Supporting Information for

Group interval-controlled polymers: an example of epoxy functional polymers via step-growth thiol-yne polymerization

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Experiments

Figure S29. Work curve of pyrene concentration dependence of absorption at 294 nm excimer emission.

Figure S30. DSC curves of **P2**, **P4**, **P6**, **P8** and **P10**.

Figure S31. TGA curves of **P2**, **P6** and **P8**.

Figure S32. DTG curves of **P2**, **P6** and **P8**.

Experiments

Synthesis of epoxy GICP, P3

Glycidyl propargyl ether (0.518 g, 4.6 mmol), 1, 3-propanedithiol (0.519 g, 4.8 mmol), and DMPA (35.5 mg, 0.14 mmol) were dissolved in 2.0 mL of 1, 4-dioxane. Subsequently, the mixture was added into a 10 mL round-bottom flask which was sealed by a rubber stopper. High-purity N_2 was bubbled through the solution for 30 min to fully remove O_2, and the polymerization was carried out under UV irradiation in ice-water bath for 2.0 h. Then, allyl glycidyl ether (1.0 mL, 8.4 mmol) containing 2 wt % of DMPA was injected into the reaction system through syringe. After additional irradiation for 1.5 h, the mixture was diluted with about 2.0 mL of THF and dropped into cold anhydrous ether (50 mL), affording colorless viscous precipitate. This above-mentioned process was repeated three times. After drying under vacuum, the product (0.776 g) was obtained in a yield of about 76.4 %.

Synthesis of epoxy GICP, P5

Glycidyl propargyl ether (0.360 g, 3.2 mmol), 1, 5-pentanedithiol (0.463 g, 3.4 mmol), and 2, 2-bimethoxy-2-phenylacetophenone (DMPA, 24.7 mg, 0.09 mmol) were dissolved in 1.5 mL of 1, 4-dioxane. Subsequently, the mixture was added into a 10 mL round-bottom flask which was sealed by a rubber stopper and covered by tin foil. Oxygen was removed by bubbling of high-purity N_2. Thoil-yne polymerization was carried out under UV irradiation (λ = 365 nm) in ice-water bath for 2.0 h. Then, allyl glycidyl ether (0.7 mL, 5.88 mmol) containing 2 wt % of DMPA was added in. After additional irradiation for 1.5 h, the mixture was diluted with about 1.5 mL of THF and dropped into cold anhydrous ether (40 mL), affording viscous precipitate. This above-mentioned process was repeated three times. After drying under vacuum, the product (0.519 g) was obtained in a yield of 65.2 %.

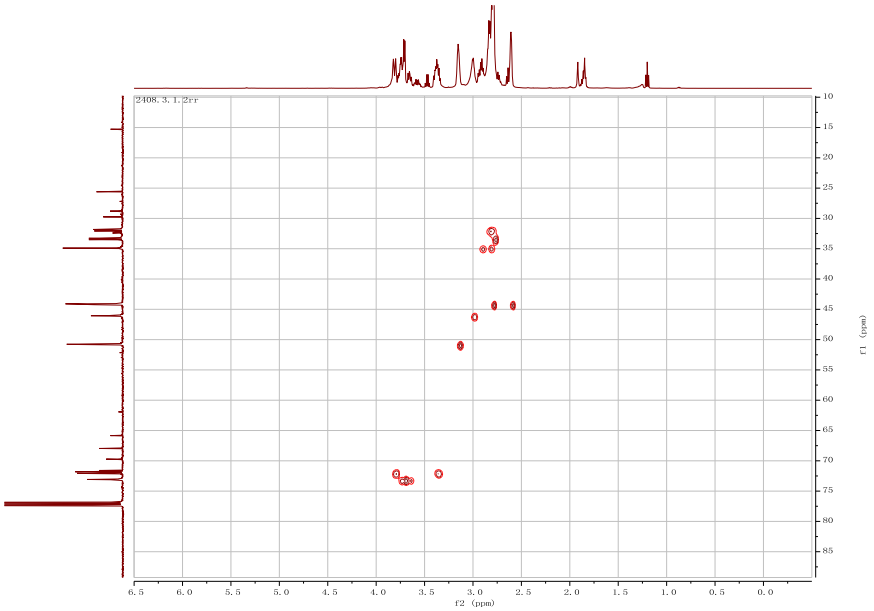
Modification of epoxy GICP, P5

Epoxy GICP, **P5**, (0.217 g, 0.9 mmol) was dissolved in 4.5 mL of dried DMF. 3-(Dimethylamino)-1-propanethiol (0.320 g, 2.7 mmol) was added into the solution and stirred at 30 ^{o}C for 48 h. After removal of most solvent, the residual solution was

precipitated into 40 mL of anhydrous ether, centrifuged, separated, and dried under vacuum. Viscous liquid (0.148 g) with a yield of 45.7% was afforded.

P5 (0.265 g, 1.1 mmol) was dissolved in 4.5 mL of dried DMF. 3-Mercapto-1, 2-propanediol (0.357 g, 3.3 mmol) was added into the solution and stirred at 35 ^{o}C for 48 h. After removal of most solvent, the residual solution was precipitated into anhydrous ether and dried under vacuum. Viscous liquid (0.262 g) with a yield of 68.2% was afforded.

P5 (0.338 g, 1.4 mmol) was dissolved in 4.5 mL of dried DMF. Thiolacetic acid (0.387 g, 4.2 mmol) was added into the solution and stirred at 30 ^{o}C for 48 h. After removal of most solvent, the residual solution was precipitated into 40 mL of anhydrous ether, centrifuged, separated, and dried under vacuum. Viscous liquid (0.247 g) with a yield of 52.7% was afforded.



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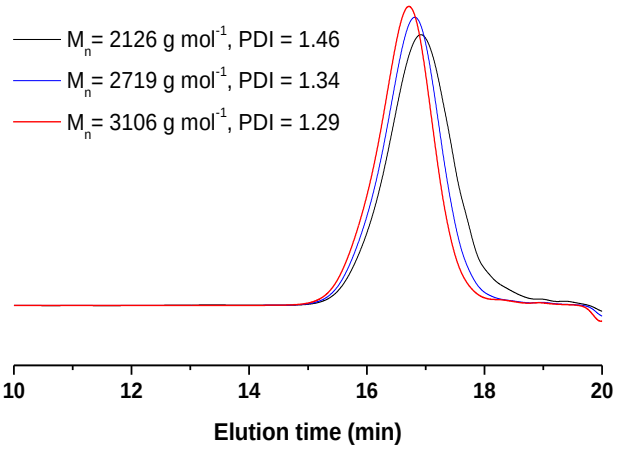
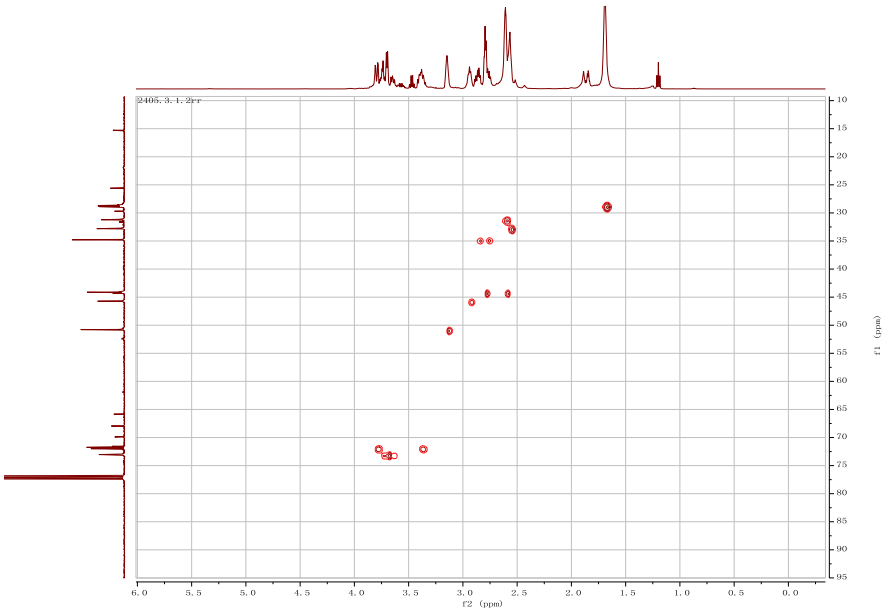


Figure S2

Figure S3



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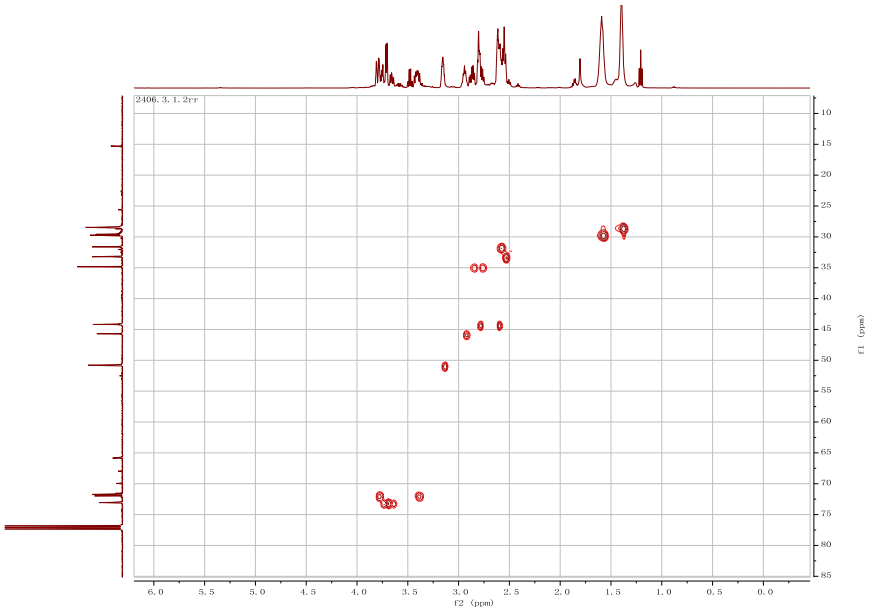

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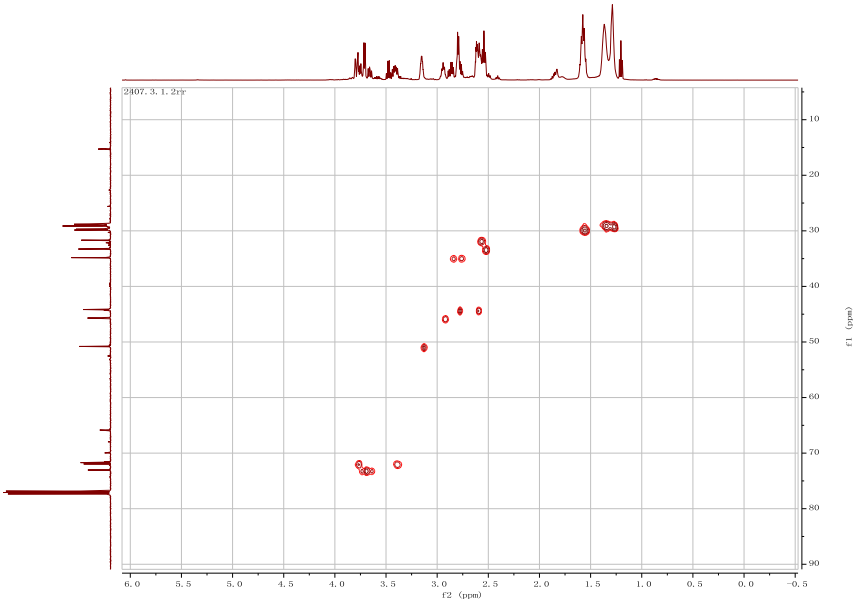

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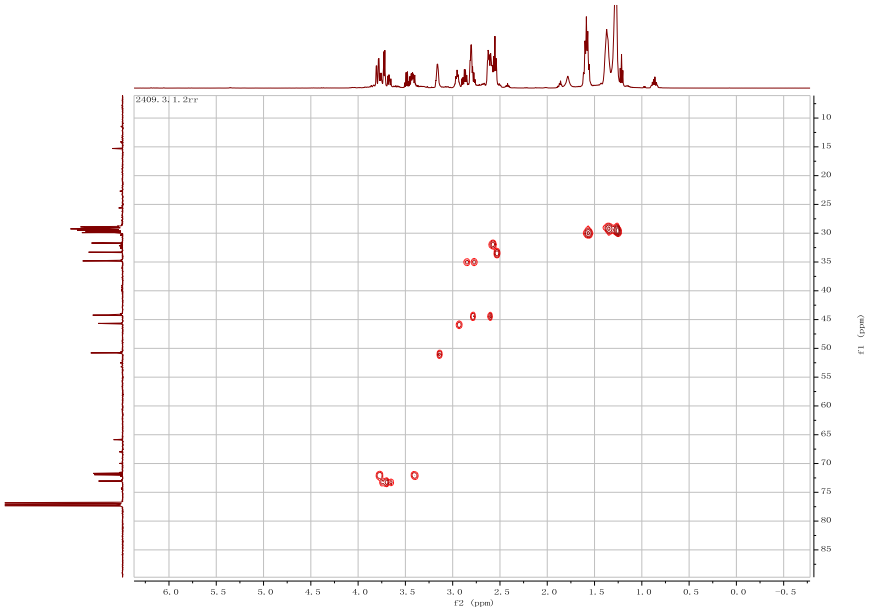

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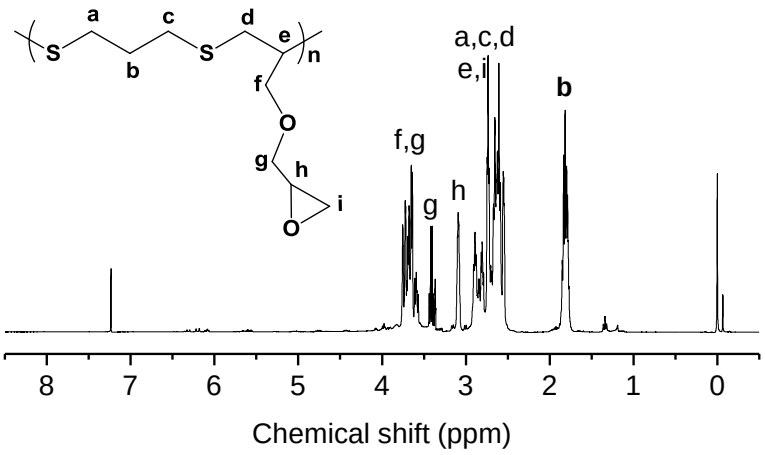

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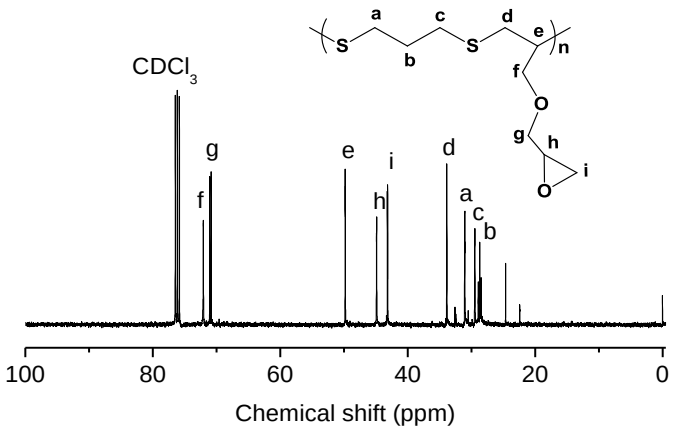

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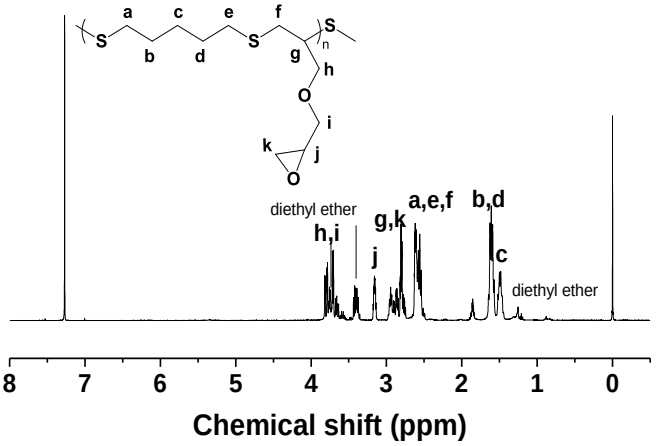

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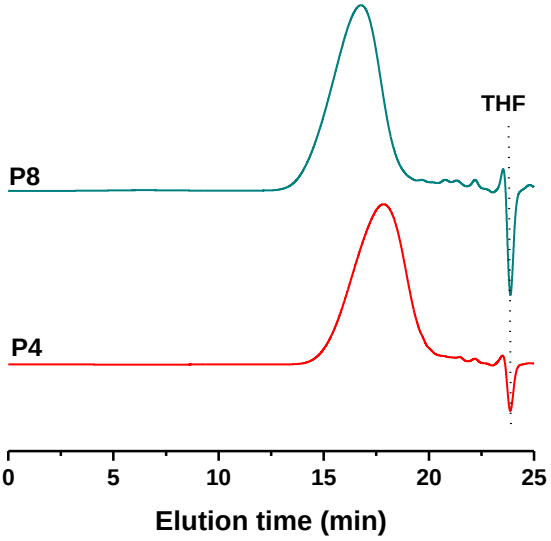

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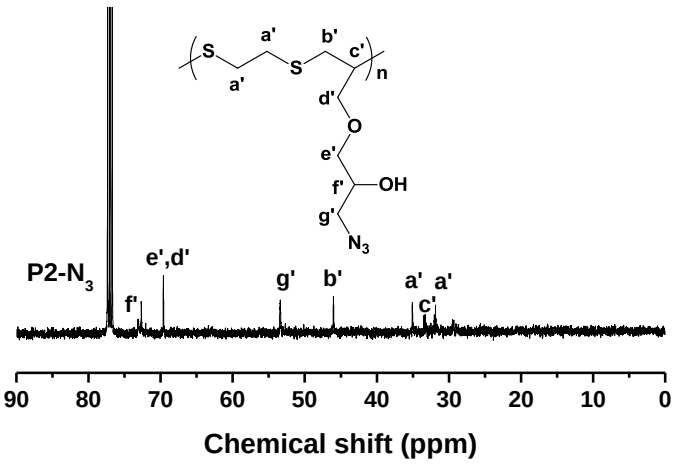

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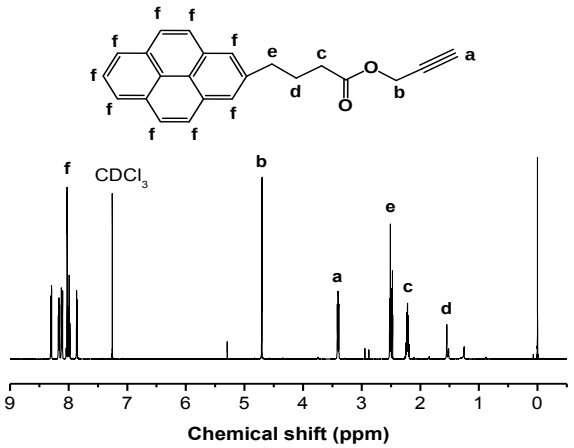

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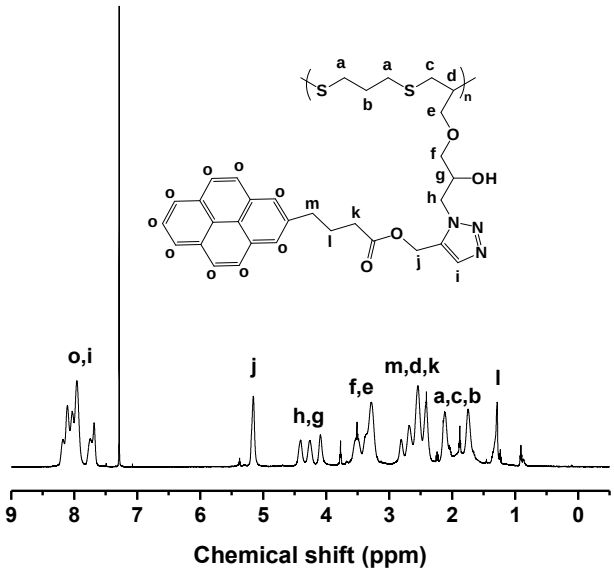

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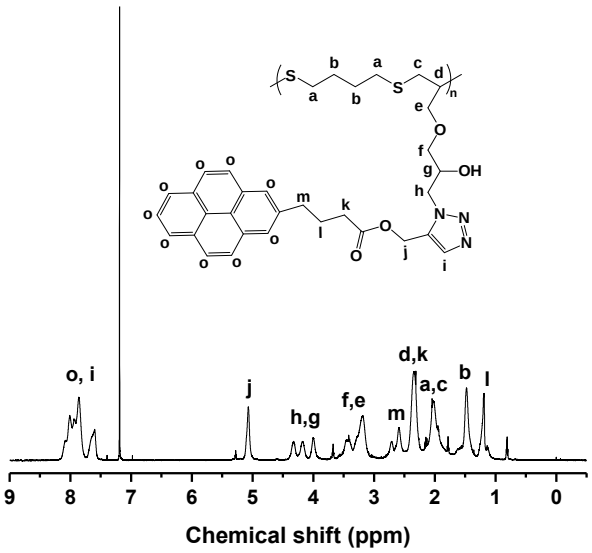

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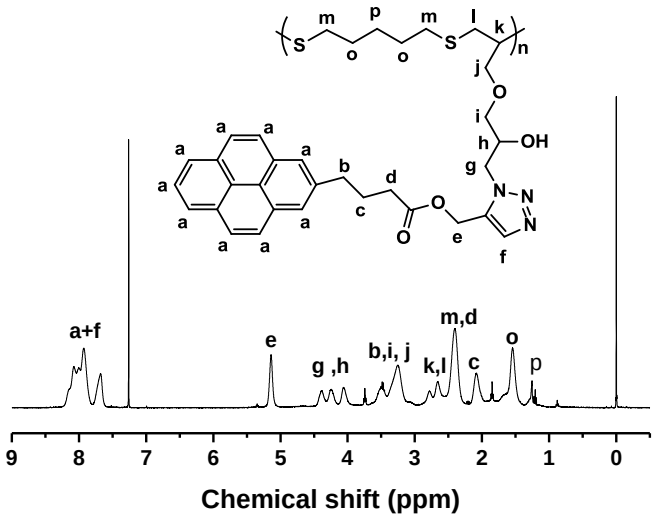

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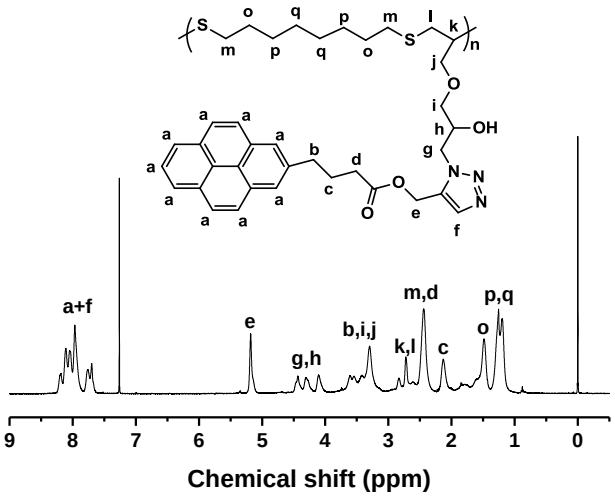

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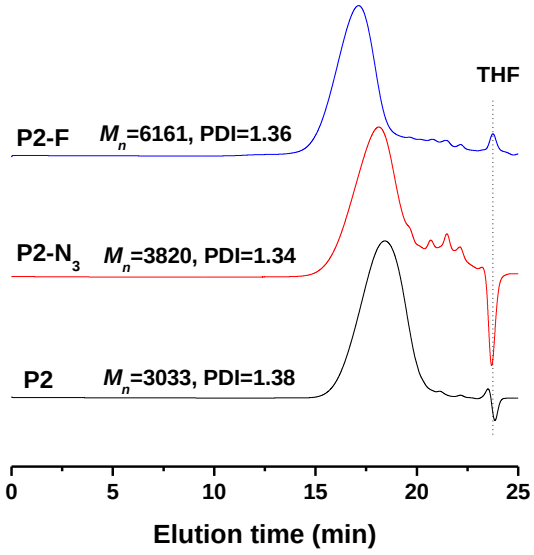

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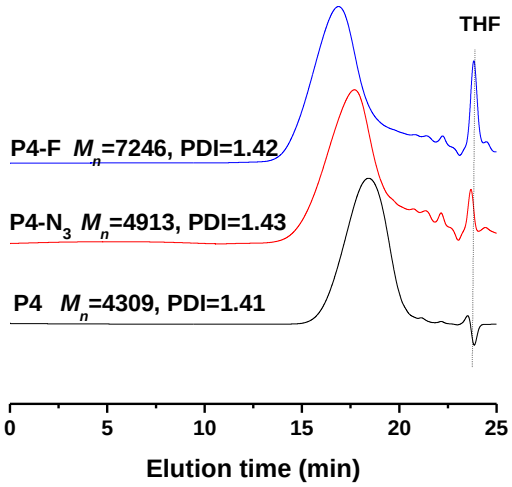

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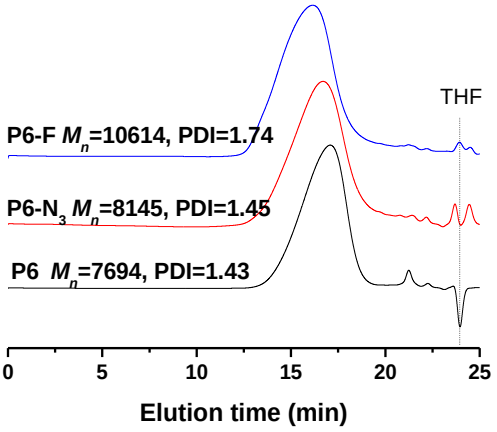

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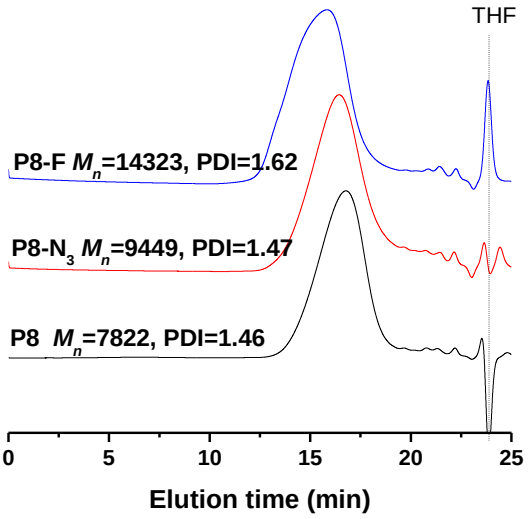

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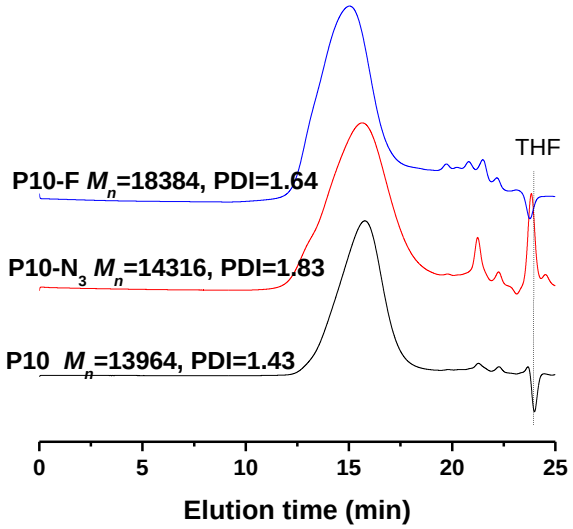

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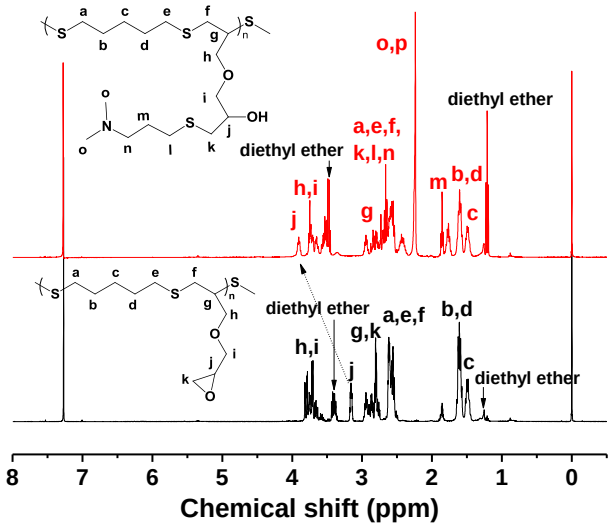

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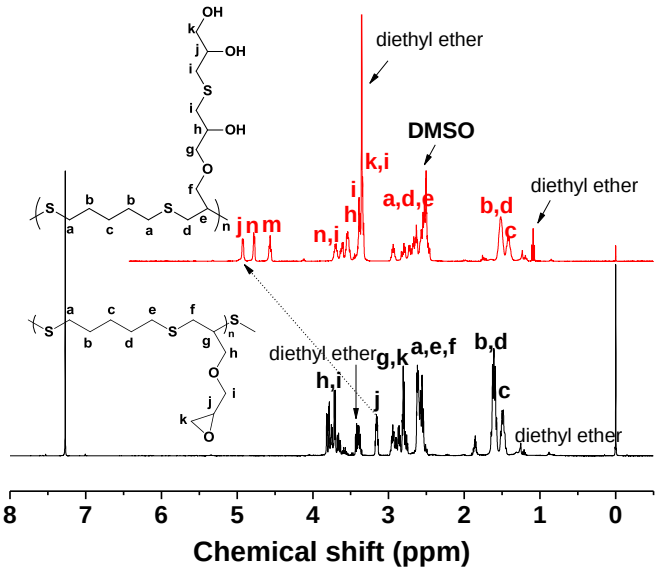

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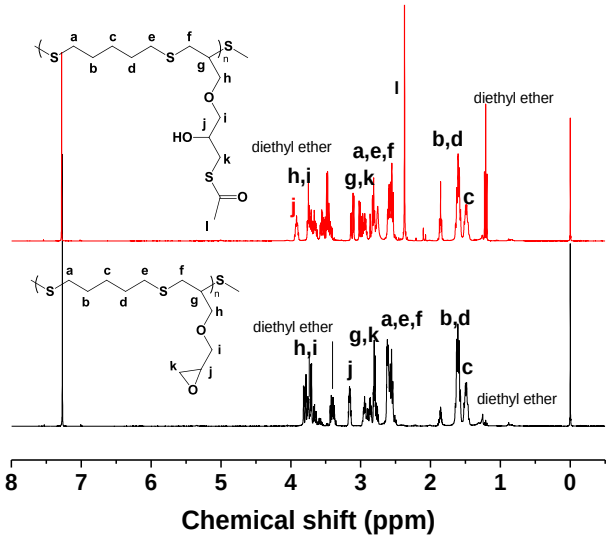

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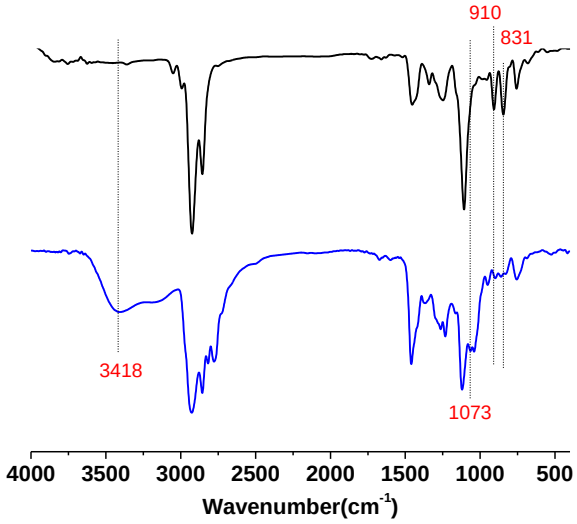

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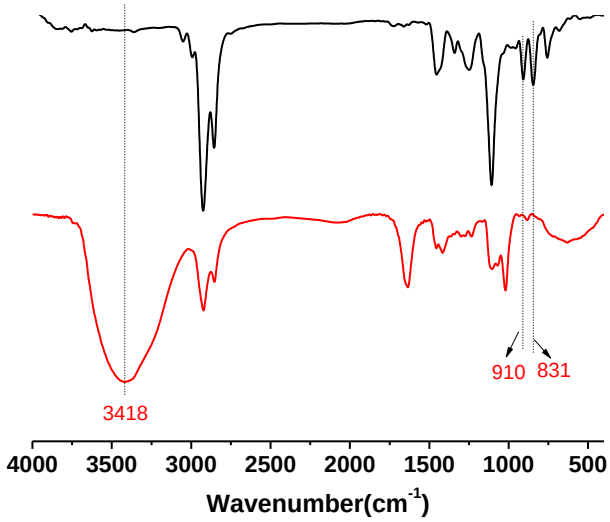

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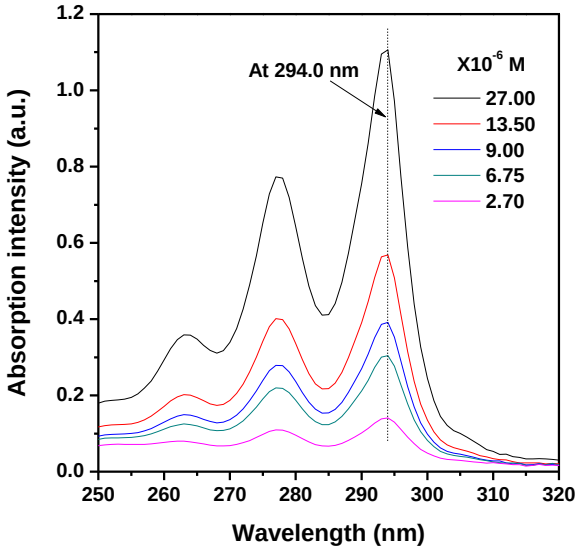

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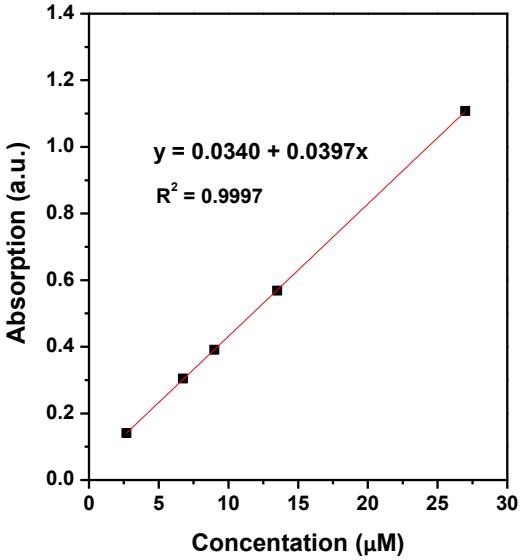

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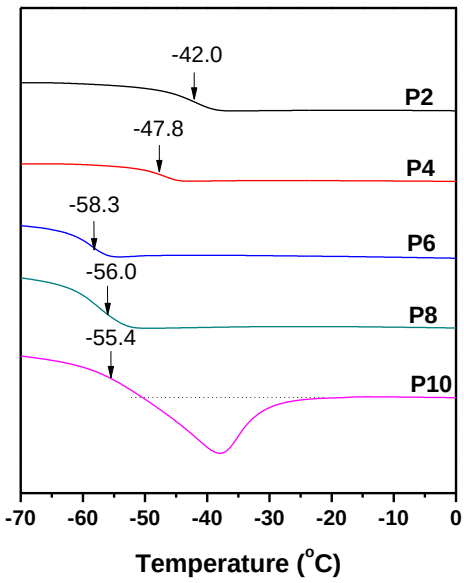

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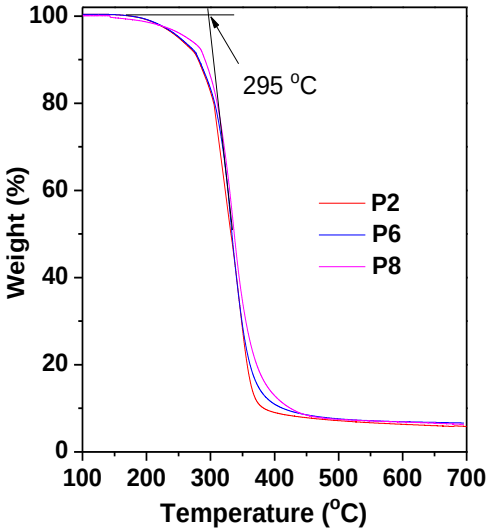

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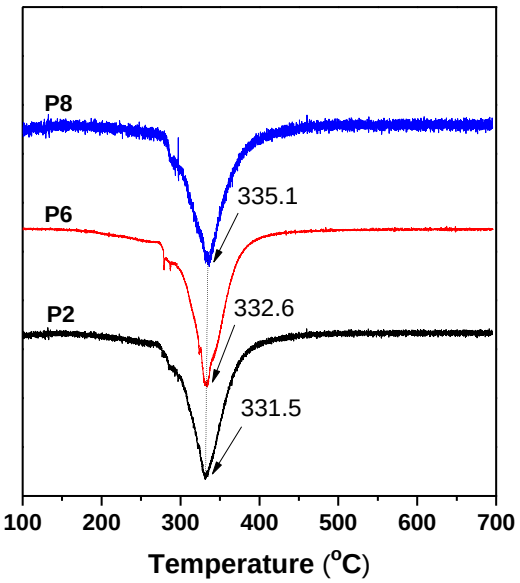

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