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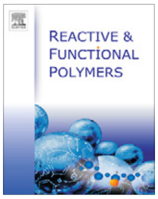

Synthesis and *in situ* core reorganization of smart polymers

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ABSTRACT

A smart poly(ethylene oxide) polymer containing two thermally reversible groups located at the chain center (F2-PEO) was synthesized by a maleimide–furan (MF) [4 + 2] Diels–Alder (DA) reaction between one bis[(furan-2-yl)methyl] terephthalate (F2) and two maleimide-terminated poly(ethylene glycol) methyl ethers (MI-PEOs). MF adducts underwent retro-DA (rDA) addition at a higher temperature, and the maleimide–anthracene (MA) addition reaction could occur simultaneously. Therefore, when F2-PEO and bis((anthracen-10-yl)methyl) succinate (AN2) were refluxed in toluene for 48 h, the cores of F2-PEOs were replaced with the MA adducts *in situ* to give new polymers AN2-PEOs. Moreover, when F2-PEOs were mixed with the molecules containing four anthracene units (AN4), the rDA reaction of the MF adducts and the MA addition reactions occurred simultaneously, generating four-arm star PEOs. The core reorganization of polymers has been confirmed by SEC, UV, ^{1}H NMR, and MALDI-TOF mass spectra.

1. Introduction

In recent years, polymer chains that can be reconstructed by responding to environmental influences have attracted significantly increased attention. Such polymers have covalent linkages that may be cleaved and reformed in response to external stimuli. This property has been applied to the discovery of biologically active materials [1,2] and to the development new stimulus-responsive functional materials [3]. Chemical groups such as disulfide linkages [4,5], acylhydrazone bonds [6–8], 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) groups [9–12], and [4 + 2] addition bonds from maleimide–furan Diels–Alder (DA) reaction [13–16] can be used as chemical linkages for such polymers.

The polymers with disulfide –S–S– bonds can be cleaved into smaller segments with terminal thiol groups in the presence of reductants such as tri-*n*-butylphosphine or dithiothreitol (2,3-dihydroxy-1,4-butanethiol), and the disulfide linkages can be reformed under oxidation [17,18]. After a cycle of cleavage and regeneration, the polymer chains can be recovered. Additionally, radical exchange reactions of disulfides in the absence of oxygen can proceed in high efficiency under photoirradiation conditions [4]. The DA reaction is a well-known thermally reversible reaction, which generally involves the coupling of a “diene” and a “dienophile”. Because it can proceed under mild conditions without a catalyst, this reaction is attractive for designing reversible covalent bonds and has been widely used in polymer synthesis [19–22], hydrogel synthesis [23–25], modification of linear and dendronized polymers [26–28], the development of reversible cross-linking systems [29–33], and the development of organic–inorganic hybrids [34,35]. One interesting feature of the DA reaction is that the adducts may undergo a reverse reaction at higher temperature. The maleimide-furan (MF) DA reaction has been thoroughly studied. The MF DA reaction occurs at a mild temperature of approximately 40 °C and undergoes the retro-DA (rDA) reaction at a higher temperature. However, the addition product between maleimide and anthracene (MA) is much more stable, and the reverse reaction does not occur even at a higher temperature [36]. The difference in the stability of the two adducts above can endow the polymers that are based on MF addition with interesting properties.

Herein, we report novel polymers with replaceable cores based upon the different properties of the MF and MA adducts. As shown in Scheme 1, linear poly(ethylene oxide) with a core of MF adducts (F2-PEO) was obtained by a coupling reaction of the maleimide modified PEO (MI-PEO) and a bis-furan derivative (F2) (2:1 M ratio). When the mixture of F2-PEO and a dianthracene functional agent (AN2) in toluene was heated to reflux, the F2-PEO cleaved via a rDA reaction yielding two MI-PEO intermediates, which reacted with AN2 *in situ* to form another linear PEO (AN2-PEO) with a core of MA adducts. Moreover, when treating F2-PEO with tetra-anthracene derivatives (AN4) at a ratio of F2-PEO:AN4 = 2:1, a star-shaped PEO with four arms could be obtained by *in situ* core reorganization. Therefore, this work supplied a new method not only to introduce new components into the polymer chains but also to reorganize the polymer chain architecture through an *in situ* process of chain cleavage and regeneration.

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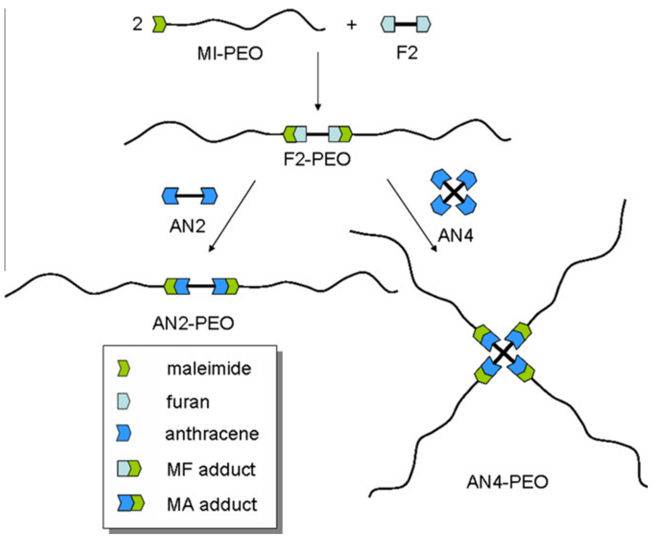


Scheme 1. Formation of smart polymers and the process of core replacement.

2. Experimental

2.1. Materials

9-(Hydroxymethyl)anthracene (97%, Aldrich), 4-(dimethylamino)pyridine (DMAP; 99%, Alfa Aesar), N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC; Aldrich), terephthalic acid ($\geqslant$99%, Aldrich), pentaerythritol ($\geqslant$97%, Aldrich), succinic acid ($\geqslant$99%, Aldrich), and furfuryl alcohol (98%, Alfa Aesar) were used as received. Other reagents were commercialized chemicals and used as received. Poly(ethylene oxide) with a terminated carboxylic acid group (PEO-COOH) was prepared by condensation between poly(ethylene glycol) monomethyl ether (molar mass is 550) and succinic acid anhydride in toluene [37]. 4-(2-Hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (F-MI) was prepared according to literature [38]. Succinic acid mono-athracen-9-ylmethyl ester was synthesized upon reaction with 9-anthrylmethanol and succinic anhydride [39].

2.2. Measurements

^{1}H NMR spectra were recorded with a Bruker 400 MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. The average molecular weights and polydispersity indices of all the samples were measured with a size exclusion chromatography (SEC) system equipped with a Waters 515 HPLC pump, three Waters Styragel columns (HT2, HT3, and HT4), a Rheodyne 7725i sampler, and a Waters 2414 refractive-index (RI) detector. Low-dispersity PS standards were used to calibrate the GPC system. THF was used as the eluent at a flow rate of 1 mL/min at 35 °C. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. The matrix, 4-hydroxy-α-cyanocinnamic acid (CCA), and sample were dissolved in THF. Mass spectra were acquired in reflection mode and linear mode using an acceleration voltage of 19 kV. UV–vis spectra were obtained on a Shimadzu model UV-1601PC spectrometer.

2.3. Synthesis of bis(furan-2-yl)methyl terephthalate (F2)

Terephthalic acid (1.00 g, 6.02 mmol), furfuryl alcohol (1.41 g, 14.4 mmol), and DMAP (0.73 g, 6.02 mmol) were dissolved in a 30 mL of mixture of CH_2Cl_2/DMF (v/v = 1/1). Then EDC (2.34 g, 15 mmol) was added upon stirring. After 12 h, 150 mL of CH_2Cl_2 was added in the solution. The solution was washed with water three times, the CH_2Cl_2 phase was dried over $MgSO_4$, and then the solvent was evaporated to give a viscous liquid. The product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate 6:1). The solid was dried at 25 °C under vacuum to give 1.07 g of product (55% yield). ^{1}H NMR ($CDCl_3$, δ_H ppm) 8.09 (s, 4H), 7.45 (s, 2H), 6.50–6.48 (d, 2H), 6.39 (s, 2H). 5.32 (s, 4H). ^{13}C NMR ($CDCl_3$, δ_C ppm) 165.4, 149.2, 143.4, 133.8, 129.7, 111.1, 110.6, 58.8. Elemental analysis: Calcd for $C_{18}H_{14}O_6$: C, 66.26; H, 4.29. Found: C, 65.80; H, 4.48.

2.4. Synthesis of the F2-PEO

MI-PEO (0.80 g, 1.03 mmol) and F2 (0.168 g, 0.50 mmol) were dissolved in $CHCl_3$ (3 mL). The resulting mixture was stirred at 40 °C for 72 h and then the solvent was removed by evaporation under vacuum. The residue was purified by column chromatography (silica gel, dichloromethane/methanol 10:1). Removal of the solvents under reduced pressure gave F2-PEO crude product, and the purified product was obtained by fractionation. ^{1}H NMR ($CDCl_3$, δ_H ppm) 8.14–8.07 (m, $4H_a$), 6.59–6.40 (m, $4H_c$, *endo*/*exo*), 5.62–5.35 (dd, $2H_f$, *endo*/*exo*), 5.22–4.68 (dd, dd, $4H_e$, *endo*/*exo*), 3.8–4.8 (m, PEO and $1H_b$, *endo*), 3.37 (s, $6H_c$), 3.10–3.03 (dd, $1H_b$, *exo*), 2.65–2.55 (m, 8H).

2.5. Synthesis of the bis((anthracen-10-yl)methyl) succinate (AN2)

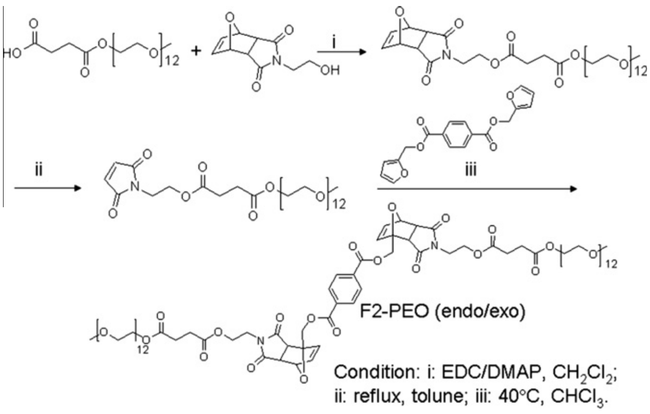
Succinic acid (1.18 g, 10 mmol), 9-(hydroxymethyl)anthracene (6.24 g, 30 mmol), and DMAP (0.61 g, 5 mmol) were dissolved in a 60 mL mixture of CH_2Cl_2/DMF (v/v = 1/1). Then EDC (4.68 g, 30 mmol) was added upon stirring. After 12 h, 250 mL of CH_2Cl_2 was added into the solution, which was then washed with water three times. The CH_2Cl_2 phase was dried over $MgSO_4$, and then the solvent was evaporated to give a viscous liquid. After precipitation in methanol, the crude product was purified by recrystallization in ethyl acetate to yield a yellow solid (3.73 g, 75%). ^{1}H NMR ($CDCl_3$, δ_H ppm) 8.50 (s, 2H), 8.27–8.23 (d, 4H), 8.04–8.01 (d, 4H), 7.56–7.25 (m, 8H), 6.09 (s, 4H), 2.65 (s, 4H). ^{13}C NMR ($CDCl_3$, δ_C ppm) 172.4, 131.4, 131.0, 129.2, 129.0, 126.6, 126.0, 125.1, 123.9, 59.1, 29.2. Elemental analysis: Calcd for $C_{34}H_{26}O_4$: C, 81.93; H, 5.23. Found: C, 81.40; H, 5.29.

2.6. Synthesis of the AN4

Pentaerythritol (0.136 g, 1 mmol), succinic acid mono-athracen-9-ylmethyl ester (1.54 g, 5 mmol), and DMAP (0.24 g, 2 mmol) were dissolved in 14 mL of a mixture of CH_2Cl_2/DMF ($v/v = 1/1$). Then EDC (1.56 g, 10 mmol) was added upon stirring. After 12 h, 100 mL of CH_2Cl_2 was added into the solution, which was washed with water three times. The combined CH_2Cl_2 phase was dried over $MgSO_4$, and then the solvent was evaporated to give a viscous liquid. After precipitation in methanol, the crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 1:2). ^{1}H NMR ($CDCl_3$, δ_H ppm) 8.44 (s, 4H), 8.33–8.30 (d, 8H), 8.27–8.24 (d, 8H), 7.53–7.40 (m, 16H), 6.09 (s, 8H), 4.06 (s, 8H), 2.60 (s, 16H). ^{13}C NMR ($CDCl_3$, δ_C ppm) 172.3, 171.6, 131.3, 130.0, 129.2, 129.0, 126.6, 126.0, 125.1, 123.9, 62.3, 59.1, 42.0, 29.0. Elemental analysis: Calcd for $C_{81}H_{68}O_{16}$: C, 74.94; H, 5.24. Found: C, 73.71; H, 5.34.

2.7. Replacing core reaction to form an AN2-PEO

The AN2 (44 mg, 0.088 mmol) was added to a solution of F2-PEO (0.17 g, 0.088 mmol) in 5.0 g of toluene. The mixture was bub-



Scheme 2. Synthesis of F2-PEO with a replaceable core.

bled with nitrogen for 30 min and refluxed in the dark for 48 h under nitrogen. The solvent was removed under high vacuum; the residual solid was dissolved in CH_2Cl_2 and subsequently precipitated with diethyl ether. The final product was dried for 24 h under vacuum at 25 °C. Yield: 0.15 g (81%). ^{1}H NMR ($CDCl_3$, δ_H ppm) 7.50–7.05 (m, H_c, phenyl), 5.50 (s, $4H_b$), 4.77 (s, $2H_a$), 4.25–4.16 (m, $8H_{d,h}$), 3.8–3.48 (m, PEO), 3.37 (s, $6H_f$), 3.0–2.8 (s, $4H_e$), 2.64–2.50 (m, $12H_{l,m,n}$).

2.8. Replacing core reaction to form star polymers AN4-PEO

The same procedure as above was performed. ^{1}H NMR ($CDCl_3$, δ_H ppm) 7.50–7.05 (m, H_c, phenyl), 5.49 (s, $8H_a$), 4.77 (s, $4H_b$), 4.25–4.16 (m, 24H), 3.8–3.48 (m, PEO), 3.35 (s, $12H_j$), 2.85–2.50 (m, $32H_{f,g,h,i}$).

2.9. Monitoring efficiency of core replacement with UV spectrum

Fifty milligrams of solution was taken from the initial toluene solution of F2-PEO and either AN2 or F2-PEO and AN4 and was diluted to 8.0 g with toluene to be measured by UV–Vis spectroscopy. After reaction for 48 h, the same amount of the solution (50 mg) was taken from the Schlenk flask and was diluted to

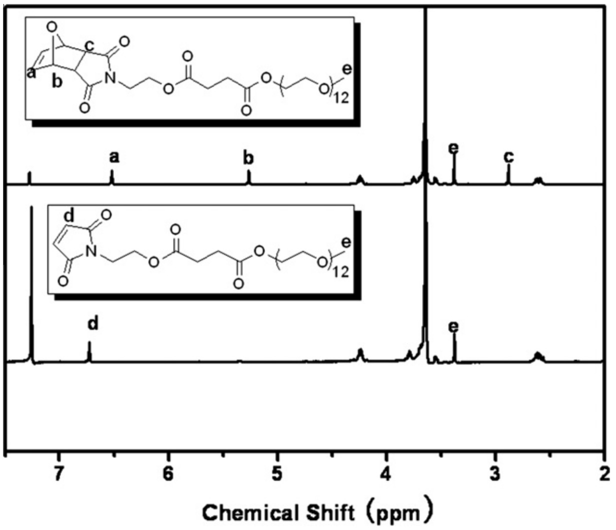


Fig. 1. ^{1}H NMR spectra of F-MI-PEO (top) and MI-PEO (bottom).

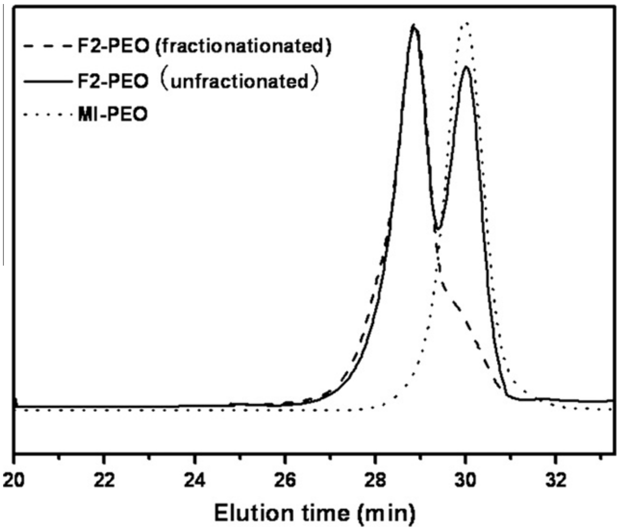


Fig. 2. SEC curves of F2-PEO before and after fractionation compared with the curves of MI-PEO.

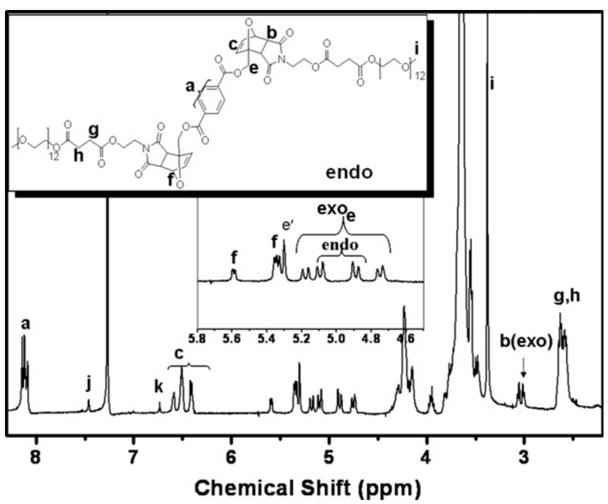


Fig. 3. ^{1}H NMR spectrum of fractionated F2-PEO prepared by the reaction of F2 and MI-PEO.

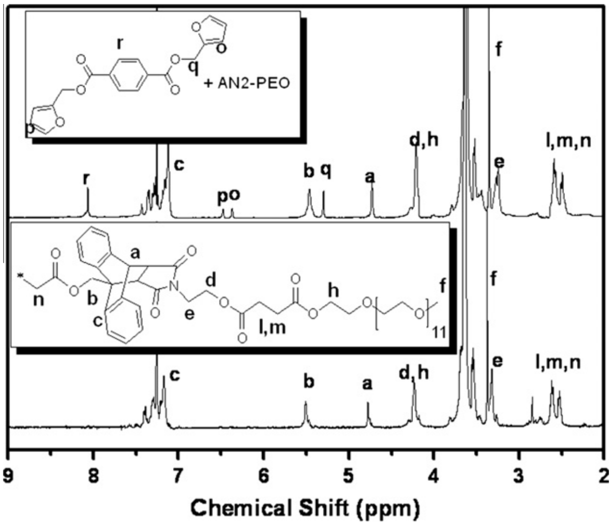


Fig. 4. ^{1}H NMR spectrum of AN2-PEO before (top) and after precipitation (bottom).

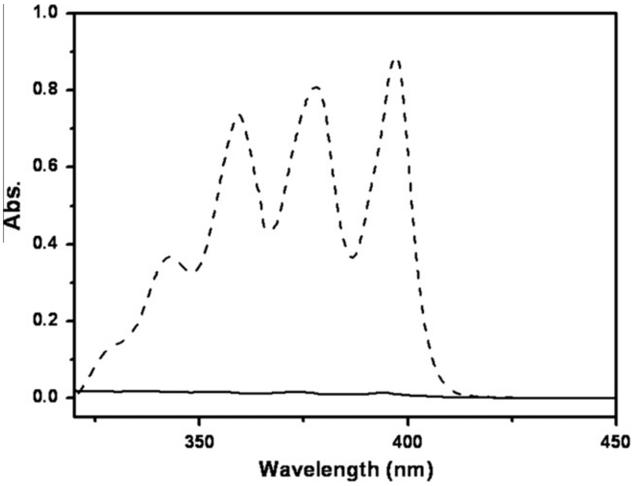


Fig. 5. UV spectra of the mixture of AN2 and F2-PEO before (dashed line) and after core exchange (solid line) in toluene.

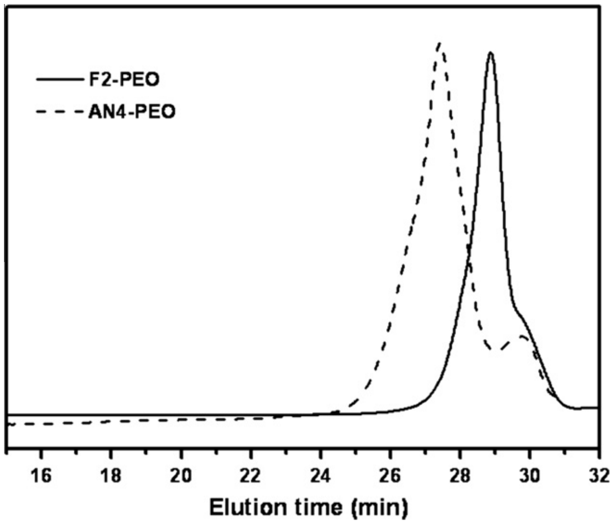


Fig. 7. SEC curves of star AN4-PEO from the reaction of F2-PEO and AN4.

8.0 g with toluene to obtain UV spectra. Comparing the intensity of absorption features due to anthracene groups in wavelength region of 300–400 nm, the efficiency of anthracene group consumption was obtained.

3. Results and discussion

3.1. Synthesis of the F2-PEO by MF DA reaction

The F2-PEO with two MF adduct units was prepared by the DA coupling reaction between two MI-PEO and an F2 unit, as shown in Scheme 2. First, the PEO with a furan protected maleimide terminal (F-MI-PEO) was easily prepared by a condensation reaction of the furan protected maleimide F-MI with PEO_{550}–COOH, which proceeded in the presence of EDC and DMAP in CH_2Cl_2 at room temperature. The structure of F-MI-PEO was identified by its ^1H NMR spectrum (Fig. 1), and the characteristic resonances from F-MI-PEO, such as vinyl proton a and bridge protons b and c, were assigned at 6.51, 5.22, and 2.82 ppm, respectively. Then by removing the furan group under reflux of toluene, the PEO with a maleimide terminal (MI-PEO) was obtained, which could also be confirmed by the disappearance of the ^1H NMR peaks a, b and c due to F-MI-PEO and the appearance of the vinyl proton d in Fig. 1. Additionally, the integration ratio between the characteristic peaks due to protons d and the methyl proton peaks e of PEO was 2:3, which indicated that all of the MI-PEO had terminal maleimide groups. Furthermore, the MI-PEO product was analyzed by MALDI-TOF mass spectroscopy, and the spectrum revealed a series of peaks in range of 700–1200 Da, corresponding to the polymer MI-PEO. The interval between neighboring peaks is 44 Da, corresponding to one ethylene oxide (EO) unit of PEO (data not shown).

Subsequently, the MI-PEO was coupled with a bis-furan molecule F2 (2:1 M ratio) to prepare a F2-PEO that has a core with two MF adduct units. The reaction proceeded in $CHCl_3$ solution at 40 °C for 72 h. From the SEC trace shown in Fig. 2, the MF reaction did not proceed with high efficiency. In addition to the new main peak, corresponding to a molecular weight that is twice that of MI-PEO, a large peak at the elution time of MI-PEO was observed, which may be attributed to unreacted MI-PEO as well as the MF monoadduct. No improvement was found when performing this reaction in other solvents, such as DMSO and THF. After the coupling reaction, column chromatography was performed to remove the fraction at 30 min, and the product after fractionation was also analyzed by SEC. As shown in Fig. 2, the peak at longer elution time has been greatly reduced and appeared as a small shoulder feature associated with the main product peak. The peak at shorter elution time with linear polystyrene as standards yielded relative M_n data (1 1 0 0) that was twice that of MI-PEO (540), which implied the formation of F2-PEO with the two MF

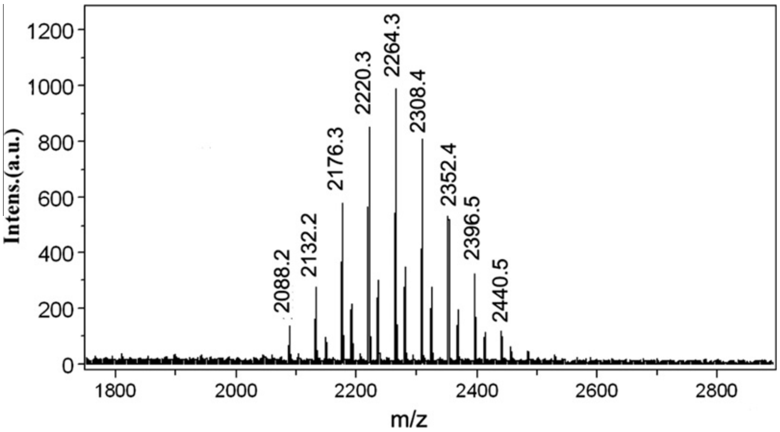


Fig. 6. MALDI-TOF mass spectrum of AN2-PEO collected in reflection mode from the reaction of F2-PEO and AN2.

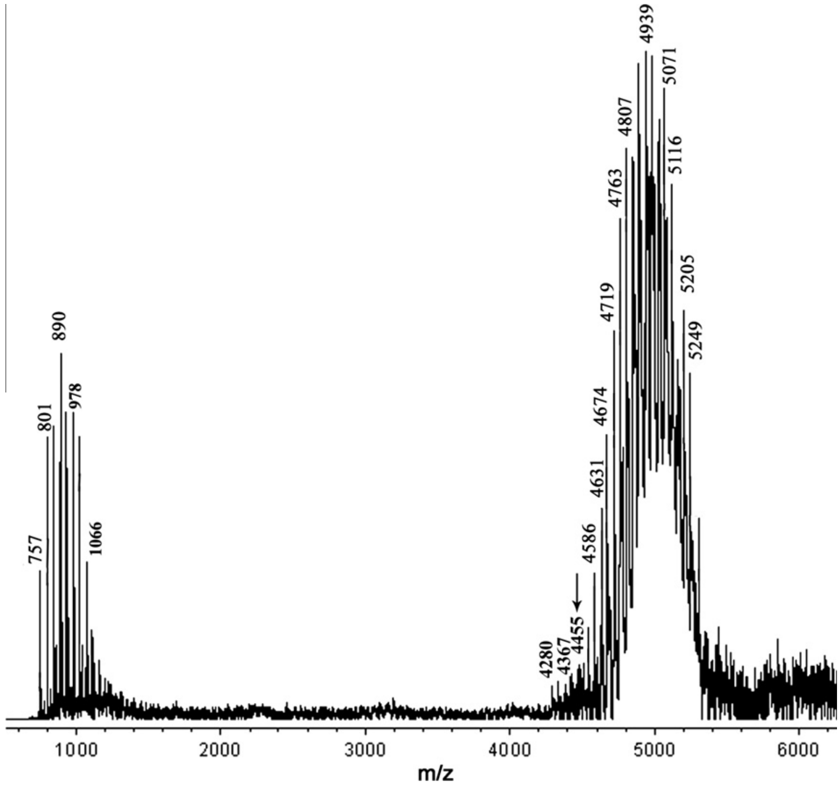


Fig. 8. MALDI-TOF mass spectrum obtained in linear mode of AN4-PEO by the reaction of F2-PEO and AN4.

adducts. As expected, the MF adduct exhibits *endo*/*exo* stereoisomers, and the ^{1}H NMR spectrum of the fractionated F2-PEO clearly displays these isomers. As shown in Fig. 3, the ratio of *endo*/*exo* adducts (57/43) was calculated by comparing the integrations corresponding to proton e (OCH$_2$C) (*endo*/*exo*) at 5.22–4.68 ppm. The peak corresponding to k at 6.75 ppm was attributed to the vinyl protons of maleimide group in the small amount of unreacted MI-PEO, in accordance with the SEC results. The peak due to proton j at 7.45 ppm was attributed to the furan group (OCH = CH) from F2. Because the bis-furan molecule F2 had been removed completely during fractionation of column chromatography, the presence of peak j indicated the presence of a small amount of the MF monoadduct during the reaction of F2-PEO and F2. By comparing the integration areas of peaks due to k, j and e, the proportion of F2-PEO in the product reached 88 mol%, and the remaining 12 mol% of included the unreacted MI-PEO and PEO with a single-MF adduct.

3.2. Replacing the core of F2-PEO to form AN2-PEO

The process of changing the polymer core was realized in the reaction of an equimolar stock of the dianthracene units of AN2 and the MF adducts of F2-PEO via an *in situ* strategy where the MF retro-DA reaction occurs, followed by a subsequent MA DA reaction as shown in Scheme 1. The reaction was conducted in toluene and refluxed for 48 h in the presence of AN2. In the ^{1}H NMR spectrum of AN2-PEO (Fig. 4, top), the proton resonances of *endo*/*exo* stereoisomers disappeared and the characteristic peaks (r, o, p and q) of F2 appeared, indicating the occurrence of the rDA reaction. Furthermore, F2 could be removed by precipitation in diethyl ether. As shown in Fig. 4 (bottom), multiplet signals corresponding to the phenyl rings appeared in the range of 7.50–7.05 ppm instead of signals due to anthracene ring protons (8.55–7.50) as a result of MA cycloaddition. Moreover, we observed signals at 5.50 and 4.77 ppm, which were attributed to the CH$_2$ adjacent to MA adduct and the CH bridge-head of the cycloaddition product.

The efficiency of the MA reaction was also monitored by the UV adsorption spectrum as shown in Fig. 5. Prior to reaction, UV absorption spectrum of the mixture was measured, and the characteristic absorption of anthracene units in AN2 was observed (dash line). After reaction, the characteristic peaks of anthracene had almost disappeared (solid line), further indicating the consumption of the AN2. The consumption efficiency of the anthracene group was estimated to be in excess of 97% by comparing the absorption values ($\lambda = 364$ nm) of the solution before and after reaction.

After reaction, the MA adducts became the core of the AN2-PEO. However, the molecular weight of the polymer AN2-PEO was similar to that of F2-PEO, precluding characterization of this reaction mixture by SEC. Therefore, the AN2-PEO product was analyzed by MALDI-TOF mass spectroscopy. Examination of the MALDI-TOF mass spectrum (Fig. 6) revealed two series of peaks in range of 2000–2500 Da. The interval between neighboring peaks of each series is m/z 44, corresponding to one EO unit of PEO. The peak observed at m/z 2088.2 (M_{obs}) was assigned as a molecule of AN2-PEO with 24 EO units. In detail, this mass of AN2-PEO can be calculated as: [24×44.04 (C_2H_4O, EO unit) + 978.9 ($C_{54}H_{46}O_{16}N_2$, core) + 2×15.0 (C_2H_6, methyl end) + 23 (Na^+), $M_{\mathrm{calc}} = 2088.8$]. Another series of peaks was observed due to the same polymer ionized with potassium instead of sodium.

3.3. Forming star polymers by core reorganization

The above results indicated that the linear F2-PEO had been converted to the AN2-PEO by core replacement *in situ*. This interesting chemistry may be applied to generate topological polymers by chain reorganization such as star polymers. When the agent containing four anthracene units (AN4) reacted with two equivalents of F2-PEO, four-arm star polymers AN4-PEO would be obtained by the rDA decomposition of MF adducts and MA formation, as shown in Scheme 1. During the reaction to form AN4-PEO, the reactant ratio of F2-PEO to AN4 was kept to 2.1. Addition of excess F2-PEO could promote formation of perfect structures of four-arm star polymers.

The SEC trace of the reaction between F2-PEO and AN4, as shown in Fig. 7, exhibits a new peak at shorter elution time, indicating the formation of higher molecular weight products. Additionally, a small peak, consistent with that observed for the MI-PEO precursor, was observed in the lower molecular weight region, which was attributed to MI-PEO cleaved by the rDA reaction of the F2-PEO at higher temperature. Spectroscopic analysis (UV and ^{1}H NMR) of this product gave similar results to those previously seen for AN2-PEO; characteristic peaks due to anthracene units in UV disappeared completely after reaction, demonstrating that the anthracene units of AN4 had been consumed completely during the MA reaction. No remaining peaks due to the anthracene ring (δ 8.55–7.50) could be found in ^{1}H NMR, further supporting the complete consumption of anthracene units. Moreover, the proton resonances of the MF adduct in F2-PEO, including the protons of the phenyl spacer and *endo*/*exo* stereoisomers, had completely disappeared in the ^{1}H NMR spectrum. This observation implied that the MF adduct core of F2-PEO was destroyed during the rDA reaction. Additionally, the signals from aromatic rings associated with the MA adducts, observed as peaks at 5.49 ppm and 4.77 ppm from methylene and methenyl of MA adduct rings, were observed, demonstrating the formation of new MA adducts. These facts strongly supported the formation of star polymers by core replacing chemistry.

The AN4-PEO product was also measured by MALDI-TOF mass spectrometry in reflection mode but could not be observed due to high molecular weight. However, the MS spectrum of AN4-PEO acquired in linear mode was obtained as shown in Fig. 8. Two series of m/z peaks with 44 Da (EO unit) intervals in two regions, 800–1200 and 4400–5400, were observed, corresponding to the two peaks in SEC trace (Fig. 7). The main peaks in the high molecular weight region were attributed to the AN4-PEO star polymers. The peak observed at 4455 Da (M_{obs}), labeled with an arrow, was assigned as the AN4-PEO molecule including four MI-PEO with 48 EO units and an AN4 unit; the detailed calculation for AN4-PEO is: [48 × 44.04 (C_2H_4O, EO unit) + 8 × 116.07 ($8C_4H_4O_4$, succinate group) + 4 × 315.3 ($4C_{21}H_{17}O_2N$, MA adduct) + 68 (C_5H_8, core) + 4 × 15.0 ($4C_2H_6$, methyl end) + 23 (Na^+), $M_{\mathrm{calc}} = 4454.7$]. Additionally, the peaks in the low molecular weights region (800–1200 Da) were attributed to excess MI-PEO. The peaks observed at 890 Da (M_{obs}) were assigned as MI-PEO with 14 EO units; the detailed calculated mass for MI-PEO is as follows: [14 × 44.04 (C_2H_4O, EO unit) + 236 ($C_{10}H_6O_6N$) + 15.0 (CH_3, methyl end) + 23 (Na^+), $M_{\mathrm{calc}} = 890.6$].

4. Conclusions

We have obtained a well-defined polymer F2-PEO that has a replaceable core of MF adducts. At a higher temperature, rDA reaction of the MF adducts within the polymer chain center occurred and the MA addition reaction simultaneously proceeded in the presence of anthracene derivatives, AN2s, to generate a new PEO polymer with a different core. Such chemistry was also applied to prepare four-arm star polymers by reacting F2-PEO with AN4. Therefore, this concept could be used to change not only the composition of a polymer chain but also chain architecture and, as a result, to tune the properties of polymer materials. This methodology could be additionally interesting if the polymers with informative functional groups were incorporated by the core exchanging strategy.

Acknowledgement

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