Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Dramatically Different Charge Transport Properties of Bisthienyl Diketopyrrolopyrrole-Bithiazole Copolymers Synthesized *via* Two Direct (Hetero)arylation Polymerization Routes

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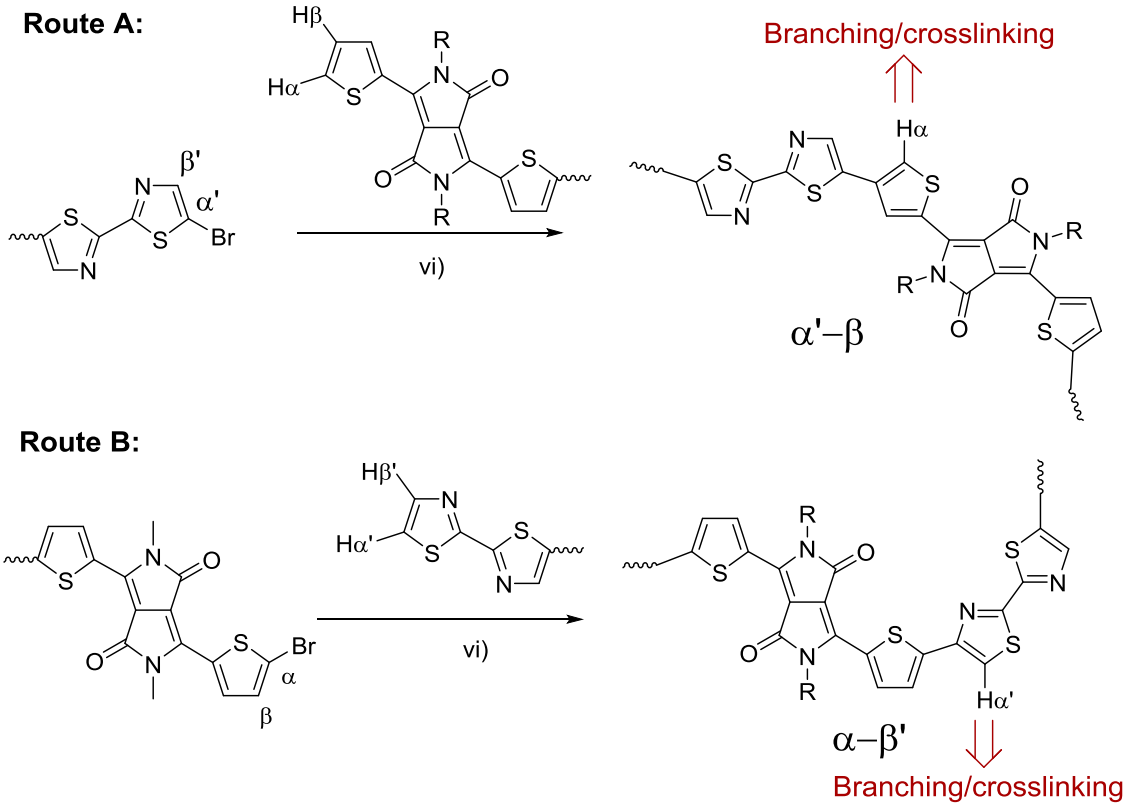
Supplementary Information



Scheme S1. Possible α'-β and α-β' coupling side reactions in Route A and Route B, respectively, between a C-Br in a terminal thiazole (α') or thiophene (α) unit of a polymer chain or monomer and a β C-H in a thiophene (β) or thiazole (β') unit of a polymer chain or monomer, where C-Hα in the α'-β defect and C-Hα' in the α-β' defect have much higher reactivity than that of other β C-H groups on the polymer backbone, resulting in branched and cross-linked structures.

Supplementary Information

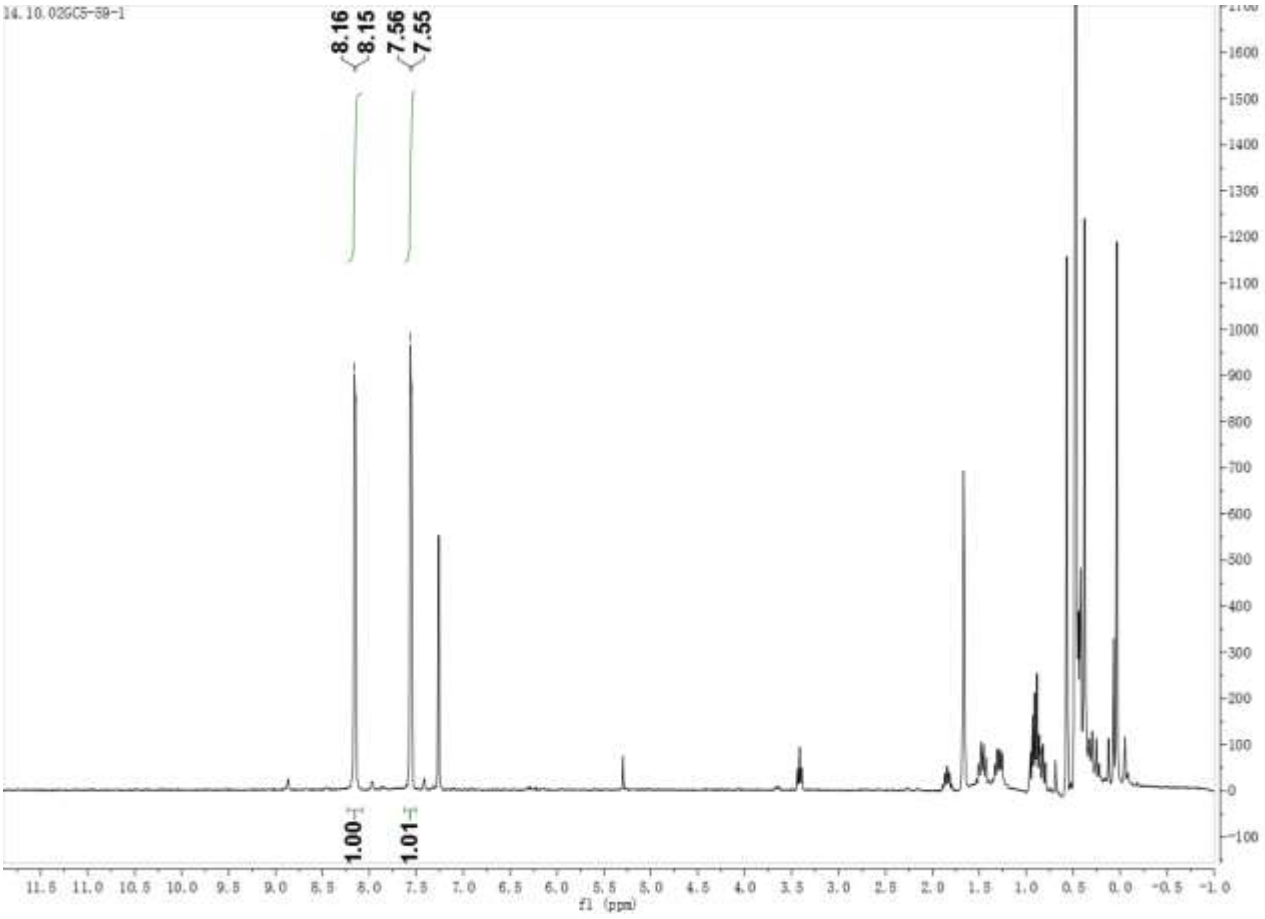


Fig. S1 The 300 MHz ^{1}H-NMR spectrum of 2-(trimethylstannyl)thiazole (**1**) measured in $CDCl_3$.

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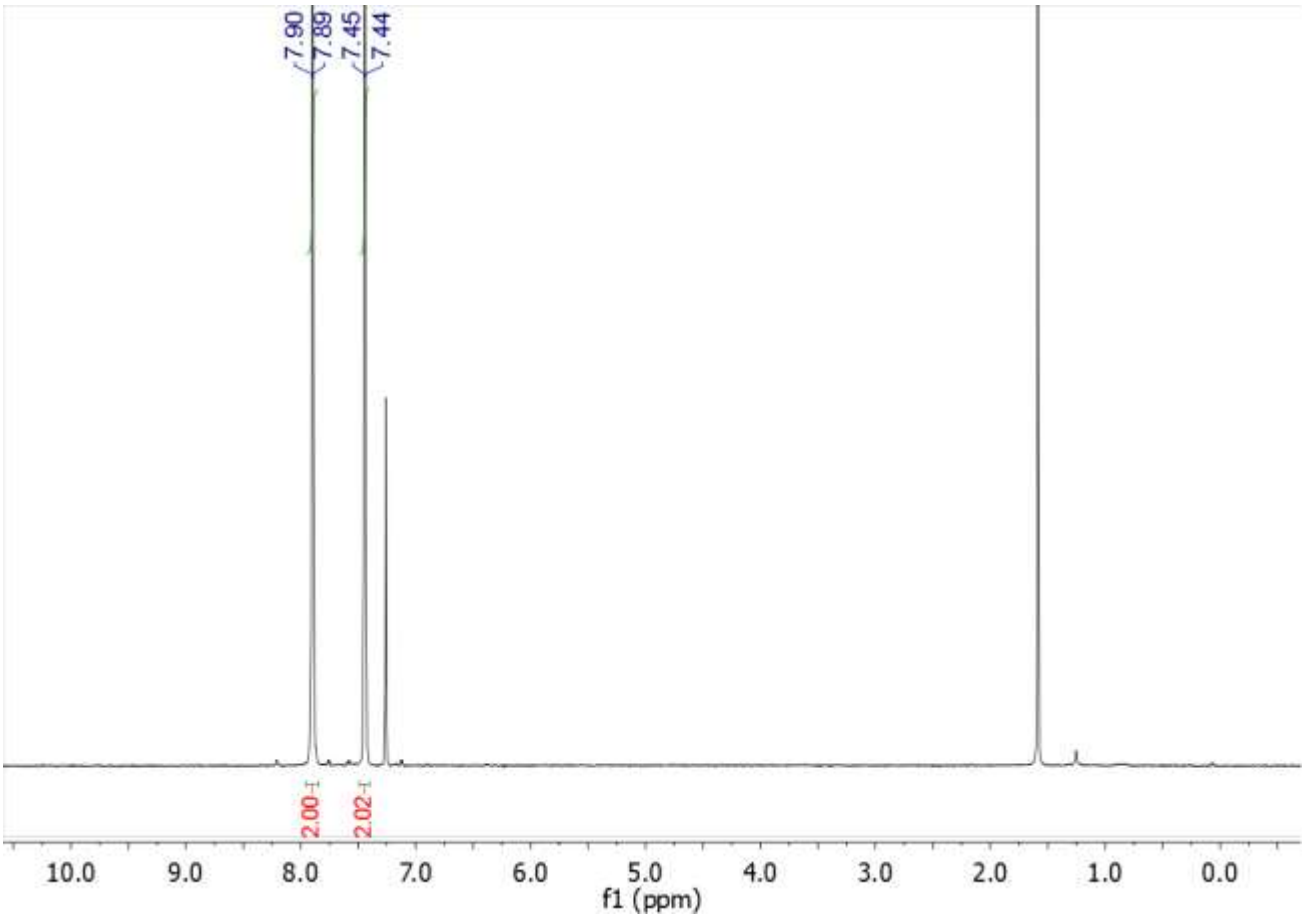

Fig. S2 The 300 MHz ^{1}H-NMR spectrum of 2,2'-bithiazole (**2**) measured in $CDCl_3$.

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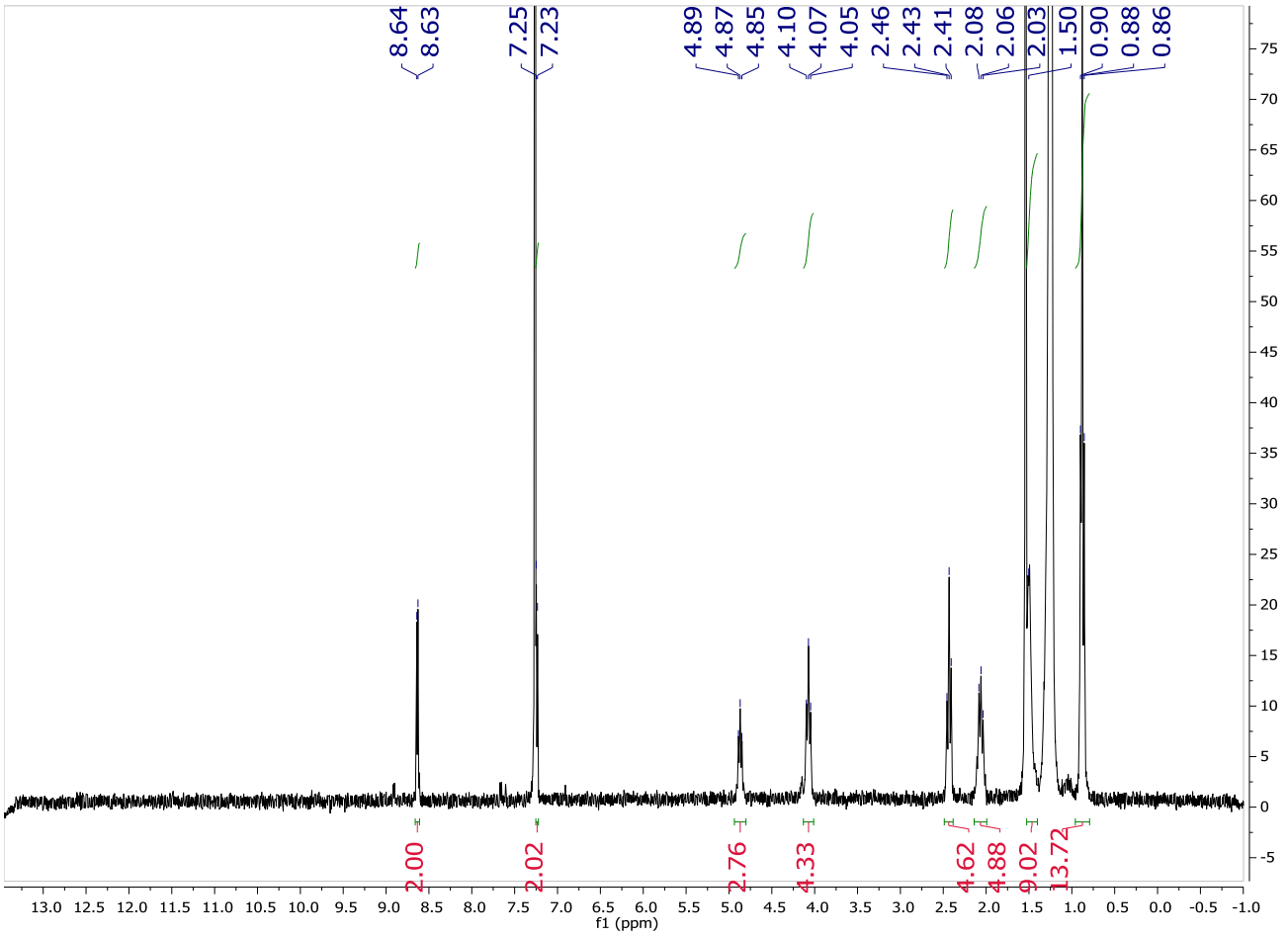

Fig. S3 The 300 MHz ^{1}H-NMR spectrum of di(tritriacontan-17-yl) 4,4'-(1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-diyl)dibutanoate (**4-2**) measured in $CDCl_3$.

Supplementary Information

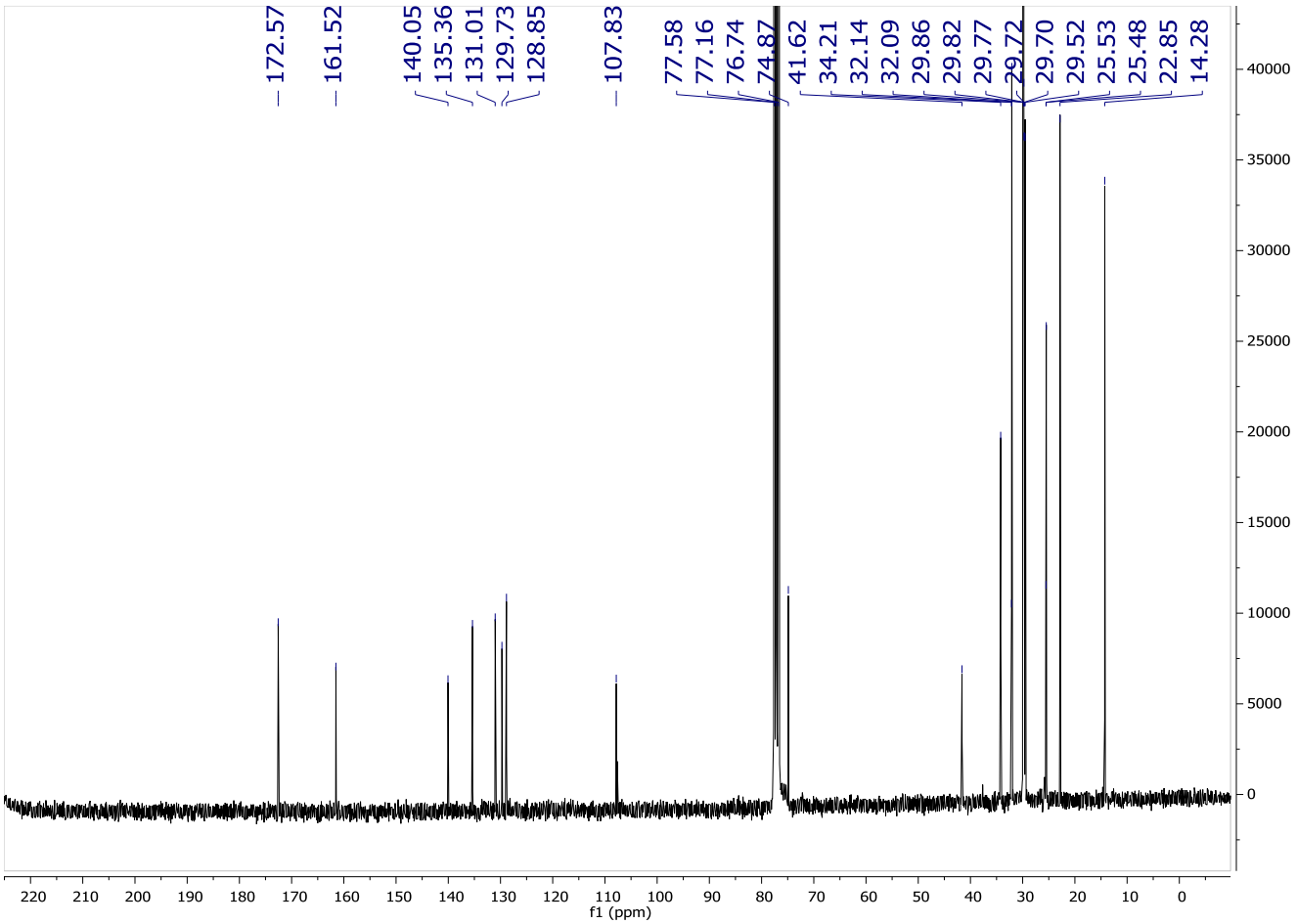

Fig. S4 The 100 MHz ^{13}C-NMR spectrum of di(tritriacontan-17-yl) 4,4'-(1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-diyl)dibutanoate (**4-2**) measured in $CDCl_3$.

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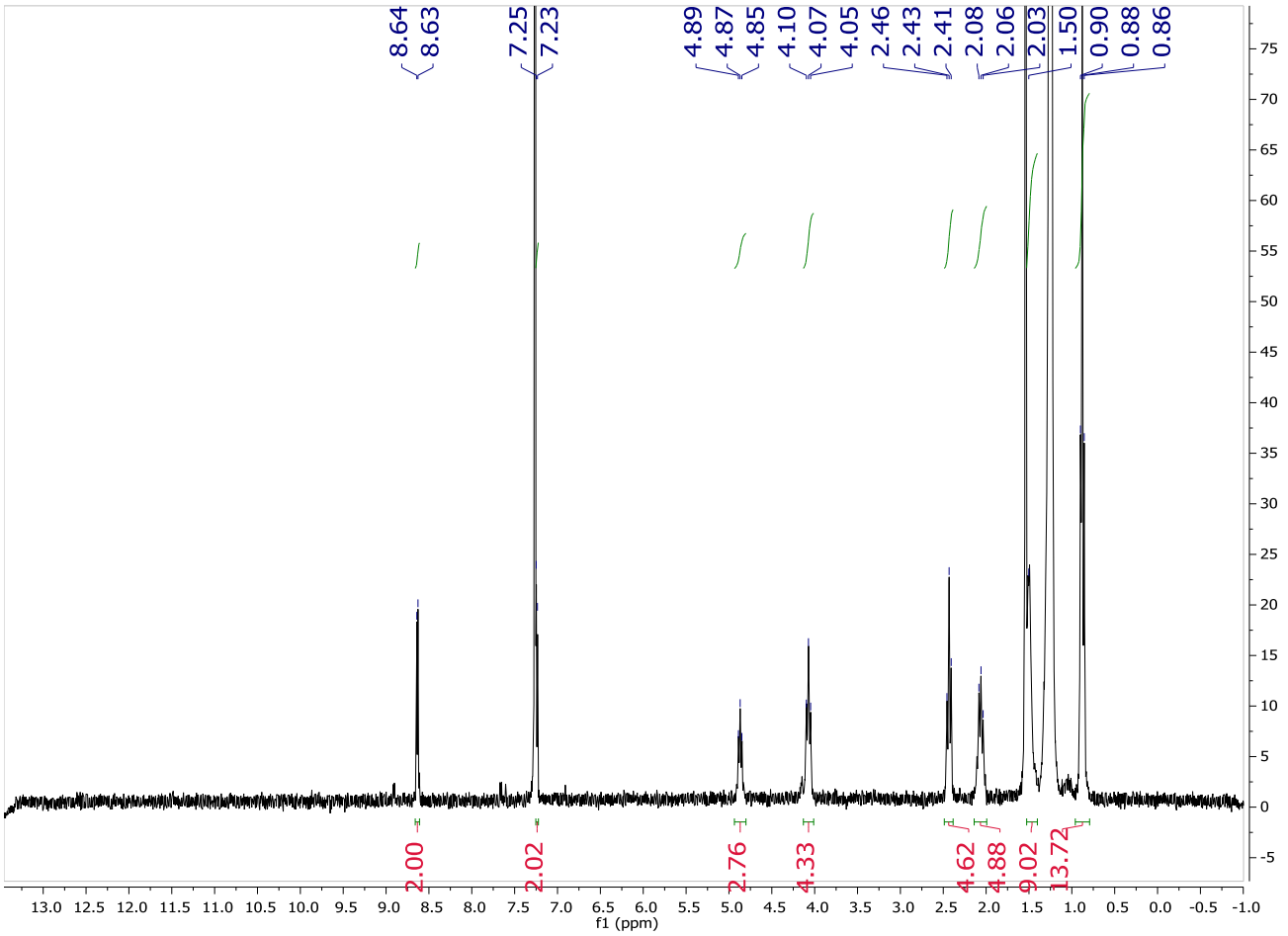

Fig. S5 The 300 MHz ^{1}H-NMR spectrum of di(tritriacontan-17-yl) 4,4'-(3,6-bis(5-bromothiophen-2-yl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-diyl)dibutanoate (**5-2**) measured in $CDCl_3$.

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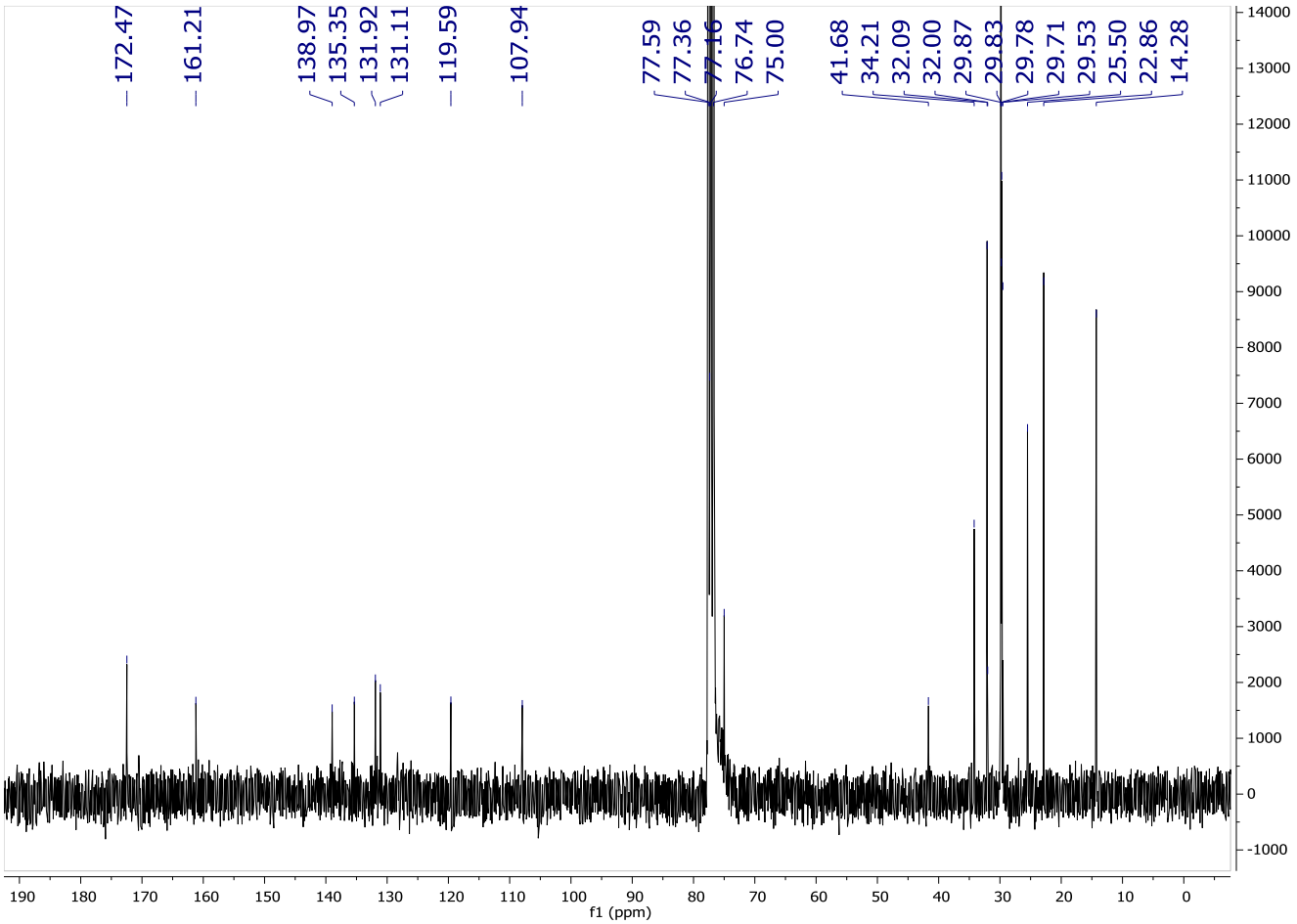

Fig. S6 The 100 MHz ^{13}C-NMR spectrum of di(tritriacontan-17-yl) 4,4'-(3,6-bis(5-bromothiophen-2-yl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-diyl)dibutanoate (**5-2**) measured in $CDCl_3$.

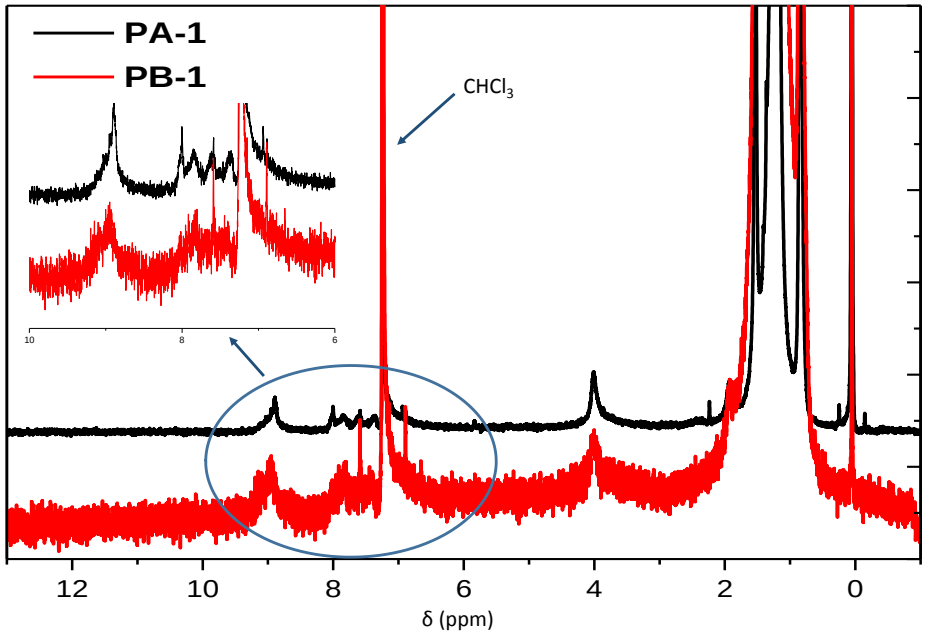

Fig. S7 The 300 MHz ^{1}H-NMR spectra of **PA-1** and **PB-1** (chloroform extracted fractions) measured at room temperature in $CDCl_3$. The poor resolution is due to the strong aggregation of polymer chains in solution.

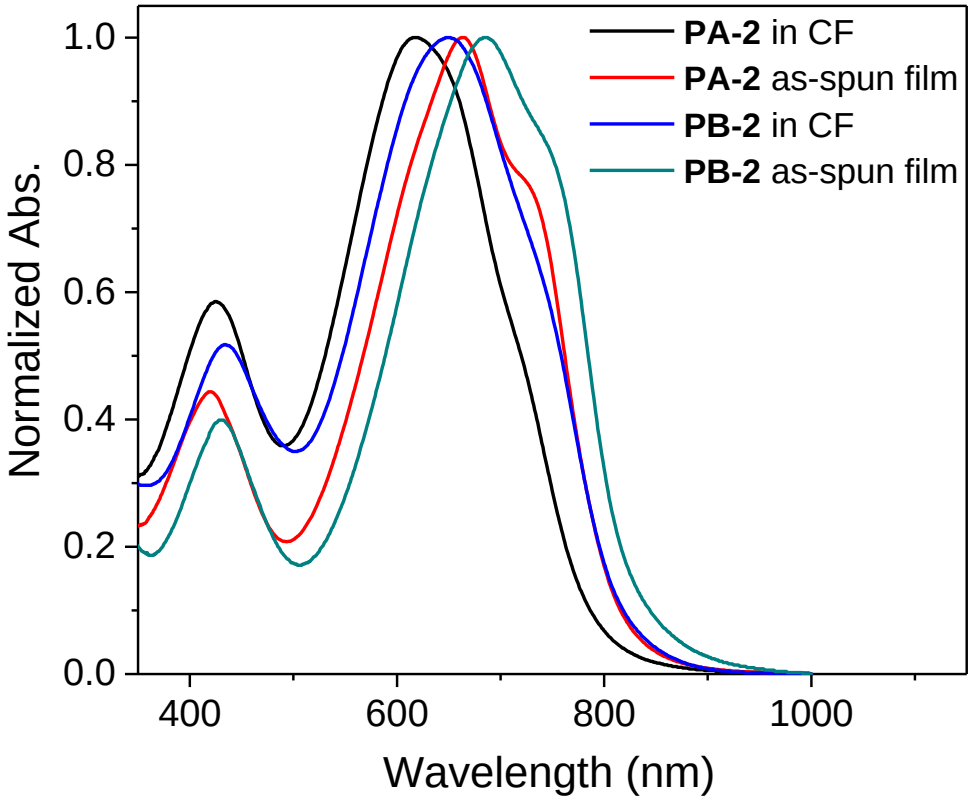

Fig. S8 UV-Vis absorption spectra of **PA-2** and **PB-2** in chloroform solutions and as thin films.

Supplementary Information

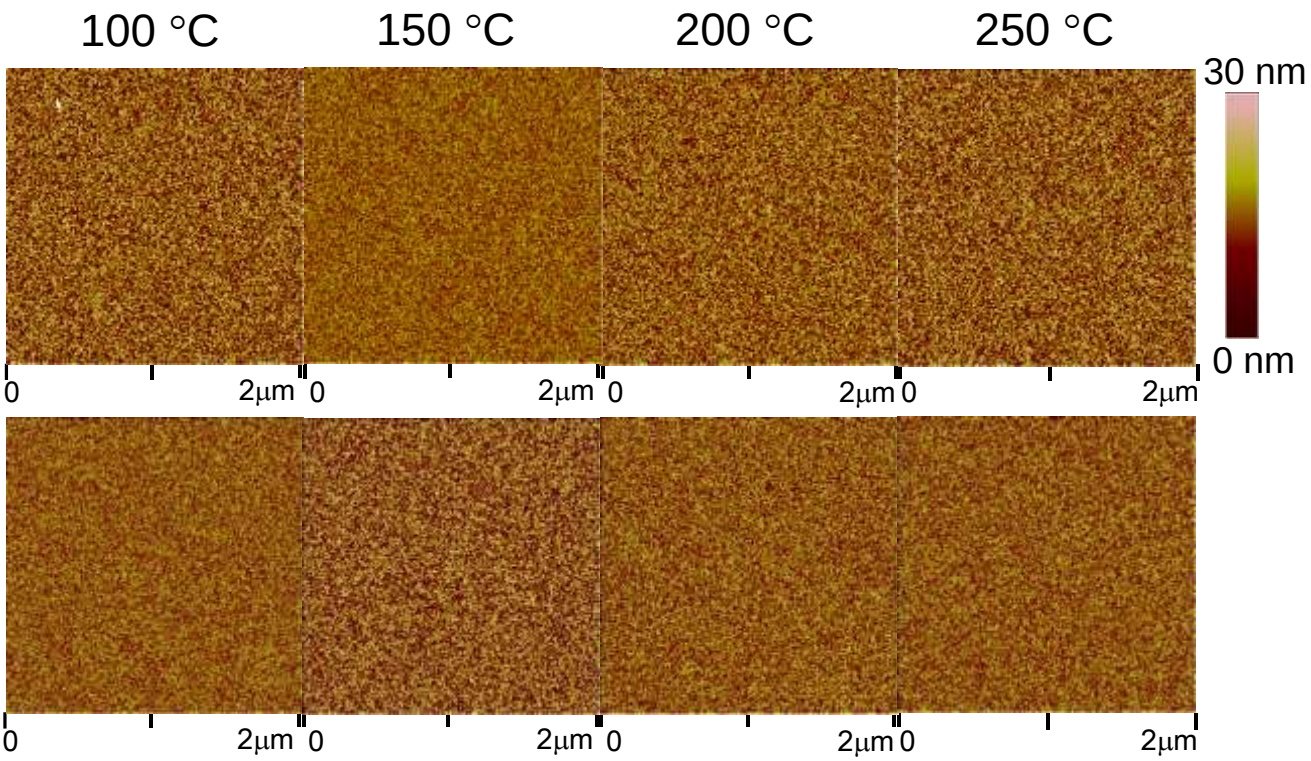

Fig. S9 AFM images (2 μm × 2 μm) of **PA-1** (top) and **PB-1** (bottom) thin films (~50-60 nm) on silicon dioxide substrates annealed at 100, 150, 200 and 250 °C

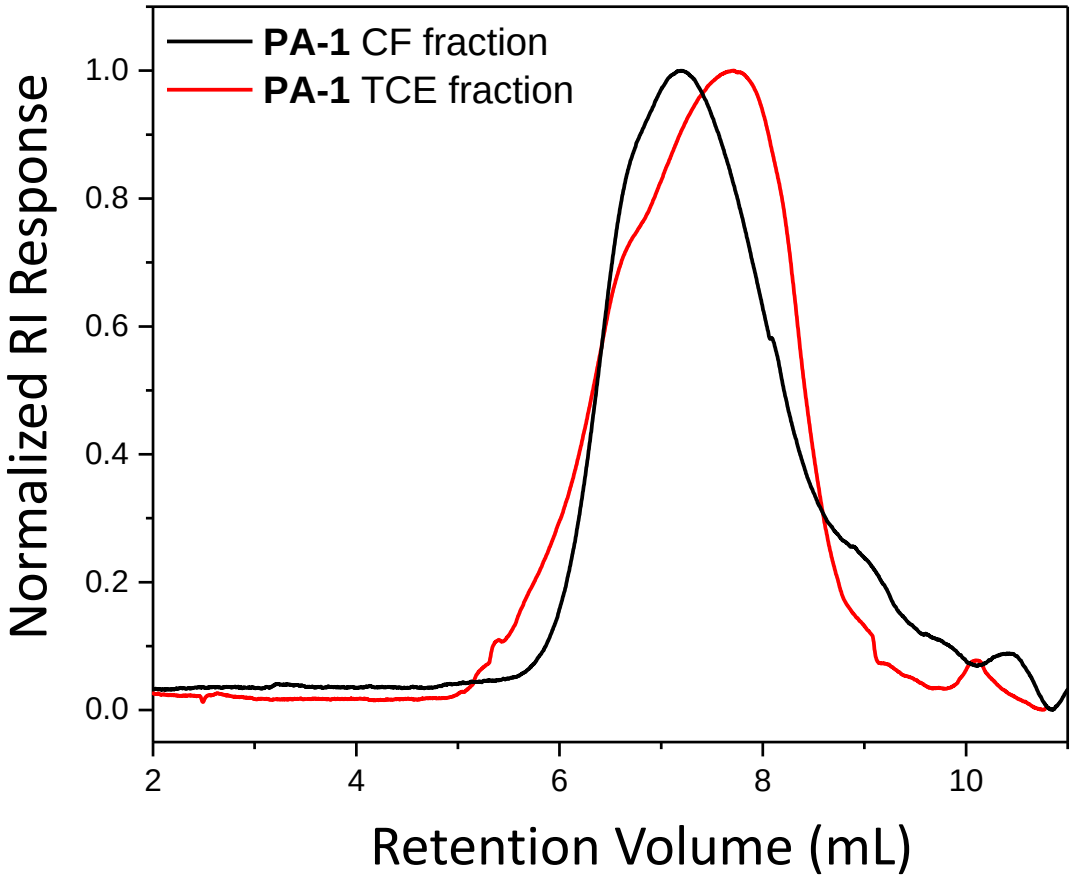

Fig. S10 GPC traces of **PA-1** chloroform (CF) and 1,1,2,2-tetrachloroethane (TCE) extracted fractions measured at 140 °C using 1,2,4-trichlorobenzene as eluent.

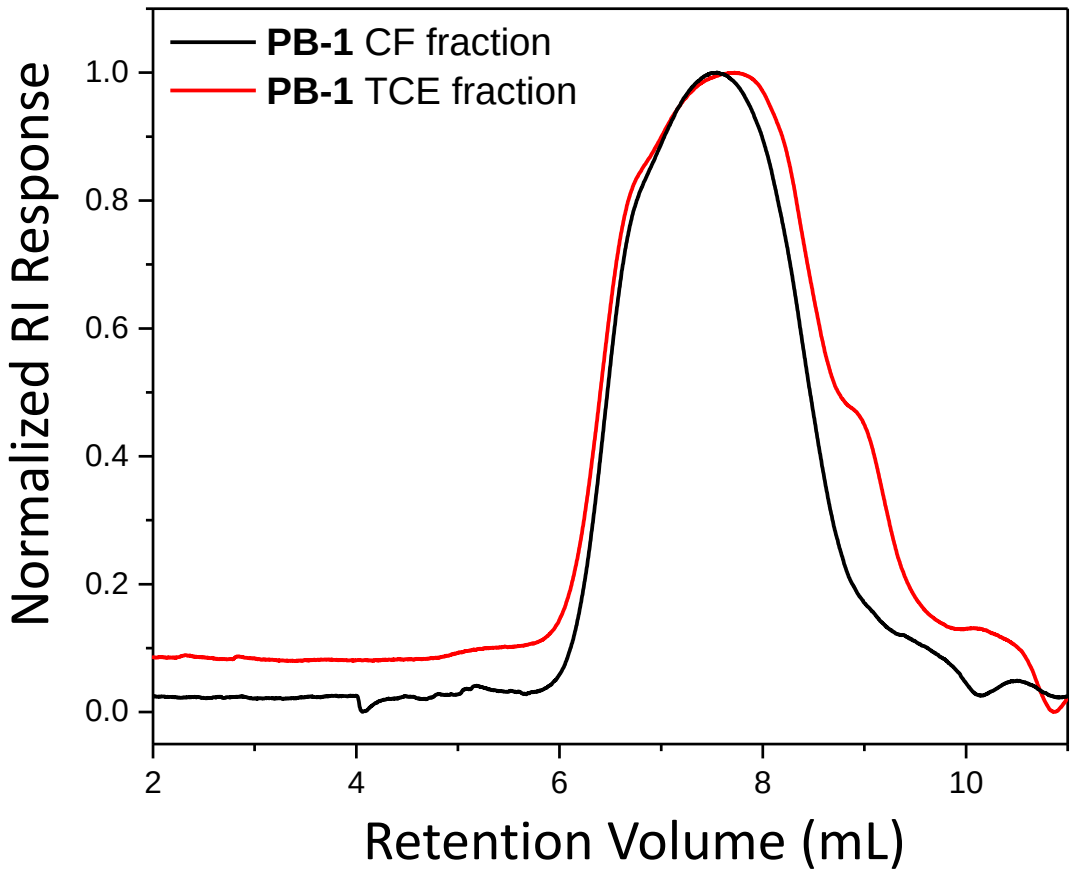

Fig. S11 GPC traces of **PB-1** chloroform (CF) and 1,1,2,2-tetrachloroethane (TCE) extracted fractions measured at 140 ℃ using 1,2,4-trichlorobenzene as eluent.

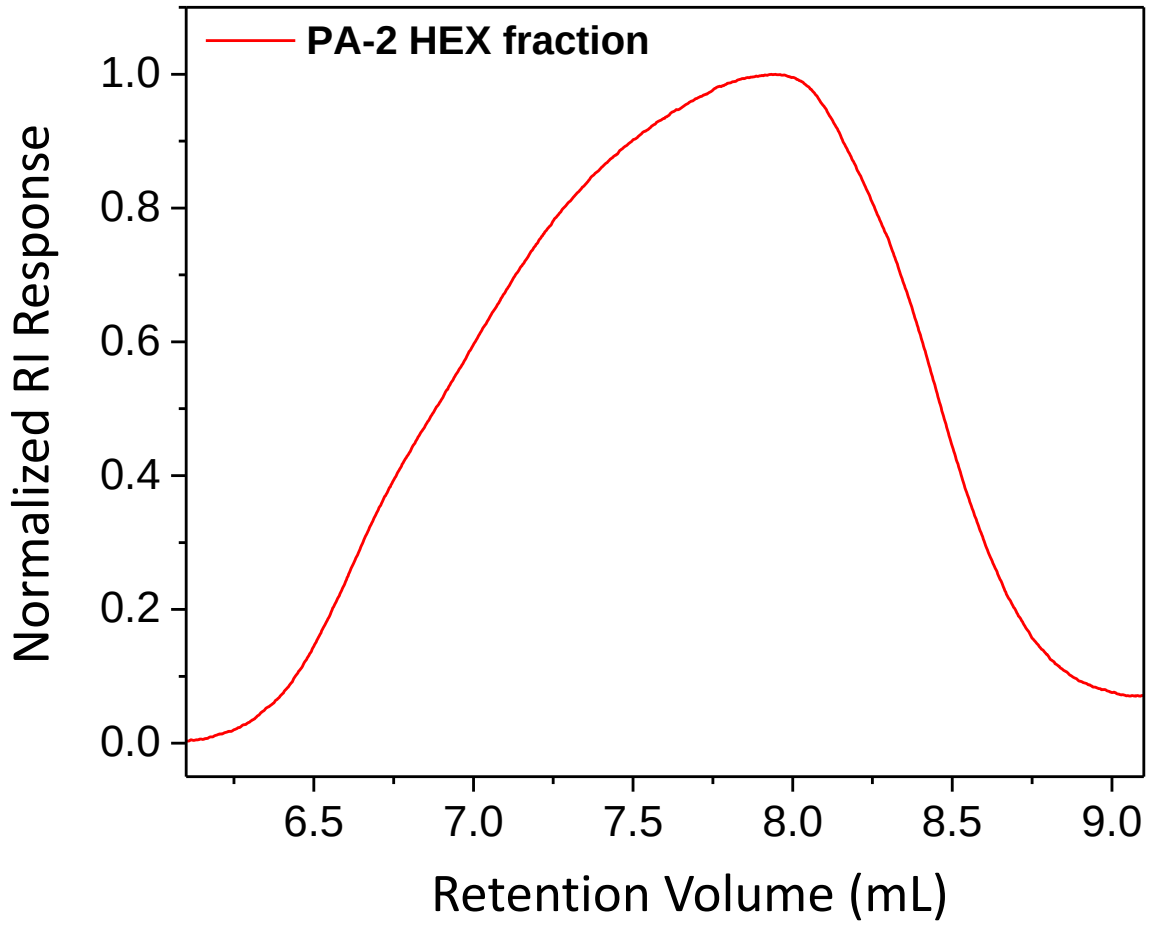

Fig. S12 GPC trace of **PA-2** (hexane extracted fraction) measured at 140 °C using 1,2,4-trichlorobenzene as eluent.

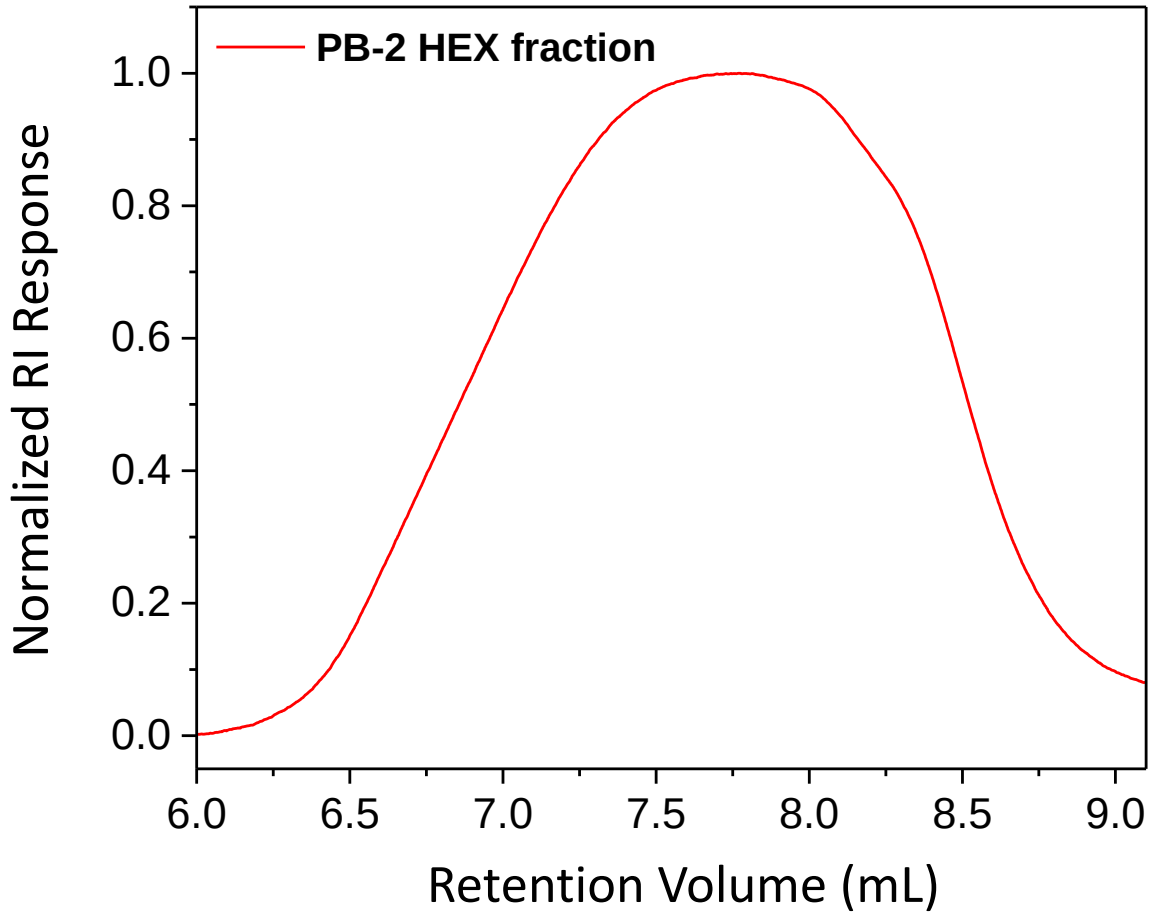

Fig. S13 GPC trace of **PB-2** (hexane extracted fraction) measured at 140 °C using 1,2,4-trichlorobenzene as eluent.

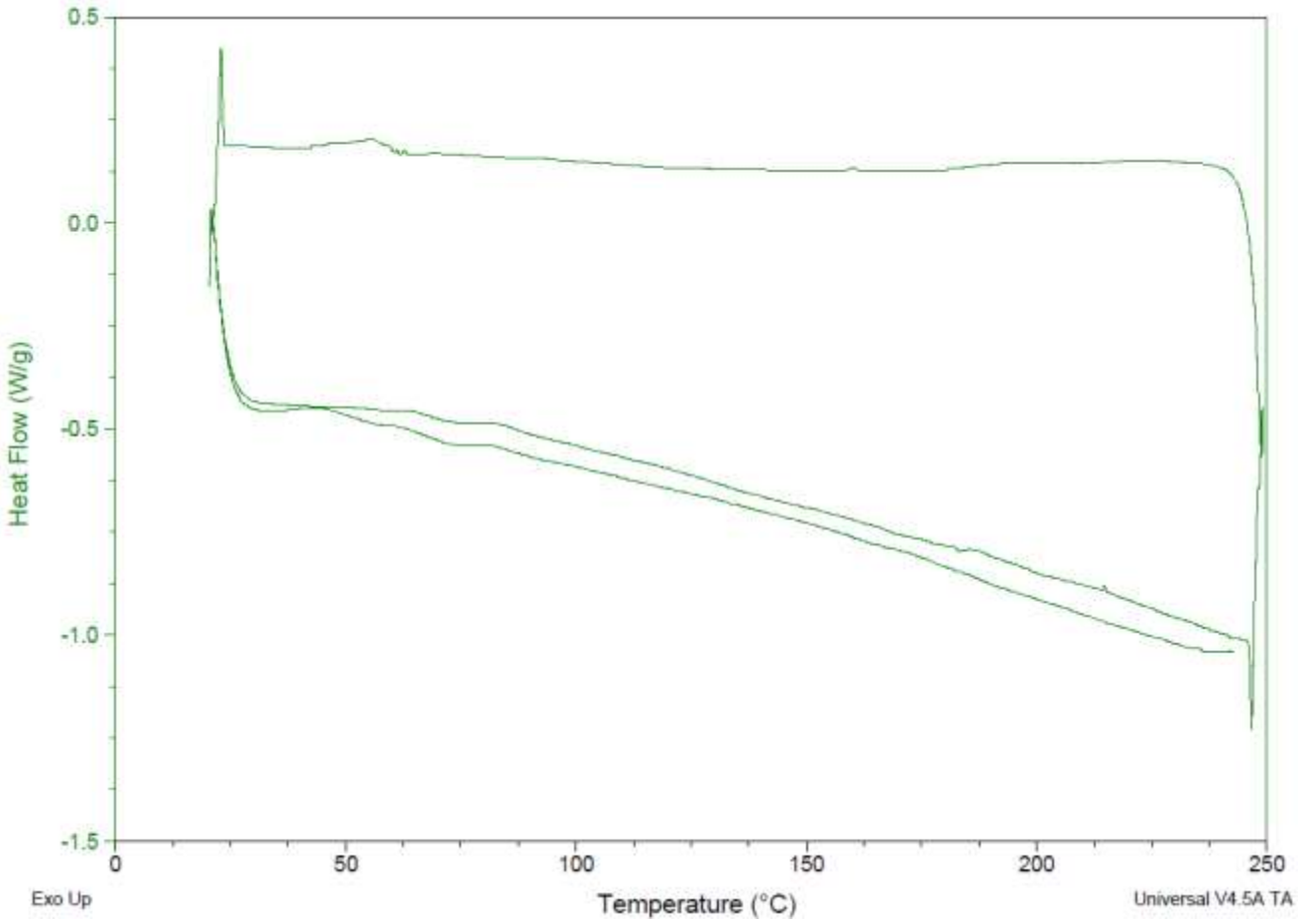

Fig. S14 DSC thermogram of **PA-1** (chloroform extracted fraction) measured with a heating rate of 10 °C min^{-1} under nitrogen.

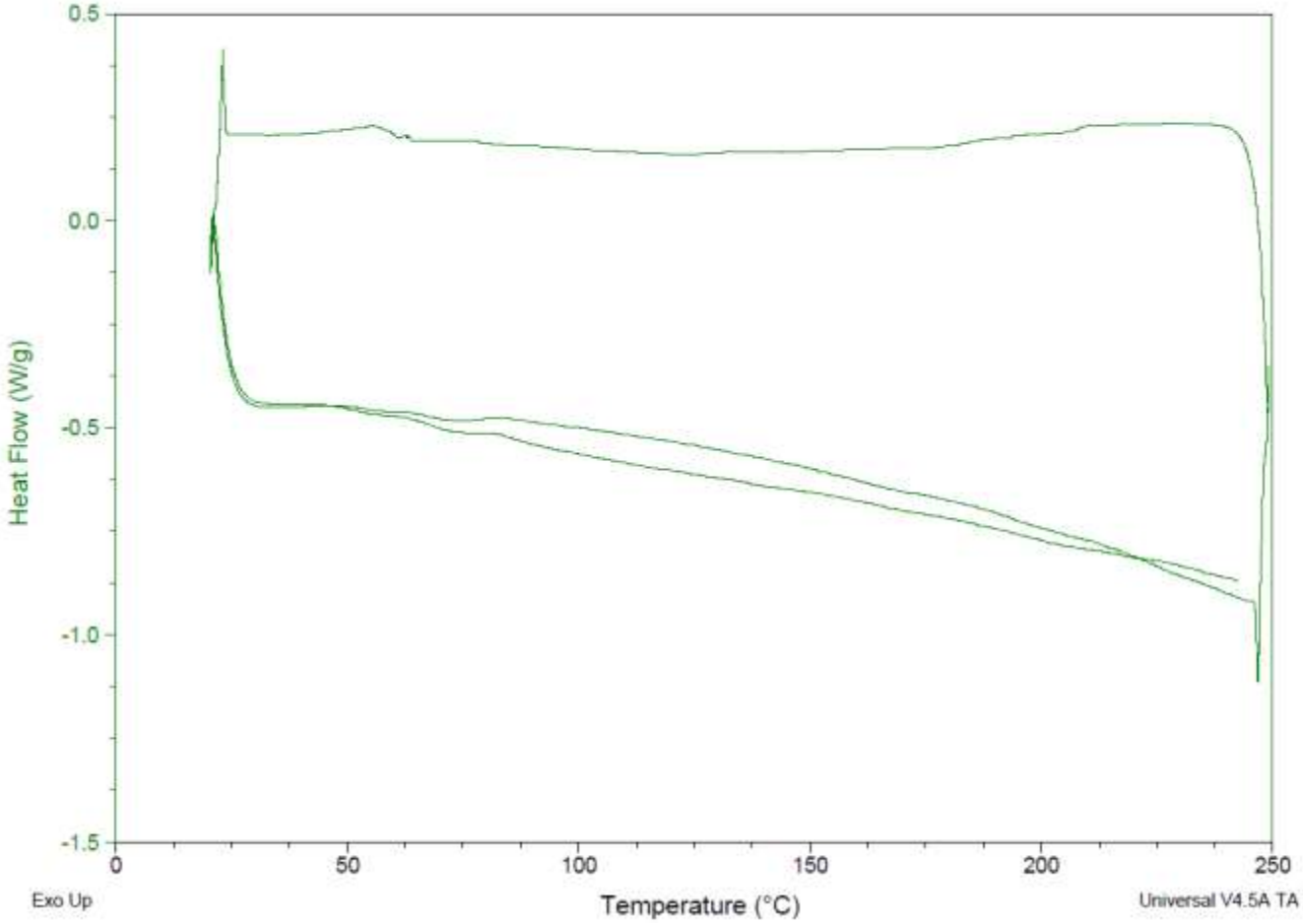

Fig. S15 DSC thermogram of **PB-1** (chloroform extracted fraction) measured with a heating rate of 10 °C min^{-1} under nitrogen.

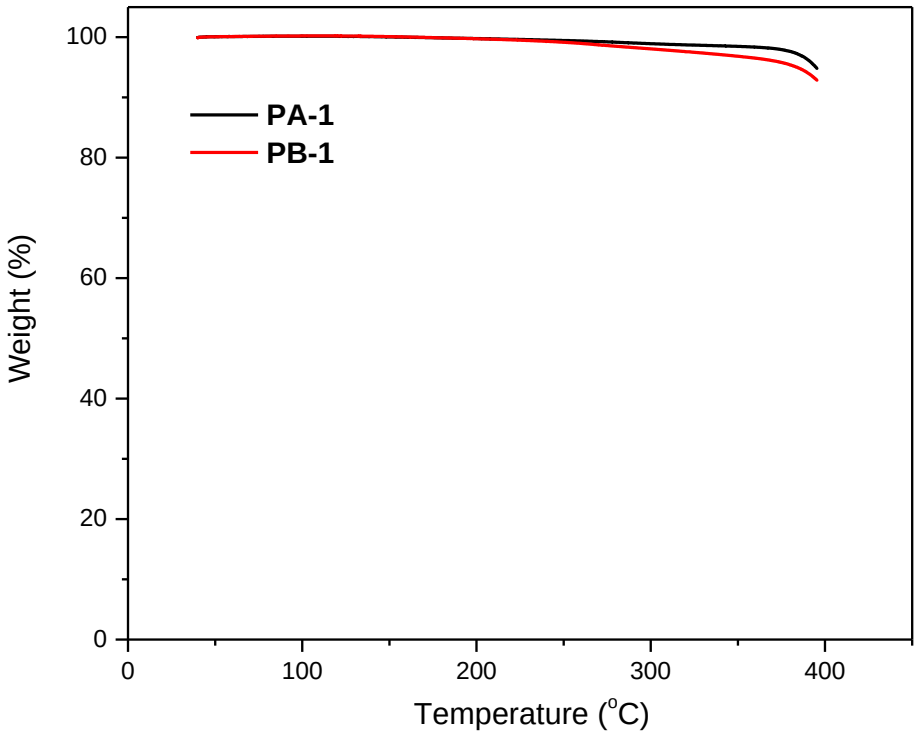

Fig. S16 TGA thermograms of **PA-1 and PB-1** (chloroform extracted fractions) at a heating rate of 10 °C min^{-1} under nitrogen.