

Supporting Information

Intrinsically Stretchable Block Copolymer Comprised of Polyisobutene and Naphthalenediimide–Bithiophene-Based π -Conjugated Polymer Segments for Field–Effect Transistors

Shuto Yamamoto,^a Megumi Matsuda,^a Chia-Yu Lin,^b Kazushi Enomoto,^a Yan-Cheng Lin,^{c,d},
Wen-Chang Chen,^{b,c*} and Tomoya Higashihara^{a,*}*

^a Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan.

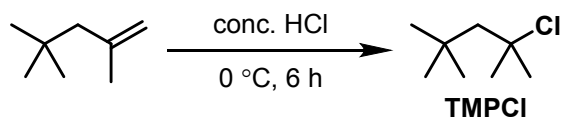
^b Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan.

^c Advanced Research Center of Green Materials Science and Technology, National Taiwan University, Taipei 10617, Taiwan.

^d Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan.

*E-mail: ycl@gs.ncku.edu.tw (Y.-C. Lin); chenwc@ntu.edu.tw (W.-C. Chen);
thigashihara@yz.yamagata-u.ac.jp (T. Higashihara).

Synthesis of 2-chloro-2,4,4-trimethylpentane (TMPCl).



Scheme S1. Synthetic route for TMPCl.

Into a 50 mL two-necked flask, 2,4,4-trimethyl-pentene (5.00 g, 44.6 mmol) was added, and then cooled down to 0 °C using an ice bath. To this flask, conc. HCl (29.2 g, 802 mmol) was added. The mixture was stirred for 6 h, followed by the addition of dichloromethane (DCM, 24.7 mL), and then stirred overnight. After the reaction, the mixture was extracted with DCM, washed with water and brine. The obtained organic phase was dried over sodium sulfate, filtered, and rotary-evaporated to afford TMPCl as a white solid (4.55 g, 69%).

¹H NMR (400 MHz, CDCl₃, δ ppm, 25 °C, **Figure S1**): 1.88 (s, 2H), 1.67 (s, 6H), 1.05 (s, 9H).

(PIB-T).



1.5 h. (iv) Thiophene in hexane/DCM, -78 °C, 4.5 h.

methanol (-78 °C) and the resulted solution was poured into methanol/ammonia hydroxide

aqueous solution (9/1, v/v). The mixture was then washed with water/isopropanol/NaCl (77.5/15/7.5, v/v/w) and water. The polymer was reprecipitated with hexane/methanol to afford PIB-T as a colorless liquid.

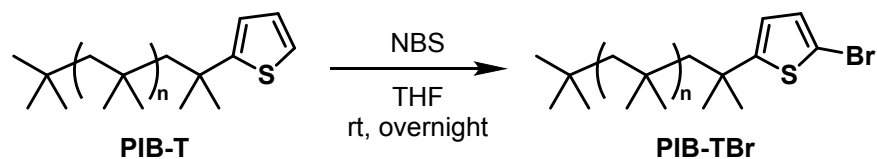
PIB-T (6.4k): Yield = 77% (1.34 g), M_n (SEC) = 6,350, M_w/M_n (SEC) = 1.16.

^1H NMR (400 MHz, CDCl_3 , δ ppm, 25 °C, **Figure S2**): 7.11-7.09 (d, J =5.0 Hz), 6.91-6.87 (t, J =1.6 Hz), 6.80-6.79 (d, J =1.8 Hz), 1.82 (s), 1.44-1.38 (m), 1.11-1.09 (m), 0.99 (s).

PIB-T (3.3k): Yield = 80% (0.56 g), M_n (SEC) = 3,260, M_w/M_n (SEC) = 1.15.

^1H NMR (400 MHz, CDCl_3 , δ ppm, 25 °C, **Figure S3**): 7.11 (dd, J = 5.0, 1.4 Hz), 6.88 (q, J = 2.7 Hz), 6.80 (q, J = 1.7 Hz), 6.55 (d, J = 2.7 Hz), 1.82 (s), 1.44-1.38 (m), 1.11-1.03 (m), 0.99 (s)

General procedure of ω -chain-end-functionalized PIB with 5-bromothieryl group (PIB-TBr).



Scheme S3. Synthetic route for **PIB-TBr**.

Into a 100 mL two-necked flask, **PIB-T** (1.34 g, 0.290 mmol) and tetrahydrofuran (THF) (50 mL) were added and nitrogen was bubbled through this solution for 30 min. After cooling the solution to 0 °C using an ice bath, *N*-bromosuccinimide (NBS) was added to the flask. The mixture was stirred overnight at room temperature. After the reaction, the solution was rotary-evaporated and extracted with hexane. After the filtration, the filtrate was concentrated and methanol was added to precipitate the polymer. The resulted polymer was reprecipitated with hexane/methanol to afford **PIB-TBr** as a colorless oil (0.610 g, 44%).

PIB-TBr (6.1 k): Yield = 44% (0.610g), M_n (SEC) = 6,130, M_w/M_n (SEC)= 1.16.

^1H NMR (400 MHz, CDCl_3 , δ ppm, 25 °C, **Figure S4**): 6.82-6.81 (d, J =3.7 Hz), 6.55-6.54 (d, J =2.7 Hz), 1.76 (s), 1.41-1.38 (m), 1.11-1.09 (m), 0.99(s).

PIB-TBr (3.3 k): Yield =94% (0.55g), M_n (SEC) = 3,300, M_w/M_n (SEC) = 1.14.

^1H NMR (396 MHz, CDCl_3 , δ ppm, 25 °C, **Figure S5**): 6.82 (d, J = 3.6 Hz), 6.54 (d, J = 2.7 Hz),

1.76 (s), 1.47-1.37 (m), 1.17-1.03 (m), 0.99 (s, 9H)

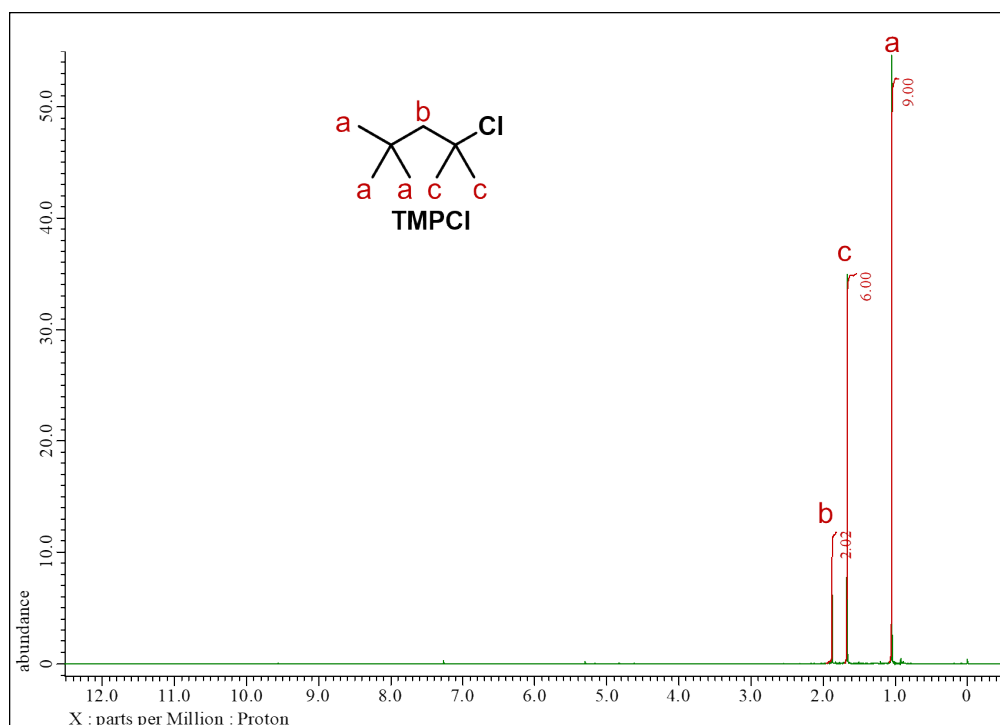


Figure S1. ^1H NMR spectrum of TMPCl.

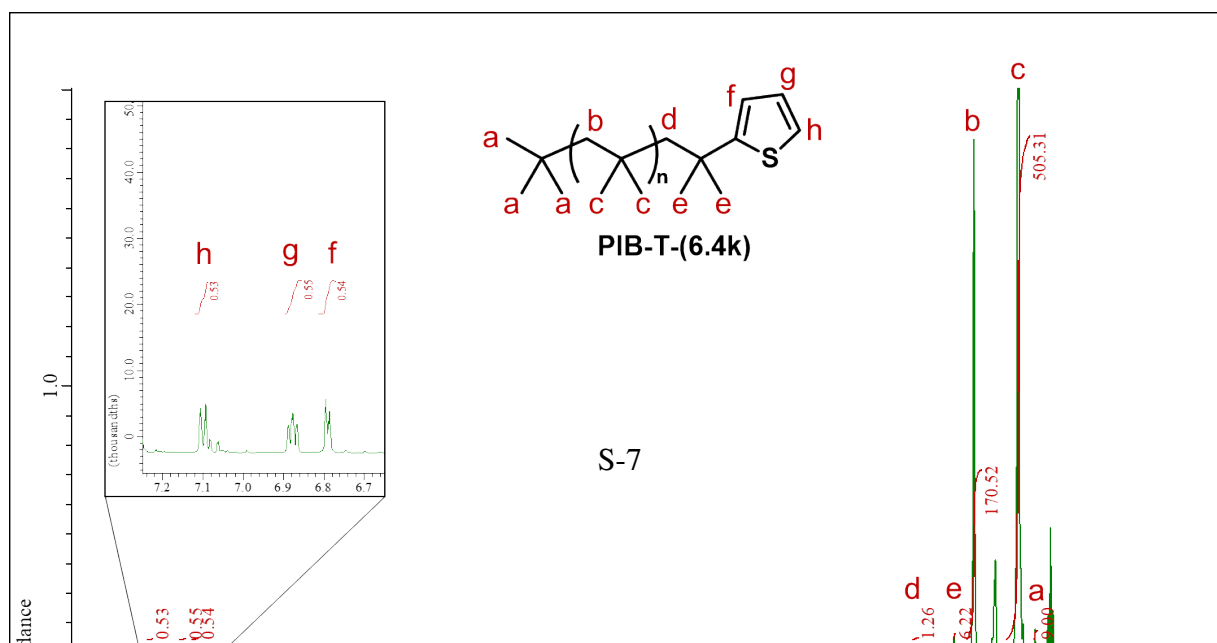


Figure S2. ^1H NMR spectrum of PIB-T (6.4 k).

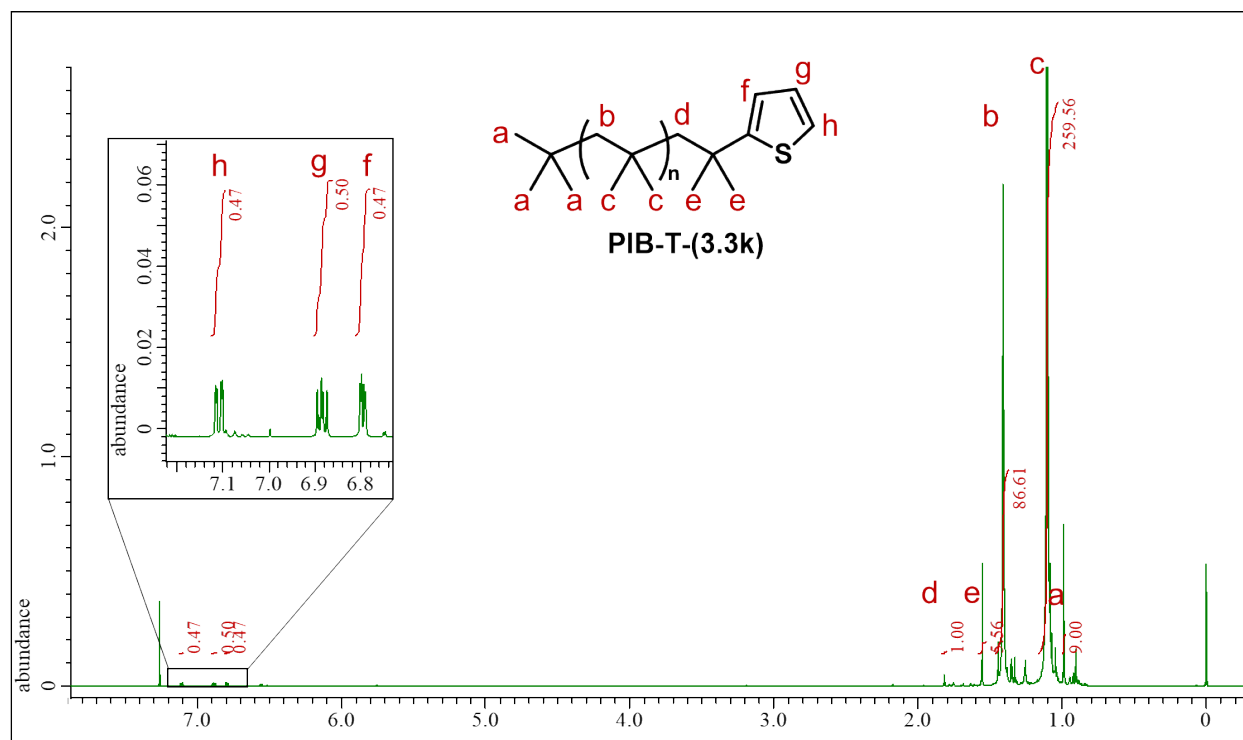


Figure S3. ^1H NMR spectrum of PIB-T (3.3 k).

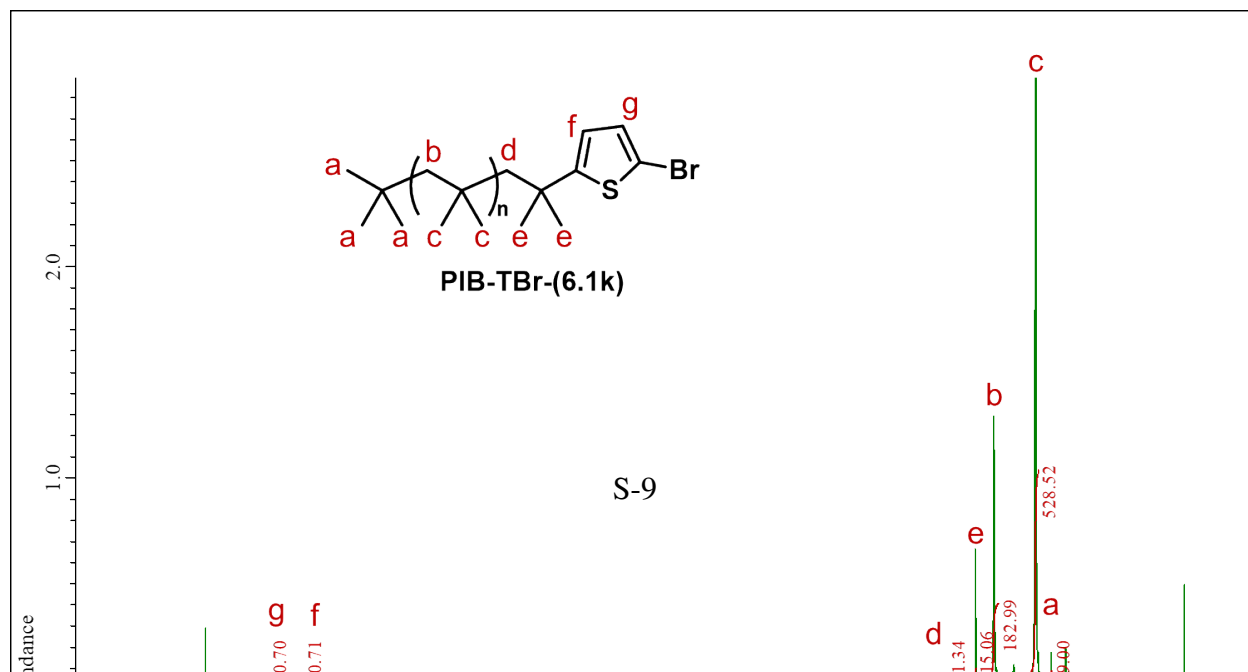


Figure S4. ^1H NMR spectrum of PIB-TBr (6.1 k).

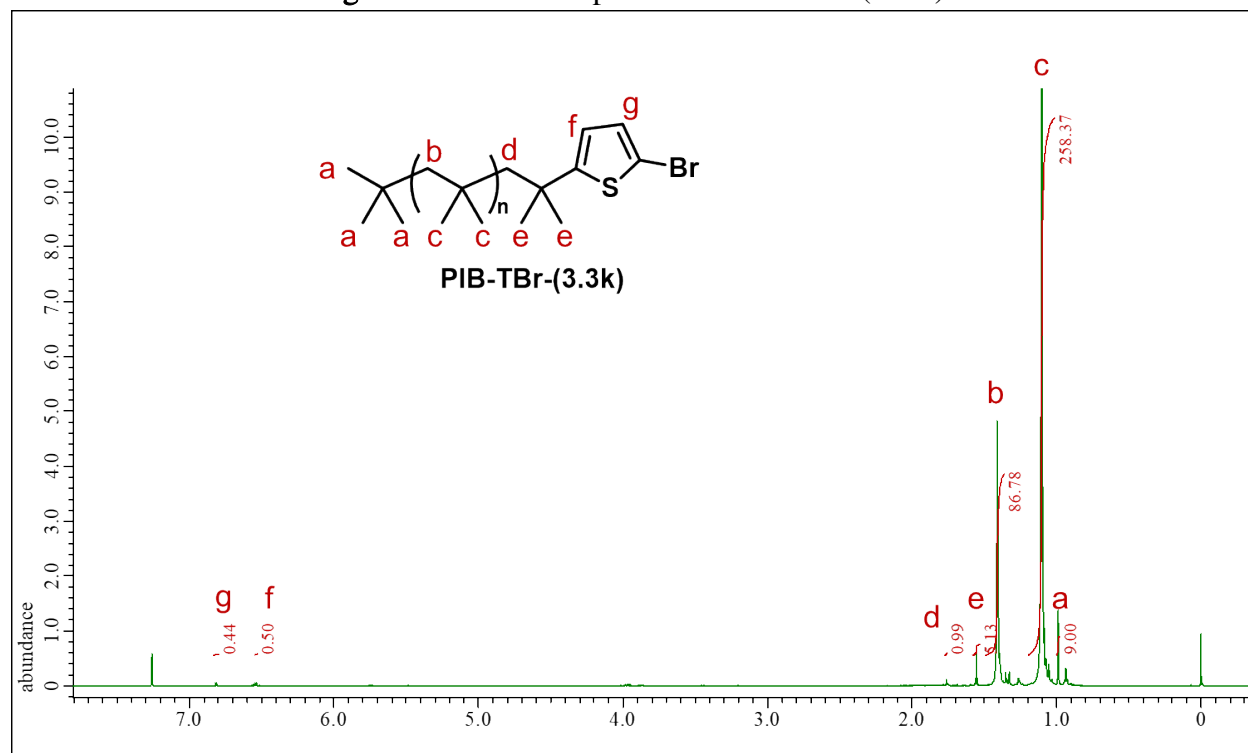


Figure S5. ^1H NMR spectrum of PIB-TBr (3.3 k).

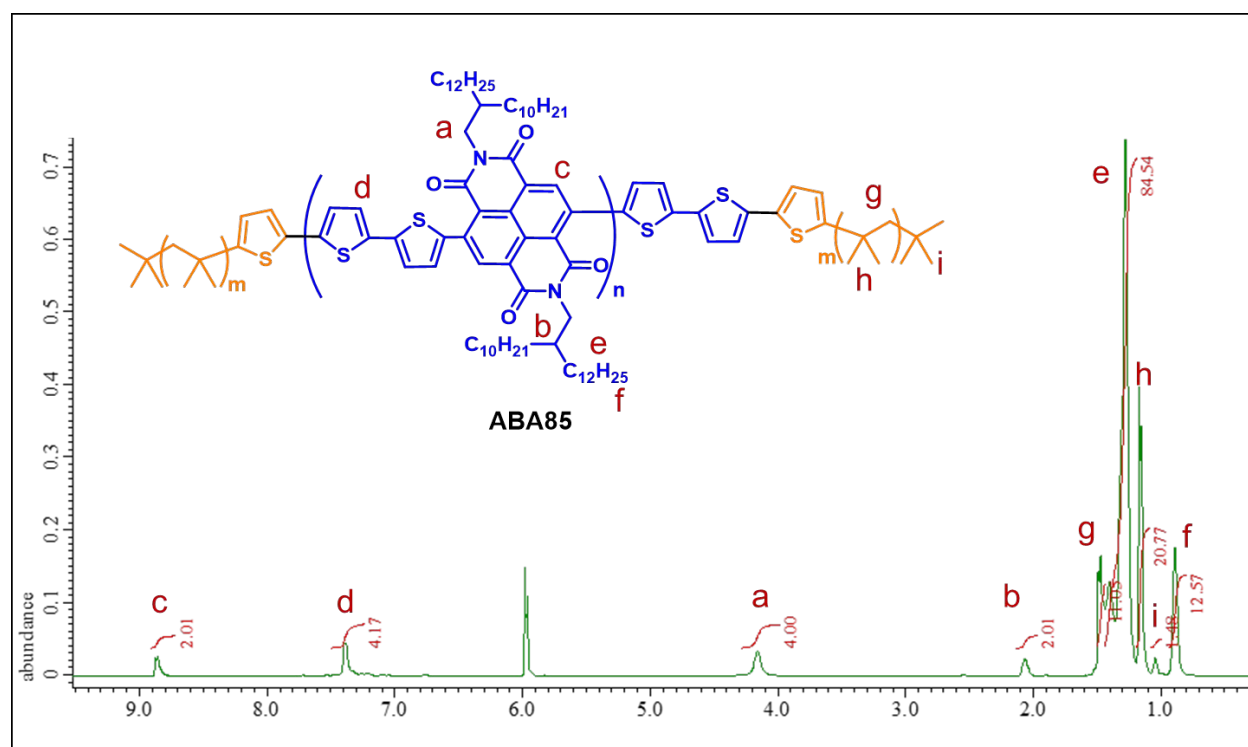


Figure S6. ^1H NMR spectrum of ABA85.

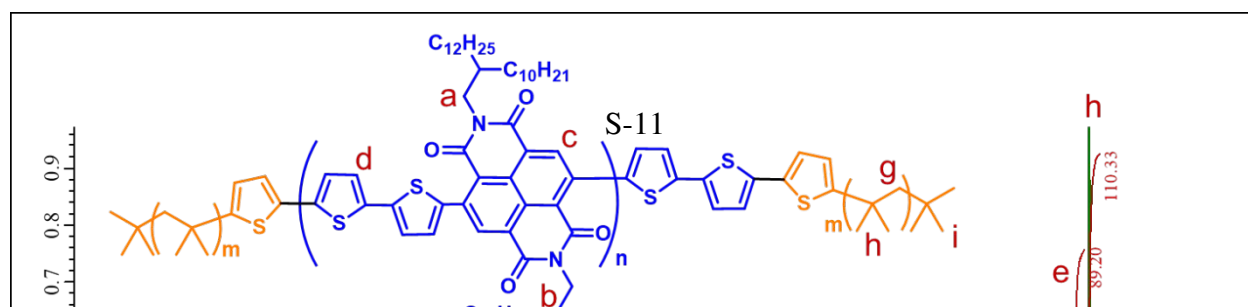


Figure S7. ^1H NMR spectrum of ABA52.

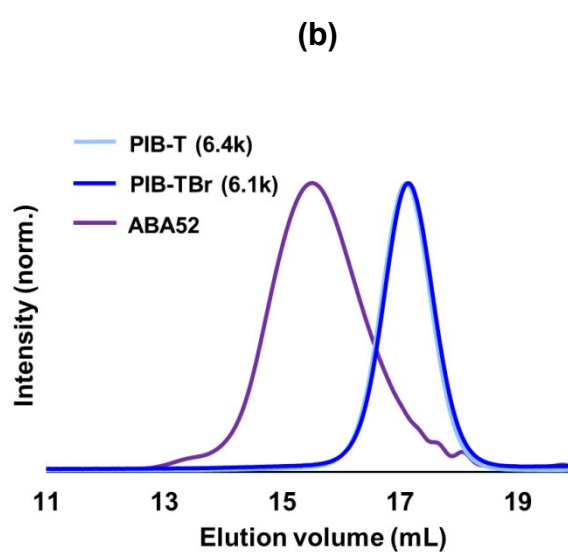
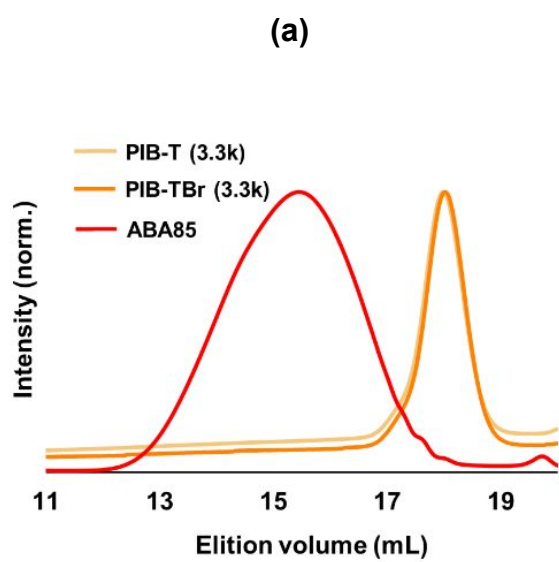


Figure S8. SEC curves of studied polymers: (a) PIB-T (3.3k), PIB-TBr (3.3k), ABA85 and (b) PIB-T (6.4k), PIB-TBr (6.1k), and ABA52.

Table S1. Structure, optical, electrochemical, and thermal characterization of the polymers studied.

	M_n	M_w	M_w/M_n	λ_{max} (nm)	E_g^{opt} (eV)	E_g^{CV} (eV)	HOMO (eV)	LUMO (eV)	$T_d^{5\%}$ (°C)
ABA100^a	27,000	85,100	3.16	395, 710	1.44	2.12	−5.90	−3.78	447
ABA85	19,500	45,600	2.34	390, 694	1.47	1.94	−5.74	−3.80	409
ABA52	20,000	29,600	1.48	395, 698	1.47	1.89	−5.70	−3.81	403

^a The structure, optical, electrochemical, and thermal parameters of the parent polymer, ABA100 were reported in the previous work.^[1]

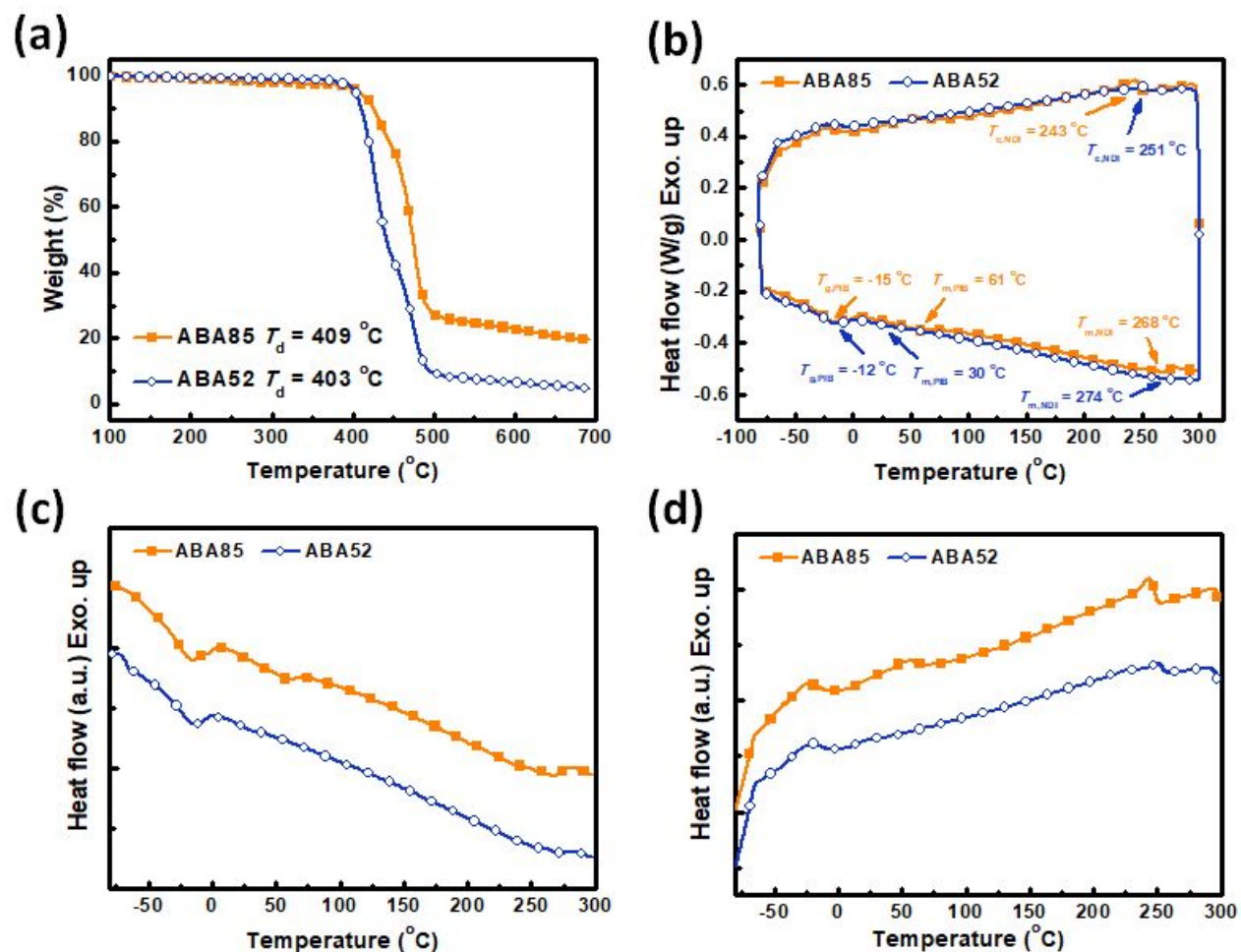


Figure S9. (a) TGA and (b) DSC profiles of the polymers studied at a ramping rate of 10 °C/min in nitrogen. The enlarged DSC profiles of the polymers in the second (c) heating and (d) cooling scans.

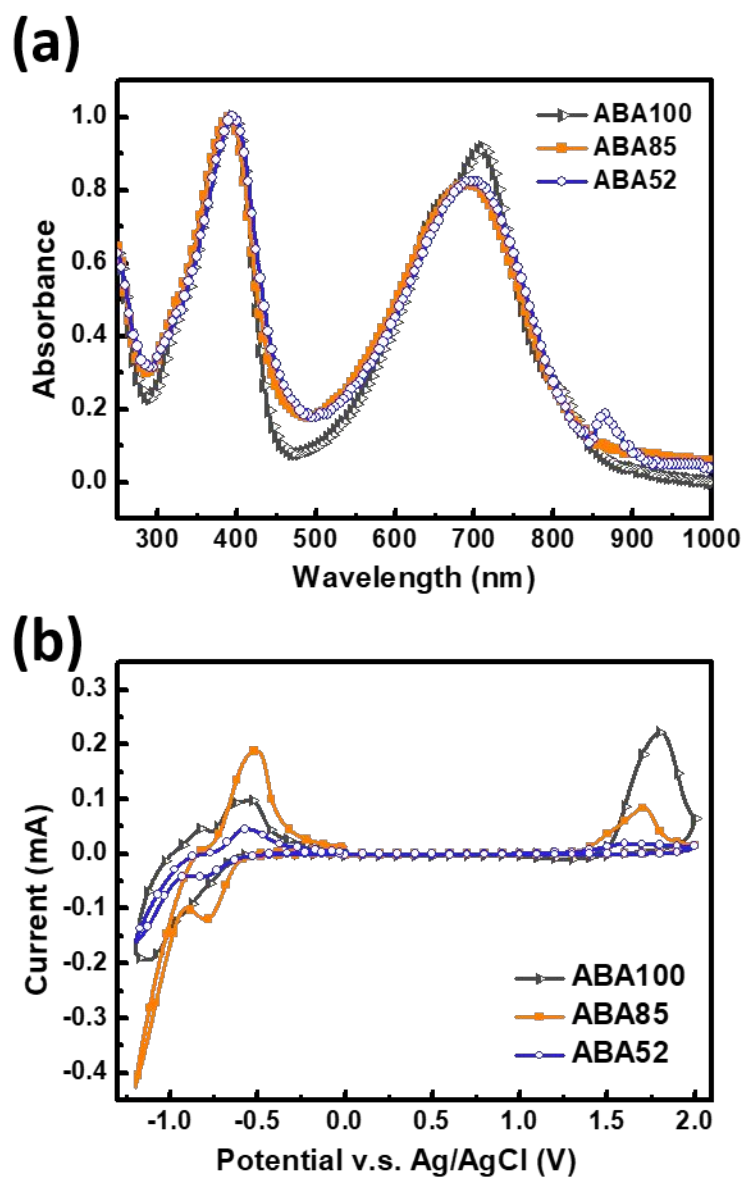


Figure S10. (a) UV-Vis absorption spectrum and (b) CV profiles of the polymer films.

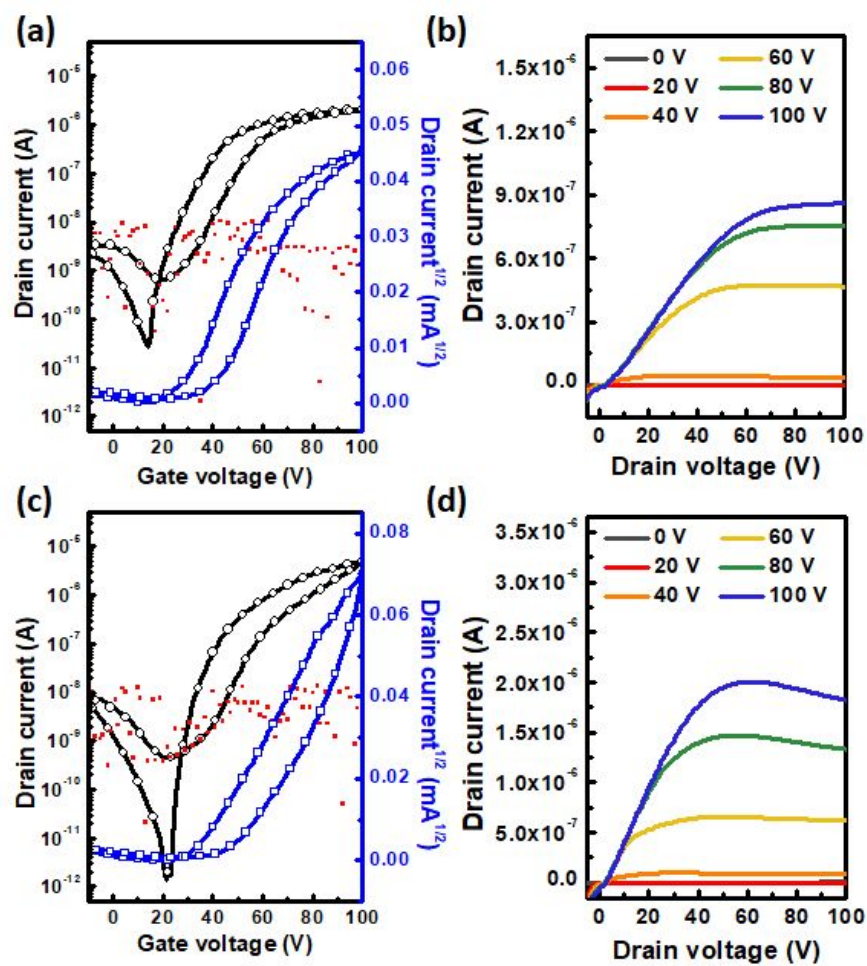


Figure S11. FET (a,c) transfer and (b,d) output characteristics of the as-cast polymer films of (a,b) ABA85 and (c,d) ABA52. Note that the drain voltage was -100 V and the sweeping of gate voltage was from -20 V to 100 V in the transfer characteristics.

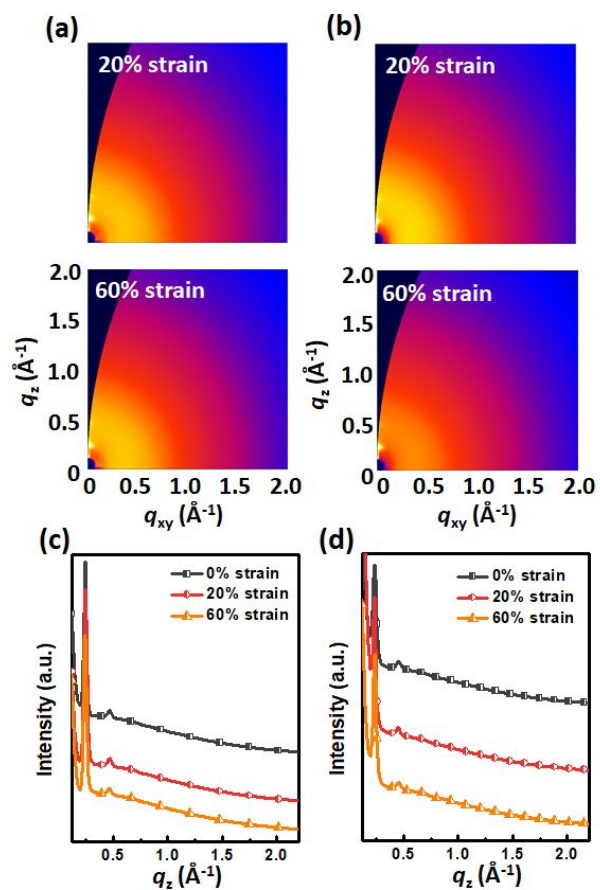


Figure S12. (a,b) 2D GIXD patterns and (c,d) 1D GIXD profiles of the transferred/stretched (a,c) ABA85 and (b,d) ABA52 films at varied strain levels with stretching direction perpendicular to the incident beam.

Table S2. Crystallographic parameters of the transferred/stretched films at varied strain levels.

		ABA100	ABA85	ABA52
Strain (%)	\parallel / \perp	Lamellar spacing (\AA)		
0	-	--	25.9	26.9
20	\parallel	25.5	25.6	27.8
20	\perp	--	25.9	27.1
60	\parallel	25.3	26.3	27.0

60	\perp	--	26.3	26.9
100	\parallel	--	27.2	27.5
100	\perp	--	--	--

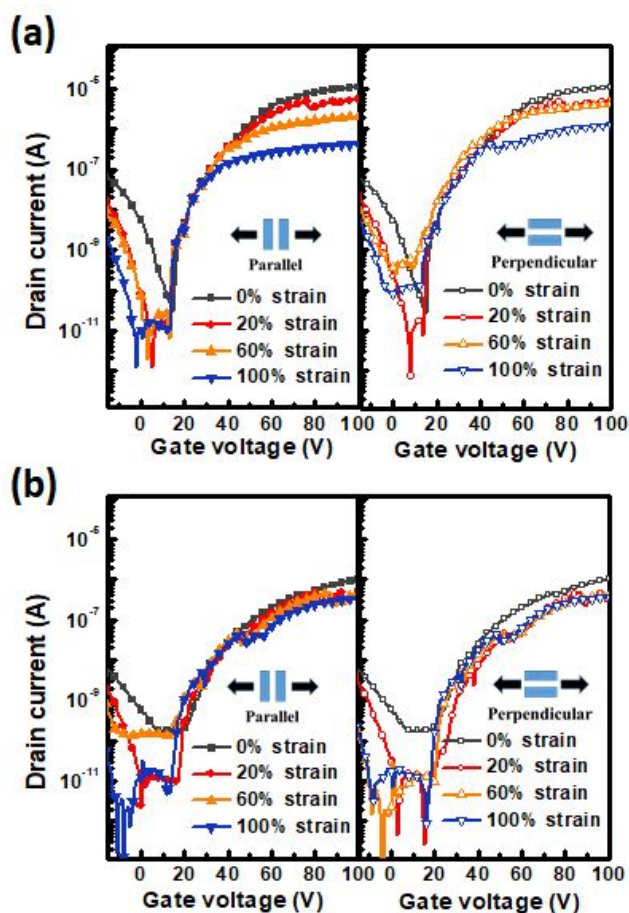


Figure S13. FET transfer characteristics of the transferred/stretched polymer films of (a) ABA85 and (b) ABA52. Note that the solid/open symbols represent that the stretching directions are parallel/perpendicular to the channel direction.

Table S3. FET device parameters of the transferred/stretched polymer films at varied strain levels.^a

Strain (%)	ABA100			ABA85			ABA52		
	μ_e (cm ² V ⁻¹ s ⁻¹)	$I_{\text{on}}/I_{\text{off}}$	V_{th} (V)	μ_e (cm ² V ⁻¹ s ⁻¹)	$I_{\text{on}}/I_{\text{off}}$	V_{th} (V)	μ_e (cm ² V ⁻¹ s ⁻¹)	$I_{\text{on}}/I_{\text{off}}$	V_{th} (V)
0	0.012 ± 0.003	1 × 10⁵	19	0.043 ± 0.008	7 × 10⁵	33	0.0032 ± 0.0008	9 × 10⁵	30
20	0.0097 ± 0.0004	2 × 10 ⁷	4	0.013 ± 0.006	8 × 10 ⁵	32	0.0021 ± 0.0004	5 × 10 ⁶	37
20 ⊥	0.010 ± 0.0009	1 × 10⁷	1	0.024 ± 0.005	4 × 10⁶	26	0.0022 ± 0.0007	2 × 10⁶	42
60	0.0077 ± 0.0053	3 × 10 ⁵	14	0.0075 ± 0.0015	7 × 10 ⁵	19	0.0017 ± 0.0010	1 × 10 ⁴	38
60 ⊥	0.0088 ± 0.0057	6 × 10⁵	7	0.017 ± 0.005	8 × 10⁵	25	0.0019 ± 0.0003	2 × 10⁶	41
100	0.0036 ± 0.0004	8 × 10 ⁴	8	0.0060 ± 0.0032	1 × 10 ⁵	18	0.0015 ± 0.0001	1 × 10 ⁵	36
100 ⊥	0.0021 ± 0.0008	8 × 10⁴	34	0.0076 ± 0.0010	1 × 10⁵	23	0.0018 ± 0.0003	2 × 10⁵	36

^a The device parameters of the parent polymer, ABA100 were reported in the previous work.^[1]

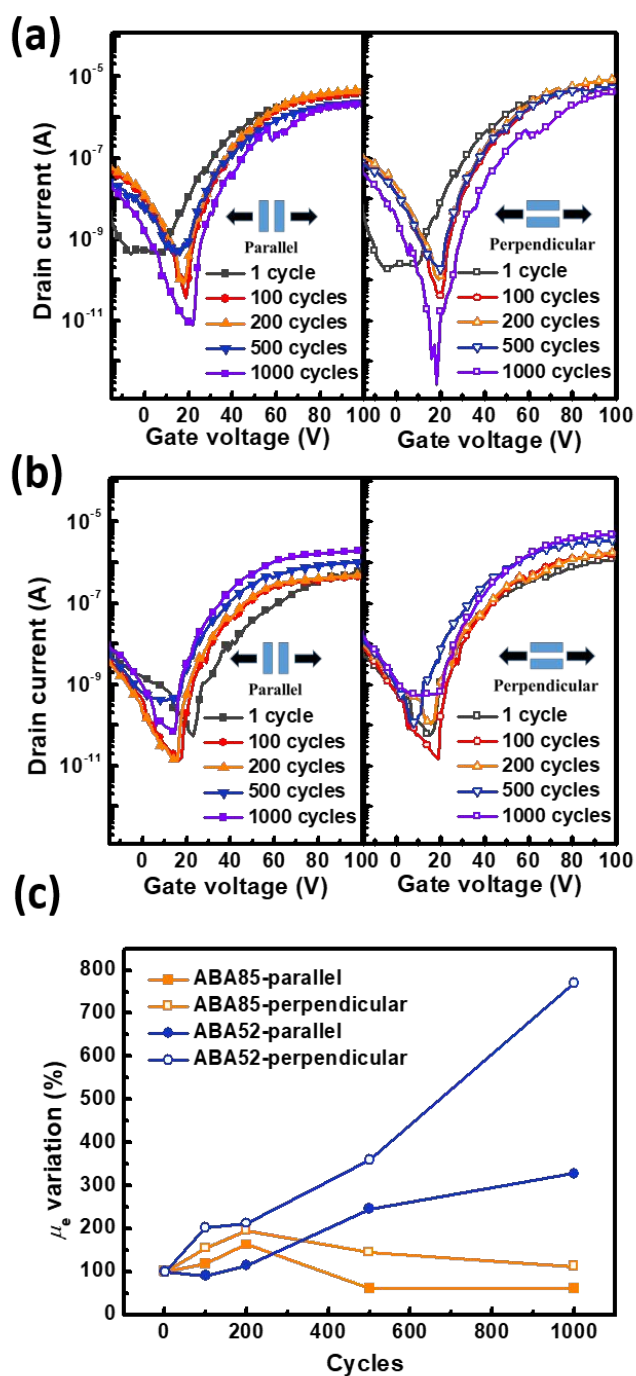


Figure S14. FET transfer characteristics of the transferred/stretched polymer films of (a) ABA85 and (b) ABA52 after stretch-release cycles at 60% strain. (c) Correlation on the μ_e variations to the stretch-release cycles of the polymer films. Note that the solid/open symbols represent that the stretching directions are parallel/perpendicular to the channel direction.

Reference

- (1) Lin, Y.-C.; Terayama, K.; Yoshida, K.; Yu, P.-J.; Chueh, P.-H.; Chueh, C.-C.; Higashihara, T.; Chen, W.-C. Strain-Insensitive Naphthalene-diimide-Based Conjugated Polymers through Sequential Regularity Control. *Mater. Chem. Front.* **2022**, 6, 891–900.