusions**

In summary, two novel thermo and competitive guest (DBrBu and hexanedinitrile) responsive PPRs have been successfully constructed via the selective recognition and threading of the PE block of PE-b-PEG with DEP5A efficiently. Due to their host-guest inclusion complexation, PPRs exhibit higher thermal stability than their precursor diblock copolymers. The self-assembled structures of PPRs are totally changed by the addition of DBrBu or hexanedinitrile in CHCl3, and exhibit its competitive guest stimuli-responsiveness. Furthermore, it is found that PSA-based host–guest chemistry and PE-based block copolymers are a perfect combination for the formation of stimuli-responsive polymeric materials. Thus, it is anticipated that this facile strategy may open up many new opportunities for accessing a new class of polyolefin materials with structural diversity and functional utility.

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**Notes and references**


