Supplementary Information

Duplex strand formation using alternating copolymers

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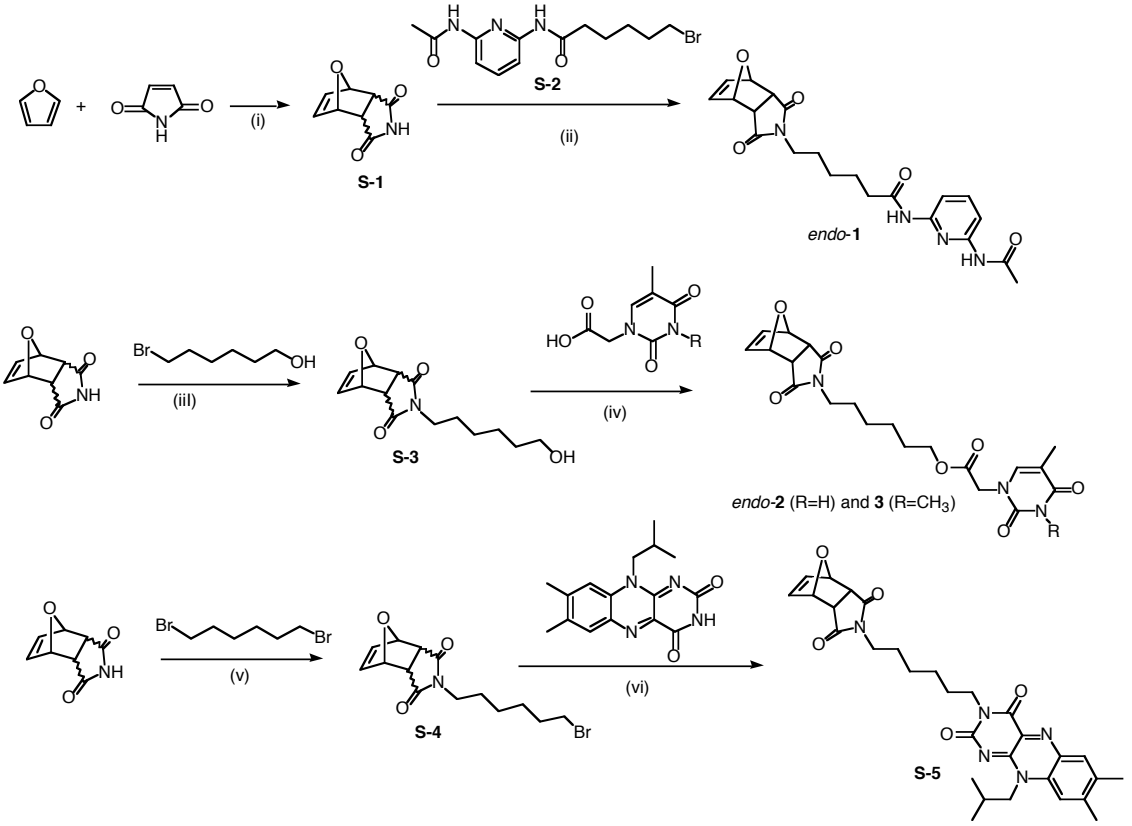
Experimental Procedures *General:* All reagents were purchased from Aldrich and used without further purification except as indicated bellow. Dimethylformamide (DMF) were purchased from VWR and used as received. All reactions were carried out under argon using oven-dried glassware. All polymerizations were carried out using standard Schlenk techniques in a dry argon atmosphere. Tetrahydrofuran (THF) was distilled from sodium and benzophenone. Dichloromethane, triethylamine and cyclooctene were distilled from calcium hydride. N-methylthymineaceticacid, acetyldiaminopyridine, N-isobutylflavin and 2-acetylamino-6-(6-bromohexanoylamino)-pyridine were synthesized according to previous reports. Deuterated chroloform was purchased from Cambridge Isotope Laboratory and used as received. Elemental analyses were performed by the Microanalytical Lab at the University of Massachusetts, Amherst.
*Instrumentation.*Molecular weights of the polymers were determined by gel permeation chromatography with a PL LC 1120 pump, a Waters R403 differential refractometer detector, and three PL gel columns (10^5, 10^4, and 10^3 Å). System was calibrated with polystyrene standards. ^{1}H NMR spectra were recorded using a Bruker Advance 400 MHz spectrometer equipped with bbi probe. Ultraviolet-Visible spectra were recorded on a Hewlett Packard 8452A photodiode array spectrometer. Leica TCS SP2 and Nicon E600 were used for visualization of the aggregates.

Synthesis of oxynorbornene monomers and their alternating copolymers with cyclooctene



Reaction conditions; (i) 4days, RT, (ii) K_2CO_3, DMF, S-2 (iii) K_2CO_3, DMF, 1-bromo-6-hexanol (iv) pentafluorophenol, DCC, DMF, thymineaceticacid or N-methylthymineaceticacid, (v) K_2CO_3, DMF, 1,6-dibromo-hexane, (vi) K_2CO_3, DMF, N-isobutylflavin

Synthesis of S-2: The synthesis of this compound was previously reported. However we improved the yield significantly, hence we report the synthesis. 6-Bromohexanoylchloride (0.96ml, 8.3mmol) was added to a solution of acetyldiaminopyridine (1.0g, 6.6mmol) and triethylamine (1.3ml, 9.2mmol) in dry dichloromethane (40ml) with cooling in an ice bath. After stirring over night, the reaction was quenched by adding a portion of water (20ml). Organic layer was washed with water and brine. Flash chromatography on silica gel with the mix solvent (Hexane:EtOAc=1:2) yielded the white solid 1.8g (80%).

Synthesis of monomer 1: K_2CO_3 (717mg, 5.2mmole) and DMF (10ml) were placed in a round bottom flask under argon. **S-1** (363mg, 2.2mmole) was added to the mixture and purged with argon. A solution of acetyl-(6-hexanoyl)diaminopyridine (S-2, 684mg, 2mmole) in DMF (1ml) was added dropwise at room temperature. After stirring over night, water was added to quench the reaction until the mixture turned to be clear. This aqueous mixture was extracted with ethylacetate and combined organic layer was washed with water and brine. Organic layer was dried with $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash column to give a white solid product (silica gel, ethylacetate). Isolated yield of*endo*-isomer was 30% (250mg, 0.61mmole). mp 143-145˚C. Calcd: C, 61.15; H, 5.87; N, 13.58. Found C, 60.90; H, 5.80; N 13.24 ^{1}H NMR ($CDCl_3$); □ 7.88 (d, 2H, 2Xpyridine-H, 8.0Hz), 7.70 (t, 1H, pyridine-H, 8.0Hz), 7.57 (s, 1H, NH), 7.52 (s, 1H, NH), 6.39 (s, 2H, 2X-CH=), 5.31 (m,

2H, >CH-O), 3.51 (d, 2H, 2X>CH-CO, 3.6Hz), 3.21 (t, 2H, N-CH_2-, 7.4Hz), 2.36 (t, 2H, CO-CH_2-, 7.4Hz), 2.20 (s, 3H, CO-CH3), 1.76-1.28 (m, 6H, 3X-CH2-).

Synthesis of S-3: A solution of K_2CO_3 (416mg, 3.0mmole) in DMF (12ml) was placed in a round bottom flask. **S-1** (495mg, 3.0mmole) was added to the mixture and purged with argon. Solution of 6-bromohexanol (550mg, 3.0mmole) in DMF (3ml) was added dropwise at room temperature. After stirring over night, water was added to quench the redish reaction mixture. This aqueous mixture was extracted with ethylacetate and combined organic layer was washed with water and brine. Organic layer was dried with $MgSO_4$ and evaporated under reduced pressure. The residual crude product was sufficiently pure for the next reaction (600mg, 2.3mmole, 75%).

Synthesis of 2: To a solution of thymineaceticacid (423mg, 2.3mmole) in DMF (8ml), was added pentafluorophenol (465mg, 2.5mmole) and cooled with an ice bath. After DCC (521mg, 2.5mmole) was added, the temperature was kept at 0˚C for 1hr and the mixture was stirred for 5hr at room temperature. The urea byproduct was filtered. To the filtrate was added a solution of **S-3** (0.6g, 2.3mmole) and triethylamine (0.32ml, 2.3mmole) in DMF (3ml) dropwise under argon. After stirring over night, water was added to quench the reaction and the aqueous mixture was extracted with ethylacetate. Organic layer was combined and washed with water and followed by brine. Flash chromatography (ethyl acetate on silicagel) was performed to obtain white solid. *Endo*-isomer isolated yield was 26% (257mg, 0.6mmole). mp 130-132˚C. Calcd: C, 58.46; H, 5.84; N, 9.74. Found C, 59.39; H, 6.20; N 8.80 ^{1}H NMR ($CDCl_3$); □ 8.32 (s, 1H, NH), 6.96 (s, 1H, -CH=, thymine), 6.40 (s, 2H, 2X-CH=, oxynorbornene), 5.33 (m, 2H, >CH-O), 4.43 (s, 2H, -CO-CH_2-N), 4.17 (t, 2H, -CH_2-O-, 6.4Hz), 3.52 (d, 2H, 2X>CH-CO, 3.6Hz), 3.31 (t, 2H, N-CH_2-, 7.4Hz), 1.94 (s, -CH_3, 3H), 1.70-1.2 (m, 8H, 4X-CH_2-).

Synthesis of 3: Synthesis procedure was adapted from the synthesis of **2**. N-methylthymineaceticacid was used instead of thymineaceticacid. Product was obtained as white waxy oil. Isolated yield of *endo*-isomer was 17% (457mg, 1.0mmole). Calcd: C, 59.31; H, 6.11; N, 9.43. Found C, 59.31; H, 6.81; N 9.06 ^{1}H NMR ($CDCl_3$); □ 6.94 (s, 1H, -CH=, thymine), 6.40 (s, 2H, 2X-CH=, oxynorbornene), 5.33 (m, 2H, >CH-O), 4.47 (s, 2H, -CO-CH_2-N), 4.17 (t, 2H, -CH_2-O-, 6.6Hz), 3.51 (d, 2H, 2X>CH-CO, 3.6Hz), 3.36 (s, 3H, N-CH_3), 3.30 (t, 2H, N-CH_2-, 7.4Hz), 1.95 (s, -CH_3, 3H), 1.80-1.2 (m, 8H, 4X-CH_2-).

Synthesis of S-4: A solution of K_2CO_3 (416mg, 3.0mmole) in DMF (50ml) was placed in a round bottom flask. **S-1** (495mg, 3.0mmole) was added to the mixture and purged with argon. Solution of 1,6-dibromohexane (732mg, 3.0mmole) in DMF (12ml) was added dropwise at room temperature. After stirring over night, water was added to quench until the mixture became clear. This aqueous mixture was extracted with ethylacetate and combined organic layer was washed with water and brine. Organic layer was dried with $MgSO_4$ and evaporated under reduced pressure. The residual crude product was purified by flash column to yield 800mg of **S-4**.

Synthesis of S-5: A solution of K_2CO_3 (717mg, 5.2mmole) in DMF (15ml) was placed in a round bottom flask. N-isobutylflavin (655mg, 2.3mmole) was added to the mixture and purged with argon. Solution of 1,6-dibromohexane (732mg, 3.0mmole) in DMF (3ml) was added dropwise at room temperature. After stirring over night, water was added to quench the redish reaction mixture. This aqueous mixture was extracted with ethylacetate and combined organic layer was washed with water and brine. Organic layer was dried with $MgSO_4$ and evaporated under reduced pressure. The residual crude

product was purified by flash column to yield 300mg of *endo*-**S-5** (25%). mp 93˚C

General polymerization: A solution of ruthenium catalyst (0.01mmol) in freeze-pump-thaw degassed dichloromethane (0.5ml) was quickly added to a solution of monomer (0.1mmol) and cyclooctene (11mg, 0.1mmol) in 2ml of degassed dichloromethane under argon atmosphere at room temperature. The resulting solution was stirred for 12h, and the polymerization was quenched by addition of ethyl vinyl ether. The polymer was obtained and purified by repeated precipitation from cyclohexane. In all cases cis-trans ratio estimated in ^{1}H NMR was about 3:2.

Table S-1. Alternating copolymerization of **1**, **2** and **3** with cyclooctene

Monomer	M_n (M_w/M_n)	Yield (%)	Alternating unit (%)
1	7400 (1.47)	95	92
2	7300 (1.54)	93	98
3	5000 (1.58)	95	94

Flavin tagged copolymer synthesis: A solution of ruthenium catalyst (0.01mmole) in freeze-pump-thaw degassed dichloromethane (0.5ml) was quickly added to a solution of **1** (0.09mmole), **S-5** (0.01mmole) and cyclooctene (11mg, 0.1mmole) in 2ml of degassed dichloromethane under argon atmosphere at room temperature. The resulting solution was stirred for 12h, and the polymerization was quenched by addition of ethyl vinyl ether. The polymer was obtained and purified by repeated precipitation from cyclohexane. Yield: 85% Mn: 9000 (1.50)

^{1}H NMR titration: A 0.5ml portion of a solution of 1mM THY copolymer (based on THY unit) in $CDCl_3$ was place in a 5mm tube and the spectrum was recorded at 20˚C. Aliquots of a solution of 10mM DAP copolymer (based on DAP unit) was added to the tube and the spectrum was recorded at 20˚C after the addition of each aliquot. Chloroform peak was used as a reference.

UV titration: A stock solution of 2mM THY copolymer (based on THY unit) was prepared and a 2.0ml portion of the THY stock was placed in 1cm quartz cell. A 8mM DAP copolymer solution (based on DAP unit) was prepared using the THY stock solution. Aliquots of the DAP copolymer solution were added to the cell and the optical density at 700nm was read after each addition.

DIC Microscopy sample preparation: Supramolecular-copolymer complexes were prepared by mixing 1mg/mL solution of DAP and THY copolymers in $CHCl_3$. The vial was shaken for complete mixing after the addition. Digital micrograph was taken at random to ensure a representative distribution was obtained. Images were collected over 5 minutes. Representative 300 discrete spheres were counted to estimate the average diameter.

LCSM sample preparation: The samples were prepared in a similar fashion as above with flavin tagged copolymer.

Job polts in UV and NMR: UV and ^{1}H NMR were recorded in $CHCl_3$ and $CDCl_3$ respectively. Two stock solutions were prepared as follows. Solution A: 2mM for UV and 1mM for ^{1}H NMR of THY in $CHCl_3$ and $CDCl_3$. Solution B: 2mM for UV and 1mM for ^{1}H NMR of DAP in $CHCl_3$ and $CDCl_3$. Concentration was based on recognition unit. Ten samples were prepared with solution A and B in the following ratio: 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3. 8:2, 9:1 and 10:0, and the optical density and ^{1}H NMR were recorded for each sample.

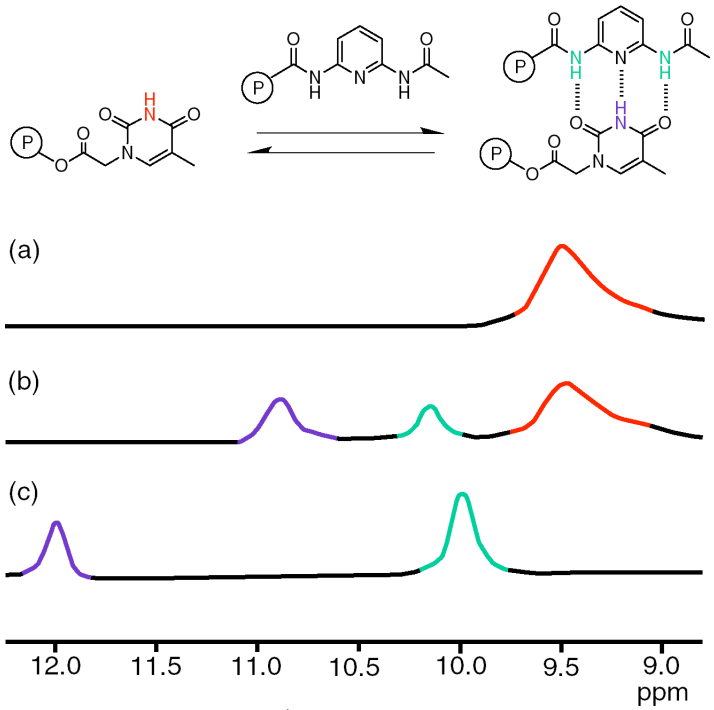


Fig S-1. Imide peak shifts during the ^{1}H NMR titration; (a) THY alternating copolymer (b) 0.2eq of DAP alternating copolymer added (c) 1eq of DAP alternating copolymer added.

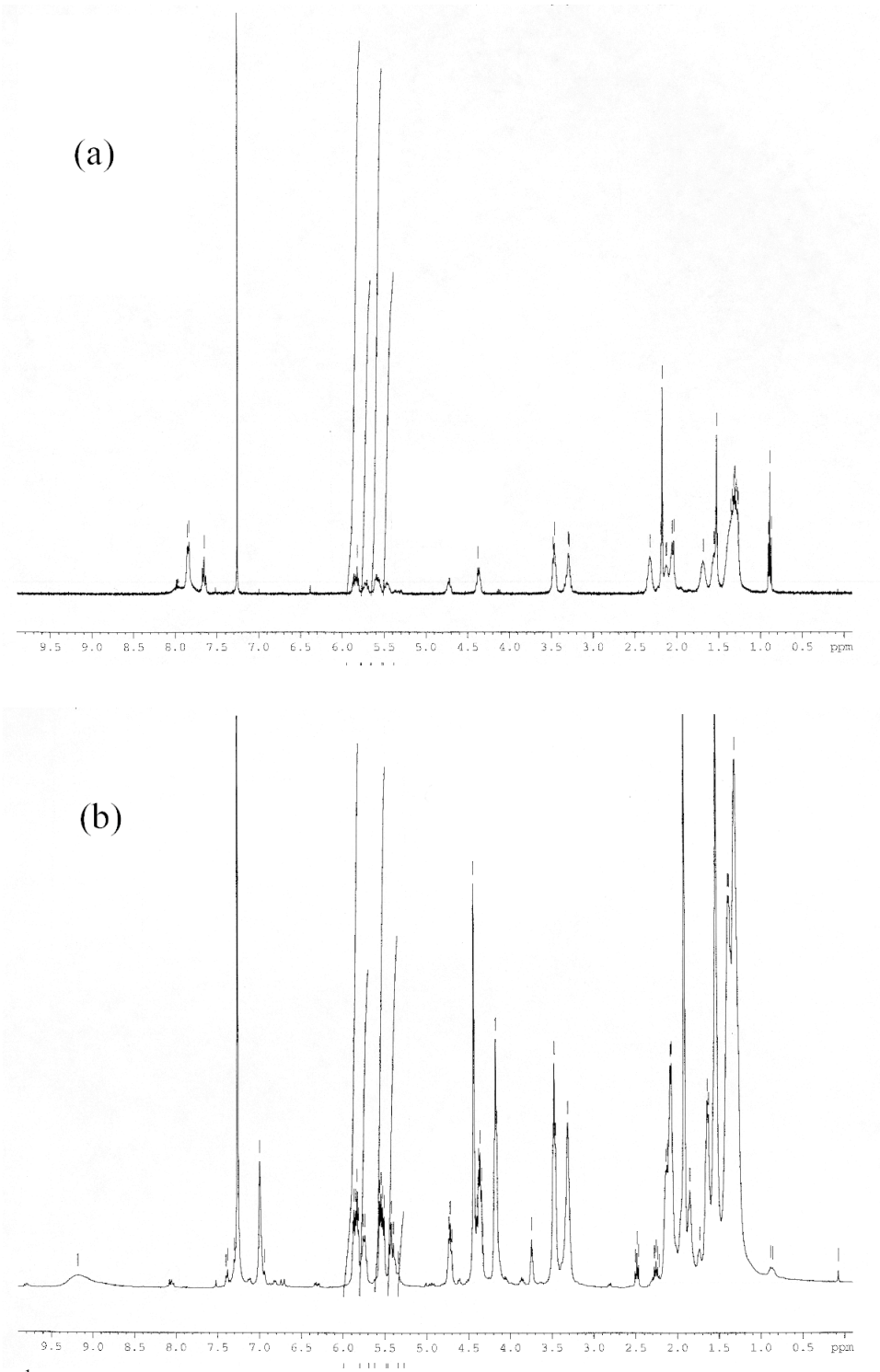


Fig S-2. ^{1}H NMR spectra of (a) DAP alternating copolymer and (b) THY alternating copolymer.

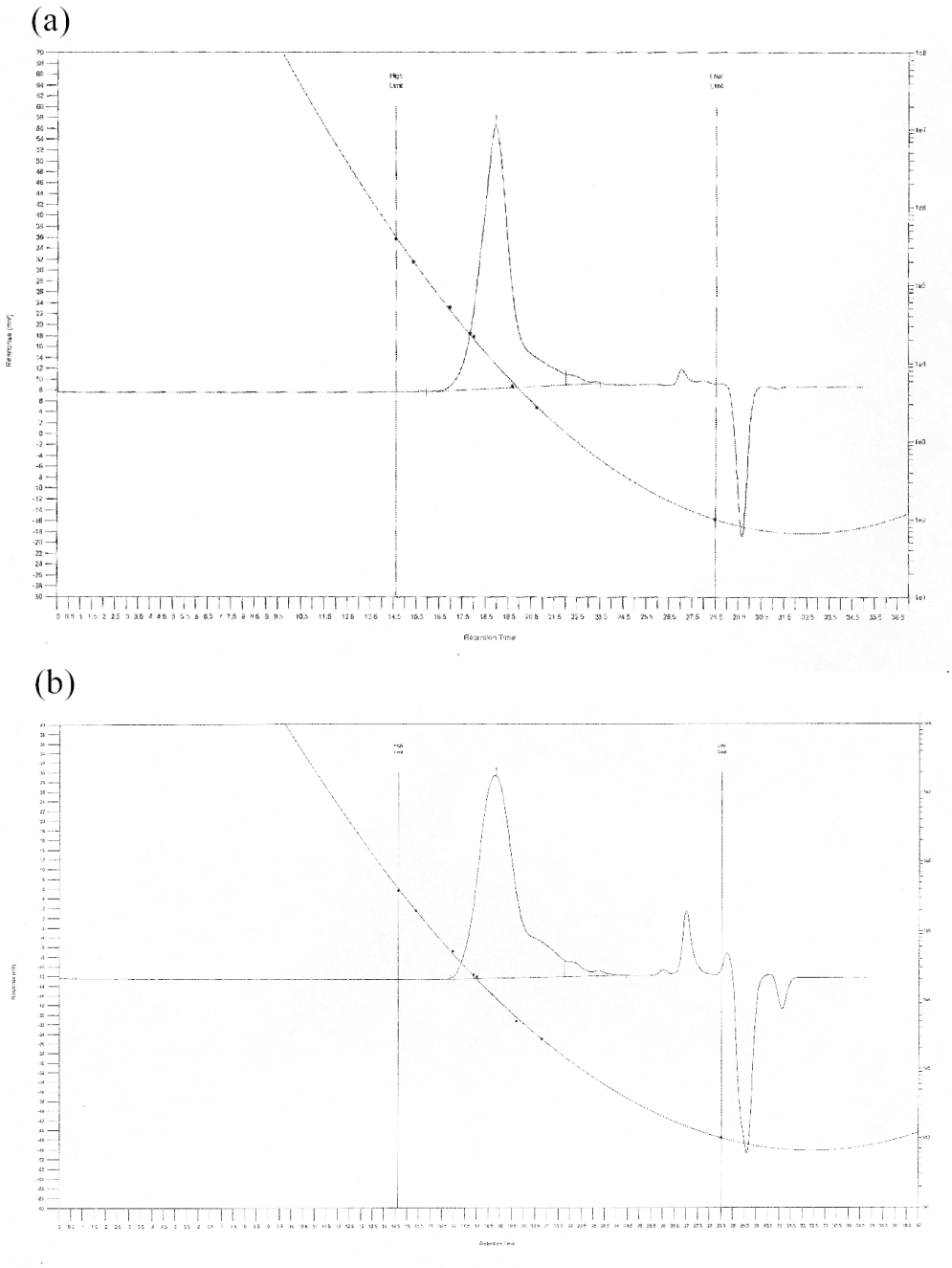


Fig S-3. GPC profiles of (a) DAP alternating copolymer (M_n: 7400, PDI: 1.47) and (b) THY alternating copolymer (M_n: 7300, PDI: 1.54).