Efficient synthesis of trefoil-shaped tricyclic polymers by a ROMP-based blocking-cyclization technique†

Hao Wang, Cuihong Ma, Zhiying Han, Xiaojuan Liao, Ruyi Sun* and Meiran Xie†

Cyclic polymers have unique physical properties and attract extensive attention, but the precision synthesis of complex cyclic polymers is a challenging subject. Herein, by using a polymeric ladderphane with six living ends as the initial motif, complex trefoil-shaped tricyclic polymers were precisely synthesized by a ring-opening metathesis polymerization-based blocking-cyclization technique in a simplified process, where three macromolecular rings consisting of multiple repeating units were covalently interconnected at a single junction point, and the ring size was readily regulated by varying the feed ratio of monomers. The topological structures and physical properties of trefoil-shaped tricyclic polymers were fully characterized. Importantly, the molecular topology of trefoil-shaped tricyclic polymers was clearly observed. Therefore, this work provides an effective strategy for the synthesis of complex cyclic polymers.

Introduction

The research on different topological polymers has become a popular subject in recent years as a result of the close relationship between physicochemical properties and topological structures of polymers.1–4 Cyclic polymers are a kind of topological polymer without chain ends,5,6 and exhibit unique physical properties, such as smaller hydrodynamic volume, lower viscosity, and higher glass transition temperature, compared with their linear polymer counterparts.7–10 Consequently, cyclic polymers have attractive application potential in the fields of drug delivery, coatings, and electronic devices.11–15

Multicyclic polymers with multiple ring units are a kind of cyclic polymer with complex topological structures, and can be divided into three basic types namely fused, bridged, and spiro (such as eight-, trefoil-, and quatrefoil-shaped) cyclic polymers.16–19 It is worth noting that the complex architectures contribute to unusual properties; for instance, the thin films of trefoil-shaped tricyclic polymers with more compact conformations show smaller domain spacing than linear and monocyclic polymers.20,21 The precision synthesis of multicyclic polymers is still a challenge due to the inherently complex topology consisting of multiple ring units connected to a single junction point,22–25 and thus multicyclic polymers have attracted more attention as synthetic targets. Until now, two traditional synthetic routes namely the ring-closure method and the ring-expansion method have been developed for multicyclic polymers. The ring-closure method is more commonly applied to synthesize multicyclic polymers. For example, the trefoil-shaped tricyclic polymers were prepared by a bimolecular ring-closure method based on the self-accelerating click reaction of azide–alkyne,23 and the quatrefoil-shaped tetra cyclic polymers were prepared through a unique monomolecular ring-closure method based on the combination of atom transfer radical polymerization with a photo-induced coupling reaction.16 In addition, the trefoil-shaped and quatrefoil-shaped cyclic polymers were successfully synthesized by the intramolecular ring-opening metathesis oligomerization of star-shaped polymers with norbornene ends.22 However, the ring-closure method for preparing multicyclic polymers possesses demerits such as requiring low concentration (<10⁻³ mol L⁻¹), the use of functionalized linear polymer precursors, products with low molecular weights, and the separation of linear polymer residues or by-products.26–29 The ring-expansion method is another attractive strategy for preparing cyclic polymers through cyclic catalysts that initiate monomers. Although the ring-expansion method does not require a linear polymer precursor and low concentration conditions,30,31 there are a few reports on the synthesis of multicyclic polymers because a cyclic catalyst cannot form multiple polymer chains simultaneously from a single reactive center.32,33 Thus, devel-
opining an efficient method to precisely synthesize multicyclic polymers is an urgent problem. Recently, a ring-opening meta-
thesis polymerization (ROMP)-based blocking-cyclization tech-
nique has been developed as a precise synthetic method to
construct cyclic polymers by using a short polymeric ladder-
phane with two living ends as the initial motif. Compared
with the above two methods, the blocking-cyclization tech-
nique has some merits such as the direct use of a commer-
cial Grubbs catalyst, nonrequirement of low concentration of
monomers, the use of a short ladderphane as the multiply
cyclizing unit for achieving cyclic polymers with high purity,
and nonrequirement of a separation process for the linear
polymer precursor residue. However, the synthetic processes of
the bicyclic and tricyclic polymers are complicated when a lad-
derphane with two living ends is used as the initial motif,
which, respectively, needs five and seven feeding steps. To sim-
plify the feeding procedure, a polymeric ladderphane with four
living ends as the initial motif was developed; thereby, the
synthesis process of bicyclic polymer was greatly simplified,
just needing three feeding steps. Thus, a polymeric ladder-
phane as the initial motif plays an important role in the con-
struction of different cyclic topologies through the blocking-
cyclization technique and the previous results indicated
that designing a rational polymeric ladderphane as the initial
motif is crucial to precisely construct a multicyclic polymer
with a complex architecture.

In this work, a novel triphenylene-based hexafunctional
norbornene monomer was synthesized and polymerized by
ROMP to obtain a polymeric ladderphane containing six living
ends, which was used as an efficient initial motif to precisely prepare a kind of trefoil-shaped tricyclic polymer through a
ROMP-based blocking-cyclization technique with a simplified
procedure containing only three feeding steps. Typically, the
hexa-, di-, and monofunctional norbornene derivatives were
successively initiated by a Grubbs catalyst for a preset time.
Notably, the short polymeric ladderphane acted as a single
junction point to covalently interconnect three ring units, and
the molecular topology of trefoil-shaped tricyclic polymers was
observed. Consequently, the effective strategy provides a new
insight into the development of complex cyclic polymers.

Experimental

Materials

Bis(norbornene pyrrolidine phenyl perylene bisimide) (BNP),
end-N-3,5-bis(trifluoromethyl)biphenyl norbornene pyrroli-
dine (TNP), endo-N-(4-hydroxy phenyl)norbornene dicarboxi-
mide (NDI), N-(4-pentafluorophenyl formate phenyl)norbor-
nene dicarboximide (PFN), (Z)-2-butene-1,4-diol bis(rhoda-
nine-N-acetic acid ester) (BRD), and the third-generation
Grubbs catalyst (Ru-III) were synthesized according to the
previous procedures. 1H and 13C NMR spectra were recorded using a Bruker 600 or
500 MHz spectrometer. UV-vis spectra were recorded using a UV-1800 spectrometer. ATR-IR spectra were recorded on a Nicolet iS50 FT-IR spectrometer. The relative molecular weight and molecular weight distribution were recorded using a gel
permeation chromatography (GPC) instrument equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refraction
index detector, and a set of Waters Styrage columns (7.8 × 300 mm, 5 mm bead size; 104, 105 Å pore size). The absolute molecular weight and intrinsic viscosity were recorded using a multi-angle detector, containing a high-per-
formance size-exclusion chromatograph (HPSEC), a Viscotek system (Viscotek TDAmax) with a differential viscometer (DV),
and right angle laser-light scattering (RALLS, Viscotek), low-
angle laser-light scattering (LALLS, Viscotek), and refractive
index (RI) detectors. A PL 10 mm guard column (50 × 7.5 mm2), one Viscotek T6000 column (8.0 × 300 mm, 10 mm bead size; 104 Å pore size) and one Viscotek T4000 column (8.0 × 300 mm, 6 mm bead size; 1.5 × 104 Å pore size) were the
important parts of the column. Dynamic light scattering (DLS)
was determined using Malvern Zetasizer Nano-ZS light scattering
apparatus (Malvern Instruments, U.K.) with a He–Ne laser
(633 nm, 4 mW). All samples were filtered with syringe filters
(0.22 μm pore size) before the test. Thermogravimetric analysis
(TGA) was performed using an SDTQ851e/SF/1100 °C TGA
instrument under nitrogen flow at a heating rate of 10 °C
min−1 from 25 to 800 °C. Differential scanning calorimetry
(DSC) was performed using a Q2000 DSC system under a nitro-
gen atmosphere. All samples for DSC measurements were first
heated from 25 to 250 °C at a rate of 30 °C min−1 and held at
this temperature for 3 min to eliminate the thermal history;
then, they were cooled to 25 °C and reheated from 25 to 250 °C
at a heating or cooling rate of 10 °C min−1. Transmission electron microscopy (TEM) images were recorded using a JEOL
JEM2100F or FEI-G2F20 at an operating voltage of 100 kV or
120 kV. All samples for TEM measurements were prepared by
dropping a THF solution of the polymer with a di
erent con-
granular carbon-coated copper grids, followed by air-drying, and then kept in a vacuum at room temperature until the test.

Synthesis of trefoil-shaped tricyclic polymers

A 50 mL Schlenk tube was charged with the hexafunctional
monomer HNHT (2.4 mg, 1.0 μmol) dissolved in 2 mL of dry
CHCl₃. The difunctional monomer BNP (4 mg, 3.0 µmol) was dissolved in 1 mL of dry CHCl₃ in a 25 mL Schlenk tube. Ru-III (1.1 mg, 1.2 µmol) and the monofunctional monomer TNP (55.1 mg, 0.13 mmol) were dissolved in 1 mL and 4 mL of dry CHCl₃ in two 50 mL Schlenk tubes, respectively. After degassing with three freeze–vacuum–thaw cycles, the solution of Ru-III was injected into the HNHT solution via a syringe under vigorous stirring at 30 °C for 1 h, and then the TNP solution was injected into the reaction mixture and stirred for 0.5 h. Finally, the solution of BNP was added to the reaction mixture and stirred for further 2 h, affording the trefoil-shaped tricyclic polymer c-[PHNHT₅-[b-PTNP₁₀b]-b-BPNP₃] (58.4 mg, 95%). GPC: $M_n = 67.2$ kDa, $D = 1.65$. ¹H NMR (500 MHz, CDCl₃, ppm): $\delta$ 8.66 (m, pery), 8.01–7.78 (m, triphenylene + F₂CCCH), 7.76–7.60 (m, F₃CCCHCCF₃), 7.58–7.33 (m, aromatic + CCCH), 7.01–6.51 (m, aromatic), 5.64–5.19 (m, CH=CH on PNB backbone), 4.32–4.07 (m, OCH₂CH₂ + NCH₂CH₂), 3.46–2.53 (m, OCCCH + CHCHCH + O=CCCH₂), 2.14–1.08 (m, CH₂CH₂CH₂ + CHCH₂CH + OCCCH₃), 13C NMR (125 MHz, CDCl₃, ppm): $\delta$ 175.54, 173.32, 166.36, 162.28, 148.37, 143.13, 132.24, 131.94, 131.77, 131.68, 127.93, 127.83, 126.75, 125.89, 125.73, 124.58, 122.41, 119.23, 113.21, 49.91, 49.70, 47.67, 46.77, 44.90, 40.21, 39.96, 39.03, 37.44, 37.20, 22.96, 16.47.

Trefoil-shaped tricyclic polymers c-[PHNHT₅-[b-PTNP₃b]-b-BPNP₃] (m = 70, 90, and 130) were prepared in a similar way following the above synthetic procedure.

Results and discussion

Synthesis and characterization of the short ladderphane

A novel hexafunctional norbornene monomer, 2,3,6,7,10,11-hexa(N-4-[phenyl norbornene dicarboximide]oxohexanooate)triphenylene (HNHT), was designed and successfully synthesized (Scheme S1†), and the details for experiment and characterization are described in the ESI and Fig. S1 and S2. The Ru-III-initiated ROMP of HNHT could be smoothly conducted at diluted concentration to form the polymeric ladderphane, poly(2,3,6,7,10,11-hexa(N-4-[phenyl norbornene dicarboximide]oxohexanooate)triphenylene) (PHNHT), which played a crucial role in the synthesis process of the complicated trefoil-shaped tricyclic topology. According to the previous procedure, the short ladderphane PHNHT₅ was prepared under the conditions of a feed ratio ([HNHT]/[Cat]) of 3:6 ([norbornene]/[Cat] = 5:1) and a low monomer concentration of $2 \times 10^{-4}$ mol L⁻¹ (1.2 $\times 10^{-3}$ mol L⁻¹ of norbornene group) for 1 h (Scheme S2 and Table S1†), also, the ladderphane PHNHT₅ with an extended chain length was obtained by increasing the feed ratio of [HNHT]/[Cat] to 5:6 ([norbornene]/[Cat] = 5:1). However, when the [HNHT]/[Cat] ratio was further increased to 10:6 ([norbornene]/[Cat] = 10:1), the polymer yield was remarkably reduced and a large amount of residual HNHT was apparently found by TLC analysis, and even if the polymerization time was prolonged to 4 h, there was no obvious improvement in polymer yield, probably due to the relatively high loading of the bulky monomer HNHT. The results of GPC analysis showed that the homopolymers PHNHT₃ and PHNHT₅ had the number-average molecular weights ($M_n$) of 2.7 kDa and 4.5 kDa accompanied by narrow polydispersions ($D$) of 1.21 and 1.24, respectively (Fig. S3a and b†), indicating the successful preparation of PHNHT₅ (n = 3, 5), and the monomodal GPC curves revealed that the homopolymers did not have branched or cross-linked structures. In addition, the absolute molecular weight ($M_n$) of PHNHT₅ was consistent with the theoretical value of 12.2 kDa. Notably, the $M_n$ value of the homopolymer PHNHT₆ (Mₙ = 4.9 kDa) (Fig. S3c†) was slightly higher than that of the homopolymer PHNHT₅ (Mₙ = 4.5 kDa), indicating that the $M_n$ value of the homopolymer PHNHT₅ does not obviously increase when the ratio of [HNHT]/[Cat] exceeds 5:6 ([norbornene]/[Cat] = 5:1). It is worth noting that the reactant concentration is also a key factor in the synthesis of a polymeric ladderphane without a flawed structure. When the monomer concentration of HNHT increased to $5 \times 10^{-4}$ mol L⁻¹ (3 $\times 10^{-3}$ mol L⁻¹ of the norbornene group), although the feed ratio ([HNHT]/[Cat]) of 5:6 ([norbornene]/[Cat] = 5:1) and the polymerization time of 1 h were unchanged, the obtained homopolymer PHNHT₅ possessing an increased $M_n$ value of 6.1 kDa and a broader $D$ value of 1.34, while the GPC curve showed a shoulder peak (Fig. S3d†), likely due to the branched structure in the homopolymer at higher monomer concentration. In addition, the homopolymer PHNHT₅ showed very poor solubility in organic solvent as the monomer concentration further increased to $1 \times 10^{-3}$ mol L⁻¹ (6 $\times 10^{-3}$ mol L⁻¹ norbornene group), indicating that a severe cross-linked reaction had occurred. However, if the monomer concentration of HNHT decreased to $1 \times 10^{-4}$ mol L⁻¹ (6 $\times 10^{-4}$ mol L⁻¹ norbornene group), the $M_n$ value of the resulting homopolymer PHNHT₅ (Mₙ = 4.4 kDa) (Fig. S3d†) was comparable to that of PHNHT₅ (Mₙ = 4.5 kDa) obtained at a monomer concentration of $2 \times 10^{-4}$ mol L⁻¹ (1.2 $\times 10^{-3}$ mol L⁻¹ norbornene group), and the GPC trace also showed a single peak. These results might be attributed to the fact that the hexafunctional monomer HNHT in solution at low concentration could be regularly arranged by the π–π interaction between the rigid triphenylene moieties, and the monomers preferred to form the polymer with a stable ladderphane structure. Furthermore, the low monomer concentration of HNHT prevented the formation of branched or cross-linked structures of homopolymers. In a word, when the monomer concentration of HNHT was reduced to $2 \times 10^{-4}$ mol L⁻¹ or below, the undesirable branched or cross-linked structures in the homopolymer PHNHT₅ could be avoided. As expected, it was observed from the 'H NMR spectrum that the new peak of olefinic protons (H₄) on the polymer backbone at 6.03–5.04 ppm appeared (Fig. S4–S6†), while the olefinic protons on the norbornenyl ring of the monomer at 6.23 ppm (Fig. S1a†) disappeared, indicating that the homopolymers PHNHT₃ and PHNHT₅ were indeed generated at a low monomer concentration of $2 \times 10^{-4}$–$1 \times 10^{-4}$ mol L⁻¹. To confirm the polymeric ladderphane structure of PHNHT₅ (n = 3, 5) possessing six active ends, which was the key point for the formation of the following six-arm star-shaped polymer, the RD group-termin-
nated ladderphanes PHNHTₙ-6RD (n = 3, 5) were also prepared by using BRD as the terminating agent at a monomer concentration of 2 × 10⁻⁴ mol L⁻¹ (Scheme S2†). The end-capped homopolymers PHNHT₃-6RD and PHNHT₅-6RD had the Mₙ values of 2.8 kDa and 4.7 kDa (Fig. S3†), respectively, which were slightly higher than those of PHNHT₃ and PHNHT₅, meaning that BRD was incorporated into the structures of PHNHT₅-6RD and PHNHT₃-6RD. Compared with the ¹H NMR spectrum of PHNHT₃, a new peak at 4.77–4.58 ppm belonging to the methylene protons (Hₘ) of –CH₂O– on the RD group appeared in the ¹H NMR spectrum of PHNHT₅-6RD (Fig. S7†), and the actual integral area ratio of protons Hₗ at 7.82 ppm to that of protons Hₘ at 7.47–4.58 ppm was calculated to be 30 : 12.01, which was consistent with the theoretical area ratio of 30 : 12 based on five HNHT units and six RD end-groups.

The result indirectly verified that PHNHT₃ had six living ends (12.01/6 = 2.01). Moreover, by comparing the actual integral area ratio of 30 : 60.39 for the protons H₁ at 7.81 ppm to the methylene protons (Hₘ) of the end-capped PHNHT₃-6RD (Fig. S4†) with that of 30 : 72.29 for the protons H₁ at 7.82 ppm to the protons Hₘ at 4.45–4.04 ppm on PHNHT₃ (Fig. S4†) with that of 30 : 72.29 for the protons H₁ at 7.82 ppm to the protons Hₘ at 4.45–3.99 ppm on PHNHT₃-6RD (Fig. S7†), the increased number of protons of about 12 (72.29–60.39 = 11.90) was attributed to the methylene protons Hₘ derived from the six RD groups, which also suggested that PHNHT₃ contained six living ends. Similarly, the shorter ladderphane PHNHT₅ (Fig. S5†) also had three HNHT units and six living ends, which can be end-capped by six RD groups to form PHNHT₅-6RD (Fig. S8†) confirmed by the ¹H NMR analysis. Lastly, the ladderphane PHNHT₅ and the end-capped ladderphane PHNHT₅-6RD formed at a further lowered monomer concentration of 1 × 10⁻⁴ mol L⁻¹ (Fig. S6 and S9†) also possessed five HNHT units and six living ends, which can be verified by the ¹H NMR analysis. It should be pointed out that for homopolymers PHNHT₃ and PHNHT₅-6RD (n = 3, 5), if polymerization is not performed following the protocol shown in Scheme 1, the resulting polymers will have complex structures that either one ladderphane PHNHT was connected with an HNHT unit by the intermolecular reaction to form the possible defective structure with a higher molecular weight and more end groups (Fig. S10a and c†), or two adjacent norbornene groups on one HNHT of the ladderphane PHNHT were connected by the intramolecular reaction to form another defective structure (Fig. S10b and d†), and thereby the methylene proton (Hₘ) numbers of the end-capped RD groups would be deviated from 12 because the number of living ends on PHNHT₃ was unlikely to be six, which were inconsistent with the actual results by ¹H NMR and GPC analyses, indicating that the proposed defective ladderphane structures should be absent. Therefore, the results fully confirmed that the homopolymers PHNHTₙ (n = 3, 5) had six living ends, and the methylene proton (Hₘ) numbers of the RD groups were only derived from the single structure of PHNHTₙ-6RD (n = 3, 5), rather than the average value for the mixture of PHNHTₙ-6RD oligomers with different living ends. Meanwhile, the ladder morphology of PHNHT₃ was observed by TEM (Fig. S11a-c†), and the black lines arranged in parallel with each other to form the ladder nanostructure with an average band spacing of nearly 0.34 nm, which was in agreement with the distance of π–π interactions between the triphenylene moieties. Noteworthily, the observed morphology was an ordered assembly rather than the single-molecule topology of PHNHT₃, because it was too short to be well observed. Besides, the diffraction spots could be observed in the relative selected area electron diffraction (SAED) diagram (Fig. S11d†), which confirmed the ordered ladderphane nanostructure of PHNHT₃, despite the SAED image not showing the conventional regular diffraction patterns due to the short ladderphane PHNHT₃ forming a short-range ordered structure. Therefore, the successful preparation of the polymeric ladderphane PHNHT₃ guaranteed the synthesis of the expected trefoil-shaped tricyclic polymer.

Synthesis and characterization of trefoil-shaped tricyclic polymers

The trefoil-shaped tricyclic polymers, cyclic-[poly(2,3,6,7,10,11-hexa(N-4′-phenyl norbornene dicarboximide)oxohexanoate)triphénylene]-block-hexa-poly[(endo-N-3,5-bis(trifluoromethyl) biphenyl-norbornene pyrrolidine)-block-bi-poly(bis(norbornene pyrrolidine phenyl perylene bisimide))] (c-[PHNHT₅(b-PTNP₉)₃]-b-PBNP₅), were synthesized by successive ROMP of hexafunctional HNHT, monofunctional TNP, and difunctional BNP in an alternating feed process, as described in Scheme 1, starting from the short ladderphane PHNHT₃ (n = 5), propagating with the chain PTNP₉m and terminating by the blocking unit of the short ladderphane PBNP₅ (k = 5) to accomplish the cyclization process. Upon extending the length of single chain PTNP₉m (m = 70, 90, 110, and 130), the Mₙ values of tricyclic polymers increased from 48.1 kDa to 98.0 kDa correspondingly (Table 1, Fig. 1a and S12†). For comparison, the representative six-arm star-shaped polymer 6a-[PHNHT₅[b-PBNP₅(b-PTNP₉)]₃] was also synthesized by adjusting the feed order of monomers BNP and TNP (Scheme S3†), and it displayed a higher molecular weight (Mₙ = 81.8 kDa) than the tricyclic polymer c-[PHNHT₅[(b-PTNP₉₁₀)₃]-b-PBNP₅] (Mₙ = 67.2 kDa), which was attributed to the smaller hydrodynamic volume of the cyclic polymer. Furthermore, the monomodal GPC curve of the tricyclic polymer indicated the absence of branched or cross-linked structures. Meanwhile, the absolute molecular weight (Mₐ) of 6a-[PHNHT₅[b-PBNP₅(b-PTNP₉₁₀)]₃] (Mₐₙₙ = 301.6 kDa) was similar to that of c-[PHNHT₅[(b-PTNP₉₁₀)₃]-b-PBNP₅] (Mₐₙₙ = 297.8 kDa) due to the same number of repeating units as each other. It was found that the Mₐₙₙ value of the trefoil-shaped tricyclic polymer was about 4.4 times larger than its Mₙ value, and Mₐₙₙ was 3.7 times its Mₐₙₙ. All polymerization reactions were conducted well with yields over 90% (Table 1).

The structure of polymers was characterized by NMR spectroscopy. For six-arm star-shaped 6a-[PHNHT₅[b-PBNP₅(b-PTNP₉₁₀)]₃] and trefoil-shaped tricyclic c-[PHNHT₅[(b-PTNP₉₁₀)₃]-b-PBNP₅], as shown in Fig. 1b and S13† the typical peak at 6.23 ppm for the olefinic protons on the norbornenyl ring of the monomer completely disappeared, and a
new broad peak at 5.64–5.19 ppm for the olefinic protons (H_a) on the polymer backbone was observed, indicating that the successive ROMP of alternating added monomers occurred successfully. By analyzing the integral areas of methylene protons (H_k+v) on the HNHT and BNP units at 4.32–4.07 ppm (for HNHT units, the integral area could be derived as S_k = S_k+v − S_v = S_k+v − 1S_w), the aromatic protons (H_q) belonged to the bis (trifluoromethyl)biphenyl group at 7.76–7.60 ppm and the aromatic protons (H_w) on the perylene imide group at 8.66 ppm, and the actual block ratios of PHNHT/PTNP/PBNP for the trefoil-shaped tricyclic and six-arm star-shaped polymer counterparts were calculated to be 5 : 659.26 : 15.18 [(60/12) : (659.26/1) : (120.72–60)/4] and 5 : 648.06 : 15.24 [(60/12) : (648.06/1) : (121.97–60)/4], respectively, which were basically in agreement with the feed ratios of 5 : 660 : 15. Similarly, for other three trefoil-shaped tricyclic polymers c-[PHNHT_{5-[(b-PTNP_{m})_2-b-PBNP]}] (m = 70, 90, and 130), the ratios of PHNHT/PTNP/PBNP were calculated to be 5 : 392.61 : 15.09, 5 : 544.19 : 15.07, and 5 : 744.18 : 15.05 (Fig. S14†), which were also close to the feed ratios of 5 : 420 : 15, 5 : 540 : 15, and 5 : 780 : 15, respectively. Importantly, the degree of polymerization for each ring of the trefoil-shaped tricyclic polymer

Scheme 1 ROMP-based blocking-cyclization process for the synthesis of trefoil-shaped tricyclic polymers with varied ring sizes.
reached up to about 250, and the total repeating units of the three rings touched 750, which was a remarkable progress in enlarging the size of multicyclic polymers compared with the results reported previously, suggesting the feasibility of the synthesis for large sized trefoil-shaped tricyclic polymers. In addition, the $^{13}$C NMR spectra revealed a single peak of aromatic carbon (C3) at 148.37 ppm and another single peak of aromatic carbon (C5) at 143.13 ppm ascribed to the triphenylene linker (Fig. S15†), indicating the successful preparation of the trefoil-shaped tricyclic polymer $c$-{PHNHT$_5$-[($b$-PTNP$_{110}$)$_2$-$b$-PBNP$_5$]$_3$}. If the polymerization does not proceed precisely as the protocol in Scheme 1, some possible (defective) structures of cyclic polymers may be formed (Fig. S16†): (i) the PTNP segment in one ring of the trefoil-shaped tricyclic polymer passes through another ring to form the defective tricyclic polymer with a similar polymer knot structure (Fig. S16a†). However, the formation of the defective tricyclic polymer was difficult because the two PTNP segments in each ring of the trefoil-shaped tricyclic polymer with a compact structure could easily come close to each other and form the intra-chain entanglement junctions by the π–π stacking interaction of the adjacent biphenyl groups, which improved the cyclization efficiency of the ladderphane PBNP for cyclizing the six-arm star-shaped polymer $6a$-[PHNHT$_5$-[($b$-PBNP$_5$-$b$-PTNP$_{110}$)$_3$] with six living ends to form the trefoil-shaped tricyclic polymer and prevented other PTNP segments from passing through the ring.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>[HNHT]/[TNP]/[BNP]/[Cat]</th>
<th>$M_n$ (kDa)</th>
<th>$D$</th>
<th>Yield (%)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$c$-{PHNHT$<em>5$-[($b$-PTNP$</em>{110}$)$_2$-$b$-PBNP$_5$]$_3$}</td>
<td>5 : 420 : 15 : 6</td>
<td>48.1</td>
<td>1.31</td>
<td>92</td>
<td>167</td>
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<td>2</td>
<td>$c$-{PHNHT$<em>5$-[($b$-PTNP$</em>{90}$)$_2$-$b$-PBNP$_5$]$_3$}</td>
<td>5 : 540 : 15 : 6</td>
<td>61.2</td>
<td>1.43</td>
<td>96</td>
<td>170</td>
</tr>
<tr>
<td>3</td>
<td>$c$-{PHNHT$<em>5$-[($b$-PTNP$</em>{110}$)$_2$-$b$-PBNP$_5$]$_3$}</td>
<td>5 : 660 : 15 : 6</td>
<td>67.2</td>
<td>1.65</td>
<td>95</td>
<td>173</td>
</tr>
<tr>
<td>4</td>
<td>$6a$-[PHNHT$_5$-[($b$-PBNP$<em>5$-$b$-PTNP$</em>{110}$)$_3$]</td>
<td>5 : 660 : 15 : 6</td>
<td>81.8</td>
<td>1.74</td>
<td>93</td>
<td>165</td>
</tr>
<tr>
<td>5</td>
<td>$c$-{PHNHT$<em>5$-[($b$-PTNP$</em>{110}$)$_2$-$b$-PBNP$_5$]$_3$}</td>
<td>5 : 780 : 15 : 6</td>
<td>98.0</td>
<td>1.71</td>
<td>91</td>
<td>176</td>
</tr>
</tbody>
</table>

*Polymerization conditions: using Ru-III as the catalyst, CH$_2$Cl$_2$ as the solvent, temperature = 30 °C; polymerization time: (60 + 30 + 120 min) for the first, second, and third added monomers, respectively, [HNHT] = 2 × $10^{-4}$ mol L$^{-1}$ refers to the initial concentration of the monomer. [TNP] = 1.5–2.5 × $10^{-2}$ and [BNP] = 4 × $10^{-4}$ mol L$^{-1}$ refer to the monomer concentrations. The feed ratios of monomers to catalysts for polymerization of hexa-, mono- and difunctional monomers in a sequential addition manner. Determined by GPC in THF relative to monodisperse polystyrene standards. Determined by DSC.
of the trefoil-shaped tricyclic polymer; (ii) the ladderphane PBNP as the cyclizing unit formed the flawed structure; thereby, the PBNP in one ring of the trefoil-shaped tricyclic polymer connected with another ring to form the complicated or defective tricyclic polymer (Fig. S16b†). According to the previous study, a high concentration of the difunctional monomer BNP (0.05 mol L\(^{-1}\)) may cause the ladderphane PBNP with a flawed structure, resulting in the formation of a cyclic polymer with a branching or crosslinking structure in the polymerization process. However, a low concentration (1 × 10\(^{-3}\) mol L\(^{-1}\)) was allowed to avoid the undesirable reaction. The ladderphane PBNP formed at a lower BNP concentration (4 × 10\(^{-4}\) mol L\(^{-1}\)) served as the cyclizing unit to cyclize the six-arm star polymer for achieving the trefoil-shaped tricyclic polymer, which effectively avoided the formation of defective structures; (iii) the ladderphane PBNP cyclized the six-arm star-shaped polymer to yield the defective trefoil-shaped tricyclic polymers with a few unreacted norbornenyl groups on PBNP (Fig. S16c†), even though a few unreacted groups have little influence on the cyclization of polymers. \(^1\)H NMR analysis of the trefoil-shaped tricyclic polymer showed no signal of olefinic protons on the norbornenyl ring at 6.23 ppm, suggesting that this defective tricyclic structure was effectively ruled out. Therefore, the proposed defective cyclic structures should be absent in the ROMP-based blocking-cyclization process.

To reveal the difference in the molecular topology of the trefoil-shaped tricyclic polymer from the six-arm star-shaped polymer, some other pieces of evidence were obtained. The curves of log(\(M_w\)) versus retention time illustrated that the trefoil-shaped tricyclic polymer eluted later than the six-arm star-shaped polymer (Fig. 1c), which was attributed to the smaller hydrodynamic volume of the cyclic polymer. Mark–Houwink–Sakurada (MHS) plots showed the lower intrinsic viscosity (\(\eta\)) of the trefoil-shaped tricyclic polymer relative to the six-arm star-shaped polymer over a wide range of molecular weights due to the unique feature of the cyclic polymer (Fig. 1d). The curves of the two polymers were parallel to each other in the whole range, indicating that the trefoil-shaped tricyclic polymer had a high cyclic topological purity. Meanwhile, the \([\eta]_\text{poly}/[\eta]_\text{sol}\) ratio of polymers was 0.83 ± 0.02 (Table S2†), which was in accordance with the reported values (0.74–0.88).\(^\text{35,41}\)

The dominating intensity-average hydrodynamic diameter (\(D_h\)) of c-[PHNHT\(_5\)-[\(b\)-PTNP\(_{110}\)-\(b\)-PBNP\(_5\)]\(_3\}) (51 nm) determined by DLS was smaller than that of 6a-[PHNHT\(_5\)-[\(b\)-PBNP\(_5\)-\(b\)-PTNP\(_{110}\)]\(_3\}) (59 nm), suggesting that the trefoil-shaped tricyclic polymer has a more compact structure than the six-arm star-shaped polymer. Besides, the trefoil-shaped tricyclic c-[PHNHT\(_5\)-[\(b\)-PTNP\(_{m}\)-\(b\)-PBNP\(_5\)]\(_3\}) (\(m = 70, 90, \text{and} 130\)) displayed controllable ring sizes with the corresponding \(D_h\) values of 24, 38, and 68 nm (Fig. 2a and Table S3†). The photophysical properties of monomers and polymers were investigated by UV-vis spectroscopy. Compared with the absorptions of monomers HNHT, TNP and BNP (Fig. S17†), the character-
istic absorptions of biphenyl groups on PTNP segments and perylene imide moieties on PBNP segments occurred at 265–385 nm and 400–600 nm, respectively (Fig. 2b). Noticeably, the absorption intensity of trefoil-shaped tricyclic c-[PHNHT5-(b-PTNP6a-b-PBNP5-b-PTNP6a)] with the same block ratios of PHNHT5/PTNP/PBNP, and the trefoil-shaped tricyclic polymers have strengthened absorption intensity at 265–385 nm with the increase of TNP units.

The differential scanning calorimetry (DSC) measurement showed that the high glass transition temperature ($T_g$) of trefoil-shaped tricyclic polymers varied from 167 °C to 176 °C with the increase in the molecular weight (Table 1 and Fig. 2c), and also the $T_g$ of the trefoil-shaped tricyclic polymer (173 °C) was higher than that of its six-arm star-shaped polymer counterpart (165 °C), revealing the remarkable effect of the trefoil-shaped tricyclic topology on $T_g$. These results might be attributed to the fact that two PTNP segments in each ring of the trefoil-shaped tricyclic polymer were easier to get close with each other, because of its more compact structure than the six-arm star-shaped polymer, and form the intra-chain entanglement by the π–π stacking interaction of the adjacent biphenyl groups, which restricted the rotation of biphenyl groups (Fig. 2d) and enhanced the rigidity of the polymer chain, thereby decreasing the absorption intensity and eventually increasing the $T_g$ of the trefoil-shaped tricyclic polymer. Thermogravimetric analysis (TGA) illustrated that the thermal decomposition temperatures ($T_d$, 5% weight loss) of the six-arm star-shaped and trefoil-shaped tricyclic polymers were 374 °C and 381 °C, respectively, indicating the excellent thermal stability of these polymers (Fig. S18†). Briefly, these results verified the feature of the trefoil-shaped tricyclic topology.

**Molecular topology of trefoil-shaped tricyclic polymers**

The visualization of cyclic topology was performed to provide the essential evidence for cyclic polymers, while the trefoil-shaped tricyclic polymer topology was often hard to observe directly because of the intra-chain entanglement of the polymer formed by the π–π interaction of biphenyl groups, and thus post-polymerization was used as an effective method to achieve the visualization of cyclic topology. Therefore, the monofunctional PFNI containing the pentfluorophenyl ester group was incorporated randomly into the backbone of trefoil-shaped tricyclic polymer by ROMP, and then, the exchange reaction of the pentfluorophenyl ester group with POSS-NH$_2$ was conducted to obtain a POSS-modified trefoil-shaped tricyclic polymer, which was significant for observing the cyclic topology (Scheme S4†). Compared with trefoil-shaped tricyclic c-[PHNHT5-(b-P(TNP85-co-PFN513)-b-PBNP5-b-PTNP6a)], the POSS-modified c-[PHNHT5-(b-P(TNP85-co-PFNI513)-b-PBNP5-b-PTNP6a)] showed a new peak at 0.72–0.49 ppm belonging to the methylene protons (H$_2$) of the POSS group in the $^1$H NMR spectrum (Fig. S19†), and three types of single peak appeared at 25.66–22.43 ppm from the POSS group in the corresponding $^{13}$C NMR spectrum (Fig. S20†). By comparing the integral area of methylene protons (H$_2$) with those of olefinic protons (H$_3$) at 6.21–5.18 ppm on the polymer backbone, the actual graft ratio of the POSS moiety was calculated to be 18%, which was close to the feed ratio of 20%, suggesting the successful graft of POSS groups to the cyclic polymer backbone. The $M_n$ values of six-arm star-shaped 6a-[PHNHT5-(b-PBNP5-b-P(TNP85-co-PFN513)-b-PBNP5)] and trefoil-shaped tricyclic c-[PHNHT5-(b-P(TNP85-co-PFNI513)-b-PBNP5)] were 78.8 kDa and 71.6 kDa, respectively (Fig. S21†). After POSS-modification, the $M_n$ values of six-arm star-shaped 6a-[PHNHT5-(b-PBNP5-b-P(TNP85-co-PFN513)-b-PBNP5)] and trefoil-shaped tricyclic c-[PHNHT5-(b-P(TNP85-co-PFNI513)-b-PBNP5)] significantly increased to 130.2 kDa and 122.8 kDa (Fig. S21b†). Besides, the six-arm star-shaped 6a-[PHNHT5-(b-PBNP5-b-P(TNP85-co-PFN513)-b-PBNP5)] had a higher $D_n$ value of 59 nm than the trefoil-shaped tricyclic c-[PHNHT5-(b-P(TNP85-co-PFNI513)-b-PBNP5)] (51 nm) (Fig. S22a†), which were also smaller than the $D_n$ values of 91 nm and 79 nm of the corresponding polymers with POSS modification (Fig. S22b†).

The TEM images of polymers were tested by dropping the solution (5 × 10$^{-4}$–1 × 10$^{-3}$ mg mL$^{-1}$ in THF) on the pure carbon film to compare the topology of different polymers. In Fig. 3a, the trefoil-shaped tricyclic c-[PHNHT5-(b-PTNP110)-b-PBNP5] exhibited a spherical morphology with an average diameter of 25 nm, whereas there was no observation of the trefoil-shaped tricyclic topology, as a result of the intra-chain entanglement of PTNP segments. Interestingly, after POSS-modification, the bulky POSS groups were introduced into the polymer chain to reduce the intra-chain entanglement; thereby, the topology of trefoil-shaped tricyclic c-[PHNHT5-(b-P(TNP85-co-PFNI513)-b-PBNP5)] was clearly observed at a low concentration of 5 × 10$^{-4}$ mg mL$^{-1}$, indicating the successful synthesis of the trefoil-shaped tricyclic polymer. Noteworthily, there are almost no reports on the molecular morphology of the trefoil-shaped tricyclic polymer by TEM measurement because the complex structure and low atomic resolution of the trefoil-shaped tricyclic polymer make it extremely difficult to observe the trefoil-shaped tricyclic topology. In Fig. 3b, the average outer and inner diameters of each single ring of the trefoil-shaped tricyclic polymer were 46 and 22 nm, respectively, and the trefoil-shaped tricyclic polymer morphology was considered to be a single-macromolecule topological structure rather than the assembly or agglomeration of some macromolecules because of its small size. Importantly, more normative trefoil-shaped tricyclic morphologies were also clearly observed in the selected range of about 2 and 1 µm (Fig. 3c and S23†), indicating that these trefoil-shaped tricyclic topology structures are not accidental, even though the morphology of partial trefoil-shaped tricyclic topology was blurred due to the low electronic contrast of the polyolefin-based backbone and the partial overlapping or twisting of three macrorings. Meanwhile, the heavy aggregation of many trefoil-shaped tricyclic polymers was clearly observed at a high concentration of 1 × 10$^{-3}$ mg mL$^{-1}$ (Fig. S24†). In contrast, the six-arm star-shaped 6a-[PHNHT5-
[b-PBNP5-(b-P(TNP85-co-POSSNI25))2-b-PBNP5]3 showed a spherical morphology with an average size of 47 nm (Fig. 3d), meaning that although the introduction of POSS groups reduced the intra-entanglement of the polymer chain, it has no contribution to the independent formation of the cyclic topology. In brief, compared with the tedious feeding process for the synthesis of the tricyclic polymer, the trefoil-shaped tricyclic polymers were efficiently prepared by the blocking-cyclization technology in three feeding steps based on the ladderphane PHNHT5 with six living ends as the initial motif.

Conclusions

In summary, benefiting from the deliberately designed multifunctional monomer and using a polymeric ladderphane with six living ends as the initial motif, a series of trefoil-shaped tricyclic polymers were precisely synthesized by a ROMP-based blocking-cyclization technique in the simplified three feeding steps. Compared with its six-arm star-shaped polymer counterpart, the trefoil-shaped tricyclic polymer exhibited a higher glass transition temperature, lower UV-vis absorption intensity and intrinsic viscosity, and smaller hydrodynamic diameter, which revealed the difference in the topological structures between trefoil-shaped tricyclic and six-arm star-shaped polymers. The ring size of trefoil-shaped tricyclic polymers could be controlled by simply adjusting the feed ratio of the monomers, and the number of repeating units in each ring of the trefoil-shaped tricyclic polymer reached up to 250. Furthermore, the visualized trefoil-shaped tricyclic topology was clearly observed. This work provides an efficient strategy for the synthesis of complex cyclic polymers using the conventional ROMP approach and a commercial Grubbs catalyst.

Author contributions

Hao Wang: experiments, investigation, formal analysis, data curation, and writing – original draft. Cuihong Ma: experiments, formal analysis, investigation, and data curation. Zhiying Han: formal analysis, investigation, and data curation. Xiaojuan Liao: formal analysis, investigation, and data curation. Ruyi Sun: conceptualization, formal analysis, writing – review & editing, and supervision. Meiran Xie: conceptualization, formal analysis, funding acquisition, writing – review & editing, project administration, and supervision. All the authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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