Supplementary Information

The Role of Sidechain Branch Position on Thermal Property of Poly-3alkylthiophenes

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Table S1. Absorption peaks and of P3AT polymers in solutions and films.

Table S2. T_m of thiophene-based polymers.

General Synthesis of 3-alkylthiophene

In an inert gas environment, a solution of alkyl bromide (0.12 mol) in 50 ml dry THF was drop wise added to a solution of Mg (0.15 mol) in 200 mL dry THF and one grain of iodine. After adding, the mixture was heated to reflux at 60 °C for 24 hours and cooled down to room temperature. In another three-necked flask, 3-bromothiophene (0.1 mol) and Ni(dppp)Cl₂ (0.001 mol) was added to 300 mL dry THF (0°C). The synthesized alkyl magnesium bromide THF solution was drop wise added to the three-necked flask. After finishing adding, the ice-bath was removed and the flask was transferred to a heated oil-bath. The reaction mixture was heated to reflux for overnight and then cooled down to room temperature. The reaction was quenched by slowly adding 1 mol/L hydrogen chloride acid solution. The organic phase was separated and water phase was extracted with ether for 3 times. Combining all the organic phases, the solvent was removed by vacuum-evaporating. The residue was purified by passing through a silica gel column using hexane as eluent. 3-alkylthiophene was obtained as colorless oil.

General Synthesis of 2-Bromo-3-alkylthiophene

3-alkylthiophene (0.1 mol) was added to a mixture of chloroform and ethyl acetic acid with a volume ratio of 1:1. Nbromosuccinimide (NBS) (0.105 mol) was portion wise added to the above solution under dark (0°C). After finishing adding, the mixture was warmed to room temperature and continued to react for 1 h under dark. Water was added, the organic phase was separated. The water phase was extracted with chloroform. The combined organic phase was washed with a diluted NaOH solution and water. The solvent was removed by vacuum-evaporation. The residue was purified by silica gel column using hexane as eluent. 2-Bromo-3-alkylthiophene materials were obtained as a light yellow oil.

General Polymerization of poly-3-alkylthiophenes

In an inert gas environment, 2-Bromo-3-alkylthiophene (3 mmol) was added to a 100 ml two-necked flask. 3 ml 1 M 2, 2, 6, 6-Tetramethylpiperidinylmagnesium chloride lithium chloride complex solution in THF was added. The mixture was stirred for 3 hours at room temperature. Then 20 ml dry THF was added. A solution of Ni(dppp)Cl₂ (1% mmol to monomer) in 3 ml dry THF was added. The reaction mixture was stirred for 1 h and quenched by adding 10 ml 1M h hydrochloric acid. The mixture was poured into 300 ml cold methanol. The precipitated solid was further purified by soxhlet extraction using methanol (24 h), hexane (24) and chloroform (24 h). The chloroform fraction was concentrated to 5 ml and passed through a pre-prepared silica gel column to remove catalyst. The elution was concentrated to 2 ml and again precipitated in a 300 ml methanol. After being filtered, the solid was dried in a vacuum box at 60 °C overnight. The ¹H-NMR and ¹³C-NMR spectra of the polymers were shown in supporting information.



Figure S1. ¹H NMR spectra of P3PT.



Figure S2. ¹³C NMR spectra of P3PT.



Figure S3. ¹H NMR spectra of P3HT.



Figure S4. ¹³C NMR spectra of P3HT.



Figure S5. ¹H NMR spectra of P3(4MP)T.



Figure S6. ¹³C NMR spectra of P3(4MP)T.



Figure S7. ¹H NMR spectra of P3(3MP)T.



Figure S8. ¹³C NMR spectra of P3(3MP)T.



Figure S9. Absorption spectra of polymers in chlorobenzene solutions.



Figure S10. Thermal property of P3AT polymers measured by DMA. The storage modulus, loss modulus, and tan δ are plotted for a) P3PT, b) P3HT, c) P3(4MP)T, d) P3(3MP)T. The backbone T_g is marked on the transition peak of tan delta. The large peak at high temperature is the melting transition for the conjugated polymer.



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Figure S13. Hole mobility of P3AT polymers measured by thin film field-effect transistors. (A) Summary of the measured mobility, (B) representative device's transfer curve.

Table S1. Absorption peaks and of P3AT polymers in solutions and films.

Polymer	λ_{max} in solutions (nm)	Peaks in films (nm)							
	-		No annealing			Annealing			
	-		0-1	0-0		0-1	0-0		
P3PT	460	537	567	612	537	568	612		
P3HT	458	537	566	609	542	566	611		
P3(4MP)T	459	538	569	611	538	568	613		
P3(3MP)T	461	540	572	617	539	573	618		

Table S2. T_m of previously reported thiophene-based polymers

Polymer	Structure	<i>Т_т</i> [°С]	Test Method	M _n [kg/mol]	PDI	Ref.
P3BT	(S n C₄H ₉	243	DSC	17	4.1	[¹]
РЗНТ	C ₆ H ₁₃	222	DSC			[²]
		234	DSC		1.1	[³]
		236	DSC	25	2.0	[⁴]
		235	DSC	32	1.9	[5]





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