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SPECIAL ISSUE

Cyclic polymers: New developments

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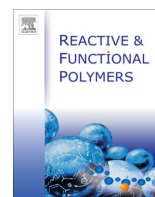
Synthesis of core-fluorescent four-armed star and dicyclic 8-shaped poly(THF)s by electrostatic self-assembly and covalent fixation (ESA–CF) protocol

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ABSTRACT

A pair of four-armed star and dicyclic 8-shaped poly(tetrahydrofuran)s, poly(THF)s, possessing a perylene diimide group at the core position (**Ia** and **Ib**, respectively) were synthesized by means of an *electrostatic self-assembly and covalent fixation* (ESA–CF) protocol. Mono- and bifunctional poly(THF)s having *N*-phenylpiperidinium salt end groups accompanying a perylene diimide tetracarboxylate as a counteranion were prepared by the ion-exchange reaction, and the subsequent covalent conversion by reflux in toluene afforded the corresponding core-fluorescent four-armed star and dicyclic 8-shaped poly(THF)s, (**Ia** and **Ib**, respectively) for the use of single-molecule fluorescence microscopy measurements.

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1. Introduction

Cyclic polymers have gained growing attention as a new class of polymeric resources, since a wide variety of well-characterized single cyclic polymers have become obtainable through a number of newly developed end-to-end polymer cyclization processes, as well as alternative ring-expansion polymerizations [1–6]. Due to their unique topological feature of the elimination of chain termini in contrast to linear and branched counterparts, unprecedented topology effects by cyclic polymers have now been demonstrated by tailored cyclic polymers having prescribed chemical structures [1,7,8].

In particular, the diffusion process of cyclic polymers is of a significant interest, as the prevailing reptation theory premises a key involvement of the chain ends in linear or branched polymers on their static and dynamic properties in a semi-dilute solution or in a melt [9,10]. Indeed, an amoeba-like, non-reptational motion has been suggested theoretically [11]. More compact conformation and less interpenetration of cyclic polymers than linear counterparts have been revealed by simulation studies in the melt state, which lead to faster diffusion of the cyclic polymers [12,13]. On the other hand, few experimental works have so far been undertaken apparently due to the limitation of the synthetic means to afford guaranteed cyclic polymer samples [14,15]. In these studies, the reported diffusion coefficients of the cyclic and linear polymer melts are often inconsistent [16,17]. Furthermore, even trace amount of the linear chains in the cyclic polymer melt affects rheological response significantly [18].

We have recently reported a single-molecule fluorescence microscopy study to reveal a remarkable topology effect on the diffusion behavior of cyclic polymers against linear counterparts in a semi-dilute solution or in a melt matrix of linear polymers [19–21]. In these studies, a pair of single cyclic and linear polymer samples having a fluorescent perylene diimide probe unit were purposely synthesized by an *electrostatic self-assembly and covalent fixation* (ESA–CF) protocol [19]. In particular, mono- and bifunctional linear poly(THF) precursors having *N*-phenylpiperidinium salt end groups accompanying an perylene diimide dicarboxylate counteranion were employed to provide the cyclic and linear polymer samples suitable for the subsequent fluorescent measurements, where the quenching of the fluorescence was prevented by eliminating the *N*-phenyl group from the final polymer structures [19,20].

In order to study further the polymer topology effect on the diffusion behavior of non-linear polymers by means of the single-molecule fluorescence microscopy technique, we report here the preparation of a *dicyclic* polymer possessing a fluorescent probe unit at the prescribed position, together with the relevant model branched polymer. We have thus selected a pair of four-armed star and dicyclic 8-shaped polymers, both of which have commonly one branch (junction) point with four outward segments, while the four free chain ends of the former are linked together in two sets to form the latter [22].

The ESA–CF process has so far been successfully applied to construct not only single cyclic but also multicyclic polymer topolo-

gies as well as star and comb-branched polymers [1,2,5,6]. In particular, a wide variety of multicyclic polymers, such as *dicyclic* polymer constructions, i.e., θ (*fused*), 8 (*spiro*), and manacle (*bridged*) forms, were effectively produced [23]. Moreover, such *tricyclic* counterparts like trefoil and tandem tricyclic (*spiro*), and three-way paddle (*bridged*), forms were constructed in conjunction with the click chemistry using *kyklo*-telechelics [23,24]. Furthermore, *tricyclic* polymers having β-, γ-, and δ-graph (*fused*) forms were also produced through the combination of click chemistry and olefin metathesis, i.e., the click and clip process, in conjunction with the ESA–CF protocol [25–27]. More recently, the synthesis of *tetracyclic* topologies, i.e., quatrefoil (*spiro*), four-way paddle (*bridged*), and unfolded tetrahedron (*fused*), was also demonstrated [26,28].

We have now applied the ESA–CF procedure to produce a pair of four-armed star and dicyclic 8-shaped poly(THF)s by employing the mono- and bifunctional linear poly(THF) precursors having *N*-phenylpiperidinium salt groups possessing a newly prepared

perylene diimide tetracarboxylate as a counteranion. (Scheme 1) The subsequent covalent conversion of the electrostatic self-assemblies, by reflux specifically under dilution in toluene for the polymer cyclization, afforded the corresponding four-armed star and dicyclic 8-shaped poly(THF)s, suitable for the subsequent single-molecule fluorescence microscopy measurements.

2. Experimental section

2.1. Materials

A monofunctional linear poly(tetrahydrofuran), poly(THF), (**1a**, M_n(NMR) = 1300, M_p(SEC) = 1900 and PDI = 1.18) and bifunctional poly(THF), (**1b**, M_n(NMR) = 2700, M_p(SEC) = 3800 and PDI = 1.17) both having *N*-phenylpiperidinium end groups at a single and both chain ends, respectively, were prepared according to the method reported before [19,29]. The peak molecular weights (M_p) of **1a**
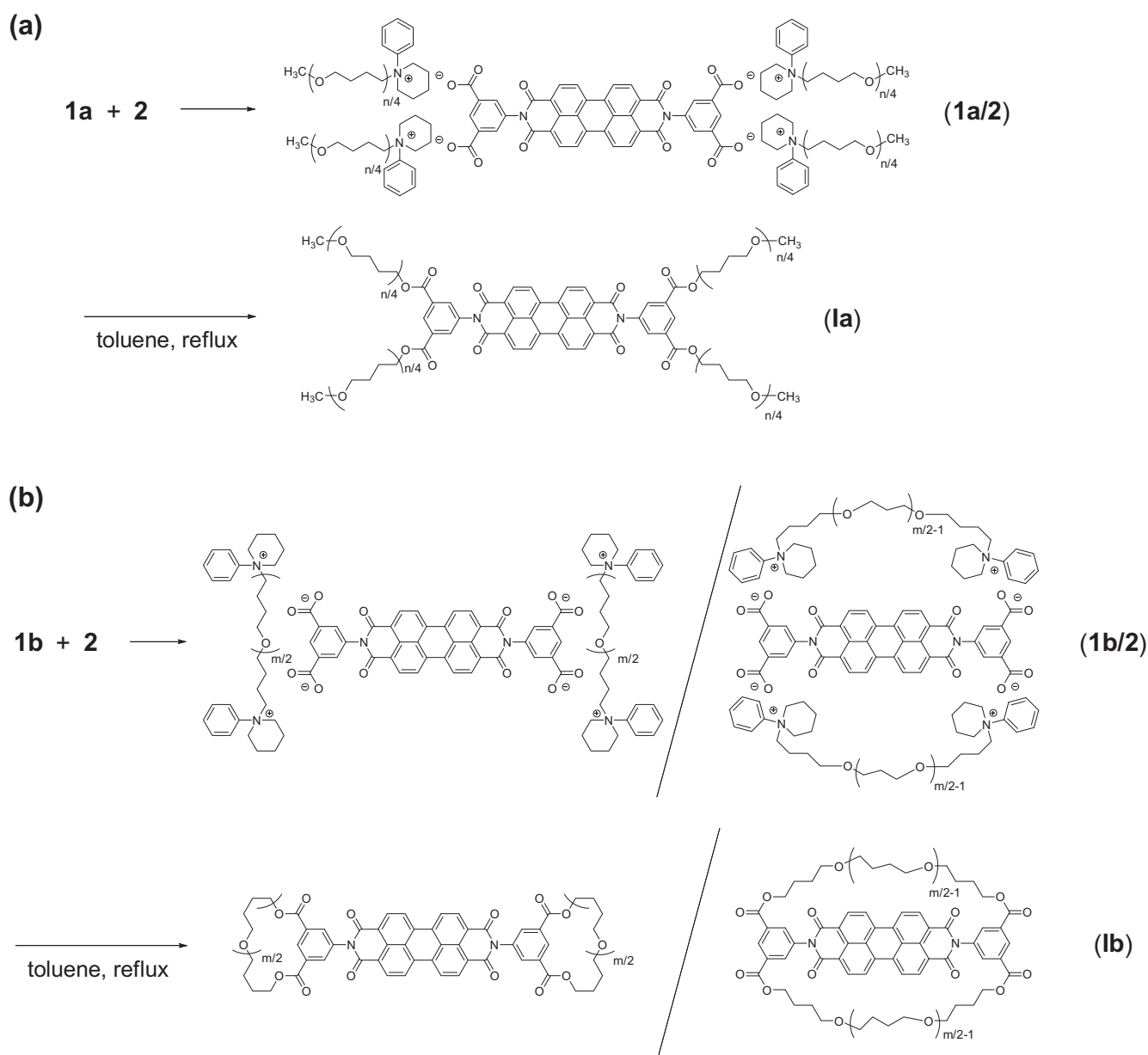
Scheme 1. Synthesis of (a) four-armed star (**Ia**) and (b) dicyclic 8-shaped (**Ib**) poly(THF)s by the ESA–CF protocol.

and of **1b** were determined by SEC after the covalent conversion reaction of the cyclic ammonium salt groups with sodium benzoate. Perylene diimide tetracarboxylate sodium salt (**2**) was prepared by modifying the reported method [30], through the reaction of perylene-3,4,9,10-tetracarboxylic dianhydride and 5-aminoisophathalic acid in the presence of zinc acetate dihydrate and imidazole, followed by the treatment with a 0.5 M NaOH solution. THF (Godo Co., Inc.) was distilled over Na wire. Wakosil C-300 (Wako Pure Chemical Industries, Ltd.) was used for silica gel chromatography. All other reagents and solvents were purchased from commercial sources, and used as received unless otherwise noted.

2.2. Four-armed star poly(THF) with a perylene diimide unit (**Ia**)

Into a vigorously stirred aqueous solution (150 mL) containing **2** (1.44 g), an acetone solution (4 mL) of **1a** (640 mg) was added dropwise. The formed precipitate was collected by filtration. This procedure was repeated four times to give an ion-exchanged product, **1a/2** (492 mg) in 72% ion-exchange yield.

^{1}H NMR(CDCl$_3$) δ: 3.33 (s, OCH_3), 4.24–4.42 (m, 8H, NCH_2CH$_2$CH$_2$), 8.12–8.19 (m, 4H, Ar-H ortho to N and CO$_2$), 8.32–8.58 (m, 8H, perylene diimide-H), 8.93–8.99 (m, 2H, Ar-H ortho to CO$_2$ and CO$_2$).

A toluene solution (100 mL) of **1a/2** (491 mg) was refluxed for 4 h. After the solvent was removed under reduced pressure, the residue was filtered through a plug of silica gel with *n*-hexane/acetone (2/1 vol/vol). The subsequent reprecipitation into an ice-cooled water to give the four-armed star polymer product, **Ia** in 206 mg yield. (M_n(NMR) = 8300, M_p(SEC) = 7600, and PDI = 1.04).

^{1}H NMR(CDCl$_3$) δ: 1.57–1.66 (m, CH_2CH$_2$O), 3.33 (s, OCH_3), 3.34–3.47 (m, CH$_2$CH_2O), 4.36–4.43 (t, J = 6.2 Hz, 8H, CO$_2$CH_2), 8.23–8.25 (m, 4H, Ar-H ortho to N and CO$_2$), 8.73–8.85 (m, 10H, perylene diimide-H, Ar-H ortho to CO$_2$ and CO$_2$).

2.3. Dicyclic 8-shaped poly(THF) with a perylene diimide unit (**Ib**)

Into a vigorously stirred aqueous solution (50 mL) containing **2** (302 mg) kept at 0 °C, a small amount of an acetone solution containing **1b** (505 mg) was added dropwise. The formed precipitate was collected by filtration. This procedure was repeated to give the ion-exchanged product, **1b/2** (473 mg) in 63% ion-exchange yield.

^{1}H NMR(CDCl$_3$) δ: 4.23–4.43 (m, 8H, NCH_2CH$_2$CH$_2$), 7.42–7.70 (m, 20H, NAr-H), 8.00–8.04 (m, 4H, Ar-H ortho to N and CO$_2$), 8.14–8.20 (m, 8H, perylene diimide-H), 8.93–9.00 (m, 2H, Ar-H ortho to CO$_2$ and CO$_2$).

A toluene solution (1.0 L) of **1b/2** (200 mg), corresponding to the concentration of 0.2 g/L, was refluxed for 4 h, and a toluene-soluble fraction (31 mg) was obtained along with an insoluble solid. Furthermore, three additional sets of CHCl$_3$ solutions (1.0 L) containing **1b/2** (each 53 mg), corresponding to the concentration of 0.05 g/L, were prepared and refluxed for 4 h to collect toluene-soluble fractions. The combined toluene-soluble products were reprecipitated from toluene to *n*-hexane, followed by silica gel column chromatography treatment with acetone/*n*-hexane (1/2 vol/vol). The recovered fraction was then reprecipitated into water to give a crude product (33 mg), which was further subjected to Bio-Beads S-X1 chromatography. The product was finally purified by preparative GPC with CHCl$_3$ to remove any intermolecular reacted products, to give a dicyclic 8-shaped product, **Ib** in 15 mg yield. (M_n(NMR) = 12,500, M_p(SEC) = 5600 and PDI = 1.10)

^{1}H NMR(CDCl$_3$) δ: 4.33 (t, J = 6.3 Hz, 8H, CO$_2$CH_2), 8.15–8.19 (m, 10H, Ar-H ortho to N and CO$_2$), 8.67–8.80 (m, 10H, perylene diimide-H, Ar-H ortho to CO$_2$ and CO$_2$).

2.4. Measurements

^{1}H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer operating at 300 MHz with CDCl$_3$ or D$_2$O as a solvent. SEC measurements were performed at 40 °C on a Tosoh model CCPS equipped with a TSK G4000HXL as a column and with a refractive index detector model RI 8020. THF was used as an eluent at a flow rate of 1.0 mL/min. Linear polystyrene standards were used for calibration, and the M_p(SEC) values were reported as poly(THF) equivalents. MALDI-TOF mass spectra were recorded on a Shimadzu AXIMA Performance spectrometer equipped with a nitrogen laser (λ = 337 nm). The spectrometer was operated at an accelerating potential of 20 kV in a linear positive ion mode with pulsed ion extraction. A THF solution (10 μL, 10 mg/mL) of a polymer sample, a THF solution (100 μL, 20 mg/mL) of dithranol, and a THF solution (100 μL, 10 mg/mL) of sodium trifluoroacetate were mixed, and a portion of the mixture was deposited onto a sample target plate. Mass values were calibrated by the three-point method using peaks from α-cyanohydroxycinnamic acid dimer plus H^{+} at m/z = 379.35, insulin β plus H^{+} at m/z = 3497.96, and insulin plus H^{+} at m/z = 5734.62.

3. Results and discussion

A pair of mono- and bifunctional linear poly(THF)s, having the molecular weights of 1300 for the former and of 2700 for the latter and having N-phenylpiperidinium salt group as a single and both end groups, respectively, were prepared according to the procedure reported before [29]. The molecular weights of the precursors were chosen so as to allow the ESA–CF process to proceed effectively [1,2,5,6]. Moreover, the rigorous MALDI-TOF characterization of the resulted four-armed star and dicyclic 8-shaped poly(THF) products, comprised of four and two units of the prepolymer, respectively, was facilitated by keeping the total molecular weights of the final polymer products below 10,000. The 6-membered cyclic ammonium, N-phenylpiperidinium, salt groups were introduced to the chain ends of polymer precursors. This is crucial for polymer samples for the single molecule fluorescent studies, as the 6-membered cyclic ammonium salts undergo the prevailed ring-emitting esterification by carboxylate anions to form simple ester units. In contrast, the selective ring-opening esterification proceeds with the 5-membered counterparts to form inherently phenylamino groups to cause the quenching of the fluorescence in the final polymer samples [19].

A tetracarboxylate having a fluorescent perylene diimide unit (**2**) was newly prepared according to the modified method reported earlier [30], and introduced as a counteranion of the mono- and bifunctional linear poly(THF)s having cyclic ammonium salt groups. The ion-exchange reaction was performed by the repeated reprecipitation of the acetone solution of the polymer precursor (**1a** or **1b**), carrying initially triflate counteranions, into an aqueous solution containing an excess amount of **2** as a sodium salt form. The ion exchange yields were 72% for the monofunctional precursor and 63% for the bifunctional counterpart, respectively. The ^{1}H NMR analysis of the ion-exchange products **1a/2** and **1b/2** (Fig. S1, top and bottom, in Supporting Information) showed evidently the signal assignable to perylene diimide protons at around 8.1–8.6 ppm and 5-aminoisophthalic protons at around 8.9–9.0 ppm.

The covalent conversion reaction of the electrostatic self-assembly product, **1a/2**, for the star polymer product, **Ia**, was performed in toluene (4.9 g/L) by reflux for 4 h. An initial attempt in CHCl$_3$ solution failed to cause the ring-opening reaction presumably due to the suppressed nucleophilic reactivity of carboxylate anions in the perylene diimide unit. The covalent product **Ia** was

recovered after the treatment of the silica gel column chromatography with acetone/n-hexane, and finally isolated after the reprecipitated into water in 42% yield (206 mg).

As for the covalent conversion reaction of the electrostatic self-assembly, **1b/2**, for the 8-shaped polymer product, **Ib**, the reaction was required to proceed under dilution to avoid the intermolecular reactions. In practice, however, the reaction of **1b/2** under considerable dilution in toluene (0.2 g/L) under reflux for 4 h yet resulted in the formation of a large portion of the insoluble fraction, presumably due to the intermolecular crosslinking by bifunctional/tetrafunctional components. The soluble portion was, nevertheless, obtained from the reaction solution after the precipitation into n-hexane, as a dark red solid. Thus, by additional sets of the relevant reaction (three times with 50 mg of **1b/2**) under the further dilution of 0.05 g/L, the recovered toluene-soluble fractions were combined and subjected to the silica gel column chromatography with acetone/n-hexane and reprecipitated into water to give a crude product in 16% yield (33 mg). Finally, the product was subjected to column chromatography with Bio-Beads S-X1, and fractionated further by preparative SEC to remove any side products by intermolecular reactions, to give the 8-shaped polymer product, **Ib**, in 15 mg yield. The quantity was sufficient for the subsequent single molecule spectroscopy measurements.

The ^{1}H NMR inspection of **Ia** and **Ib** (Fig. 1, top and bottom, respectively) showed commonly the signals due to the perylene diimide unit at 8.0–9.0 ppm, and the signal due to the methoxy chain end at 3.33 ppm only for **Ia**. In comparison with the corresponding electrostatic self-assembly precursors, **1a/2** and **1b/2**, respectively, the covalent conversion by the esterification reaction was also confirmed. Thus, the signals at 7.4–8.0 ppm due to the N-phenyl protons on the piperidinium unit both for **1a/2** and **1b/2** (Fig. S1, top and bottom, respectively) were totally removed, and a triplet signal assignable to the ester methylene protons became visible at 4.39 ppm in **Ia** and at 4.33 ppm in **Ib**, respectively. For the products, **Ia** and **Ib**, small but noticeable signals were also visible at 6.5–6.8 and 7.2 ppm due to the N-phenyldialkyl protons,

and these are ascribed to the partial ring-opening reaction. The regioselectivity ratio of the ring-emitting/ring-opening reactions was estimated as 82/18 (for **1a/2**) and 88/12 (for **1b/2**), respectively, and was consistent with previous experimental and computational studies [29,31]. Thus, the regioselectivity in the nucleophilic esterification on 6-membered and other cyclic ammonium salts was shown to be scarcely affected by the type of carboxylate species [31]. As seen in Scheme 1, two isomeric forms of the dicyclic product, **Ib**, should be produced through the present ESA–CF procedure, according to the different linking modes of the poly(THF) segments with the combination of a pair of carboxylate groups either at neighboring or at orthogonal positions in the perylene diimide tetracarboxylate [32]. These two isomeric forms were, however, undistinguishable from the NMR spectrum, as the poly(THF) chain length (ca. 250 atoms) in the product, **Ib**, was sufficiently long to assume a random coil conformation around the perylene core unit.

The MALDI-TOF mass spectra of **Ia** and **Ib** (Fig. 2, top and bottom, respectively) showed that the two major sets of a series of peaks with an interval of 72 mass units (corresponding to the repeating THF unit), and each peak exactly matched the total molar mass of the poly(THF) produced by the exclusive ring-emitting on the four esterification reactions, as a major component, while by three ring-emitting and one ring-opening, as a minor component, respectively. Thus, the peak at $m/z = 6567.3$, corresponding to the expected chemical structure of **Ia** by exclusive ring-emitting reactions (assumed to be the adduct with Na$^+$) with a DP$_n$ of 80; ($C_4H_{8-}O) \times 80 + C_{44}H_{26}N_2O_{12}$ plus Na$^+$ equals 6566.27 Scheme 1(a). The peaks due to minor components of the 4-armed star product, **Ia**, including one ($m/z = 6728.5$, $\Delta m/z = 161.2$, theoretical $\Delta m/z = 161.2$) and two ($m/z = 6888.3$, $\Delta m/z = 321.0$, theoretical $\Delta m/z = 322.5$) ring-opening (N-phenyl) groups were also observed. The observed MALDI peaks for the minor component appeared larger than their contents estimated from the ring-emitting/ring-opening ratio from ^{1}H NMR measurements [29]. This is presumably due to the higher ionization efficiency of the polymer samples
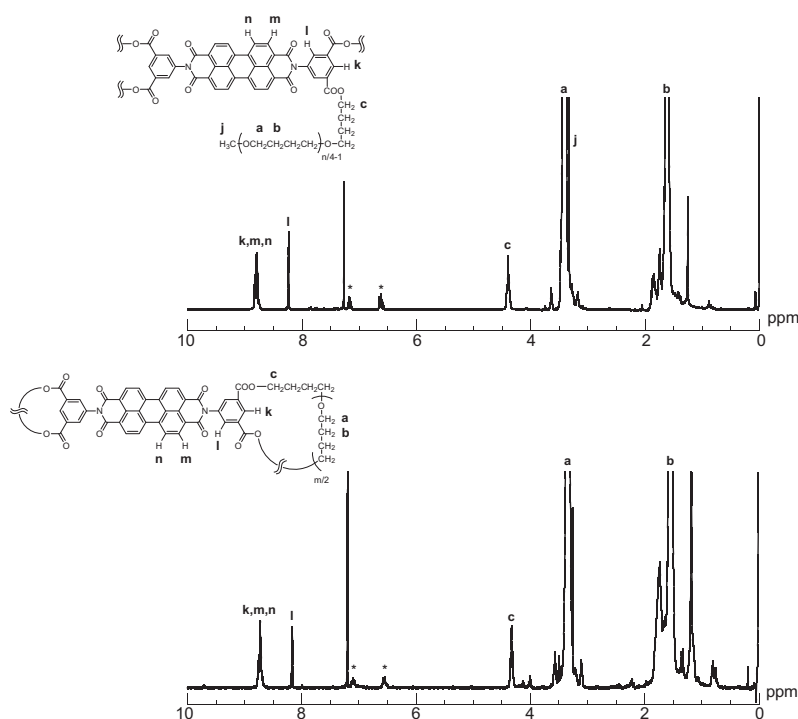

Fig. 1. ^{1}H NMR spectra of **Ia** (top) and **Ib** (bottom). Asterisk (∗) indicates N-phenylamine groups of the ring-opening products.
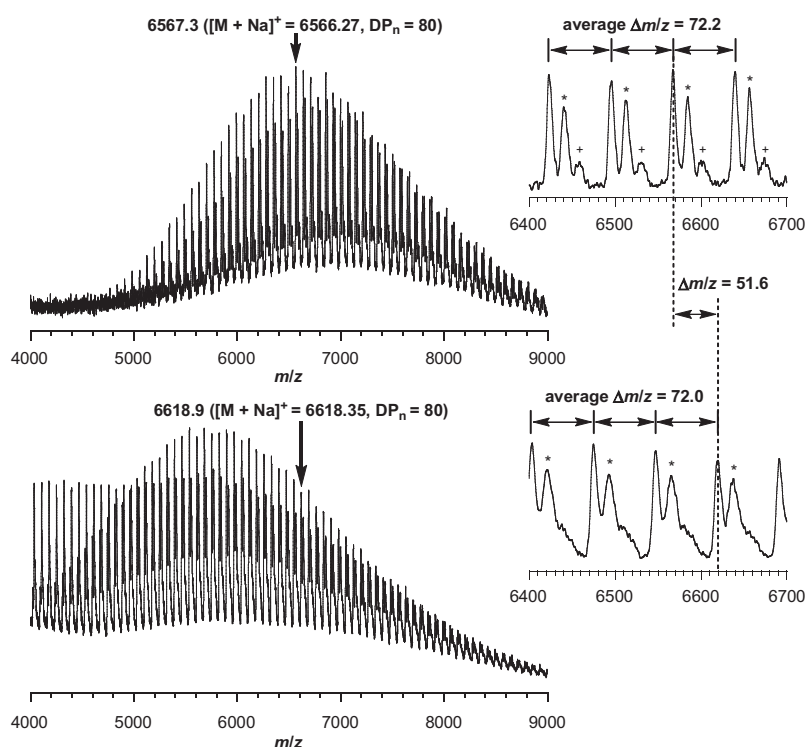
Fig. 2. MALDI-TOF mass spectra of **Ia** (top) and **Ib** (bottom). The peaks with asterisk (∗) correspond to the products involving the ring-opening reaction of one *N*-phenylpiperidinium group. The peaks with plus symbol (+) correspond to the products involving the ring-opening products of two *N*-phenylpiperidinium groups.

containing amino functions. For the 8-shaped product, **Ib**, (Fig. 2 bottom), the peak at m/z = 6618.9, corresponding to the expected chemical structure of **Ib** by exclusive ring-emitting reactions (assumed to be the adduct with Na$^+$) with a DP$_n$ of 80; (C$_4$H$_8$O) × 80 + C$_{48}$H$_{30}$N$_2$O$_{12}$ plus Na$^+$ equals 6618.35 Scheme 1(b). The peaks due to minor components of the 8-shaped product, **Ib**, including one ring-opening (*N*-phenyl) group were also observed at m/z = 6780.91, which was formed by the ring-opening of one piperidinium functionality having an additional mass of 162.03 (theoretical $\Delta m/z$ = 161.2). The observed mass difference ($\Delta m/z$ = 51.6) of **Ia** and **Ib** agrees with the calculated mass difference of their chemical structures, namely four methyl end groups against two tetramethylene linkage groups (C$_4$H$_4$, theoretical $\Delta m/z$ = 52.1). It must be emphasized that these products containing a small portion of *N*-phenylamino units are still suitable for the subsequent single molecule spectroscopic measurements, as these polymer samples are mixed into a large excess of matrix resulting in an extremely diluted condition.

Finally, the SEC analysis of **Ia** and **Ib** (Fig. 3a and 3b, bottom), in comparison with the corresponding precursors **1a** and **1b**, (Fig. 3a and 3b, top, both after the covalent conversion of the cationic end groups), respectively, showed commonly unimodal distribution. The observed peak molecular weights (M_p = 7600 for **Ia** and M_p = 5600 for **Ib**), also corresponding to the hydrodynamic volumes of the products, were substantially higher than the corresponding precursors **1a** (M_p = 1900) and **1b**, (M_p = 3800). Notably, the 8-shaped products, **Ib**, showed the contraction in their 3D sizes in comparison with the linear counterpart, estimated as 0.74(=5600/3800 × 2). This value is in good agreement with the previous observations [23,32,33], although might be considered as first approximation due to the limited accuracy of peak molecular weights of the polymer products and their precursors subjected into multistep purification processes.

As for preliminary investigation for single-molecule study, obtained **Ia** and **Ib** were mixed in a linear poly(THF) matrix to record
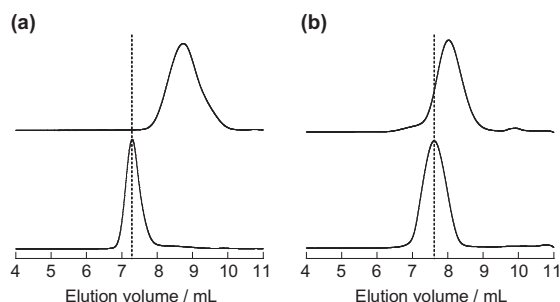

Fig. 3. SEC traces of (a) **1a** reacted with sodium benzoate (top) and **Ia** (bottom), and (b) **1b** reacted with sodium benzoate (top) and **Ib** (bottom).

fluorescence microscope images according to the method described in our preceding reports [19,20]. Indeed, illuminating spots due to the perylene diimide core of single molecules of **Ia** and **Ib** were detectable as shown in Fig. S2 of the Supporting Information. Further studies on the topology effects of the diffusion dynamics will be reported separately.

4. Conclusions

We have shown in the present study that the ESA–CF procedure was effective to produce a pair of four-armed star and 8-shaped poly(THF)s having a perylene diimide as a core functional group. A perylene diimide tetracarboxylate was introduced as a counteranion to the mono- and bifunctional linear polymer precursors having *N*-phenylpiperidinium salt group, and the subsequent covalent conversion of the electrostatic self-assemblies could produce the corresponding core-functional, four-armed star and dicyclic 8-shaped poly(THF)s. A single-molecule fluorescence microscopy

studies by making use of the obtained polymer samples are in progress.

Acknowledgment

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym. 2013.11.007.

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