Supporting Information

Bis(2-oxo-7-azaindolin-3-ylidene)benzodifuran-dione-based donor-acceptor polymers for high-performance *n*-type field-effect transistors

Guobing Zhang,[a,b,c] Yanrong Dai,[b,c] Kuychan Song,[a] Hansol Lee,[a] Feng Ge,[b,c] Longzhen Qiu[b,c] and Kilwon Cho*[a]

[a]Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH) and Center for Advance Soft Electronics (CASE), Pohang 790-784, South Korea. E-mail: kwcho@postech.ac.kr; Fax: +82-54-279-8291

[b]Key Lab of Special Display Technology, Ministry of Education, National Engineering Lab of Special Display Technology, State Key Lab of Advanced Display Technology, Academy of Opto-Electronic Technology, Hefei University of Technology, Hefei, 230009, China.

[c]Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Hefei University of Technology, Key Laboratory of Advance Functional Materials and Devices, Anhui Province, Hefei, 230009, China.

Synthesis of monomer 1

To a mixture of sodium hydride (NaH, 60% in mineral oil, 0.4 g, 9.2 mmol) in dimethhylformamide (DMF, 15 mL) was added slowly 6-bromo-7-azaindole (0.8 g, 4.1 mmol) at 0 ^{o}C. The reaction mixture was warm to room temperature and stirred for 15 min. Then 4-decyltetradecyl iodide (2.1 g, 4.5 mmol) was added to the mixture. The mixture was stirred for overnight. The reaction was quenched with water and was extracted with ethyl acetate for three times. The organic layer was dried with anhydrous sodium sulfate. Solvent was removed and the residue was purified by flash chromatography on silica gel with hexane to give the title compound as a light yellow oil (1.82 g, 83.9%). ^{1}H NMR (400 MH_Z $CDCl_3$): δ = 7.75 (d, 1H), 7.21 (d, 1H), 7.18 (d, 1H), 6.45 (d, 1H), 4.24 (t, 2H), 1.85 (m, 2H), 1.36-1.16 (m, 39H), 0.90 (t, 6H).

Synthesis of monomer 2

Pyridinium chlorochromate (PCC, 2.1 g, 9.57 mmol), silica gel (2.0 g) and monomer **1** (1.7 g, 3.19 mmol) were added in mixture solvent of acetonitrile (15 mL) and 1,2-dichloroethane (15 mL) in flask. Aluminum chloride ($AlCl_3$, 10 mg) was added and the mixture was heated to reflux for 3 h. After cooled to room temperature, solvent was removed under reduced pressure and residue was purified by flash chromatograpgy on silica gel (hexane : ethyl acetate = 1 : 20) to give the title compound as a red solid (0.67 g, 37.4%). ^{1}H NMR (400 MH_Z $CDCl_3$): δ = 7.65 (d, 1H), 7.29 (d, 1H), 3.80 (t, 2H), 1.75 (m, 2H), 1.34-1.22 (m, 39H), 0.90 (t, 6H).

Table S1 Molecular weight and thermal properties of D–A polymers.

Polymer	M_n [*kDa*]	M_w [*kDa*]	PDI	Td[a] (^oC)
PBABDF-DT	32.6	161.6	5.0	368
PBABDF-TVT	30.8	179.6	5.8	376

[a] 5% weight loss temperature measured by TGA under nitrogen atmosphere.

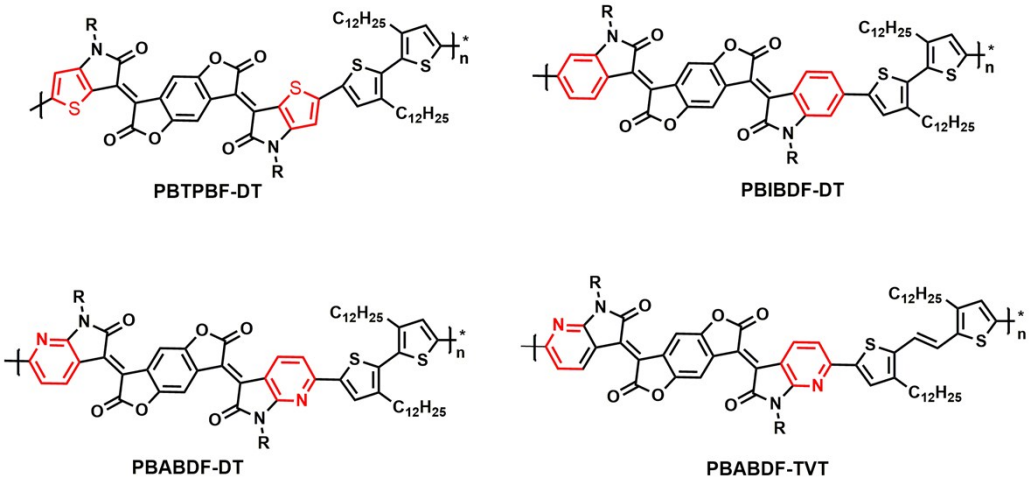


Fig. S1 The structures of four D-A polymers (**PBTPBF-DT** and **PBIBDF-DT** were reported in our previous work, [S1, 2]).

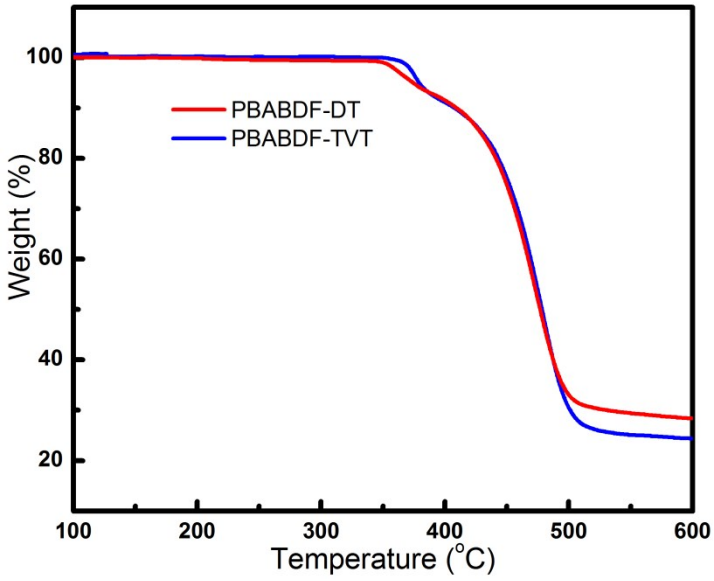


Fig. S2 The TGA plots of **BABDF**-based polymers.

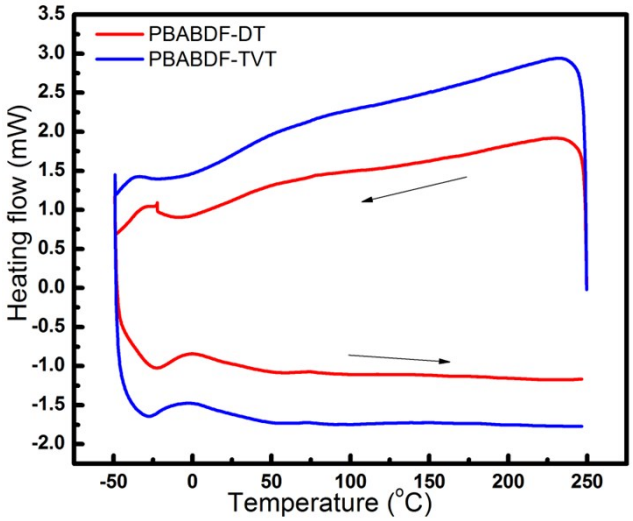


Fig. S3 The DSC plots of **BABDF**-based polymers.

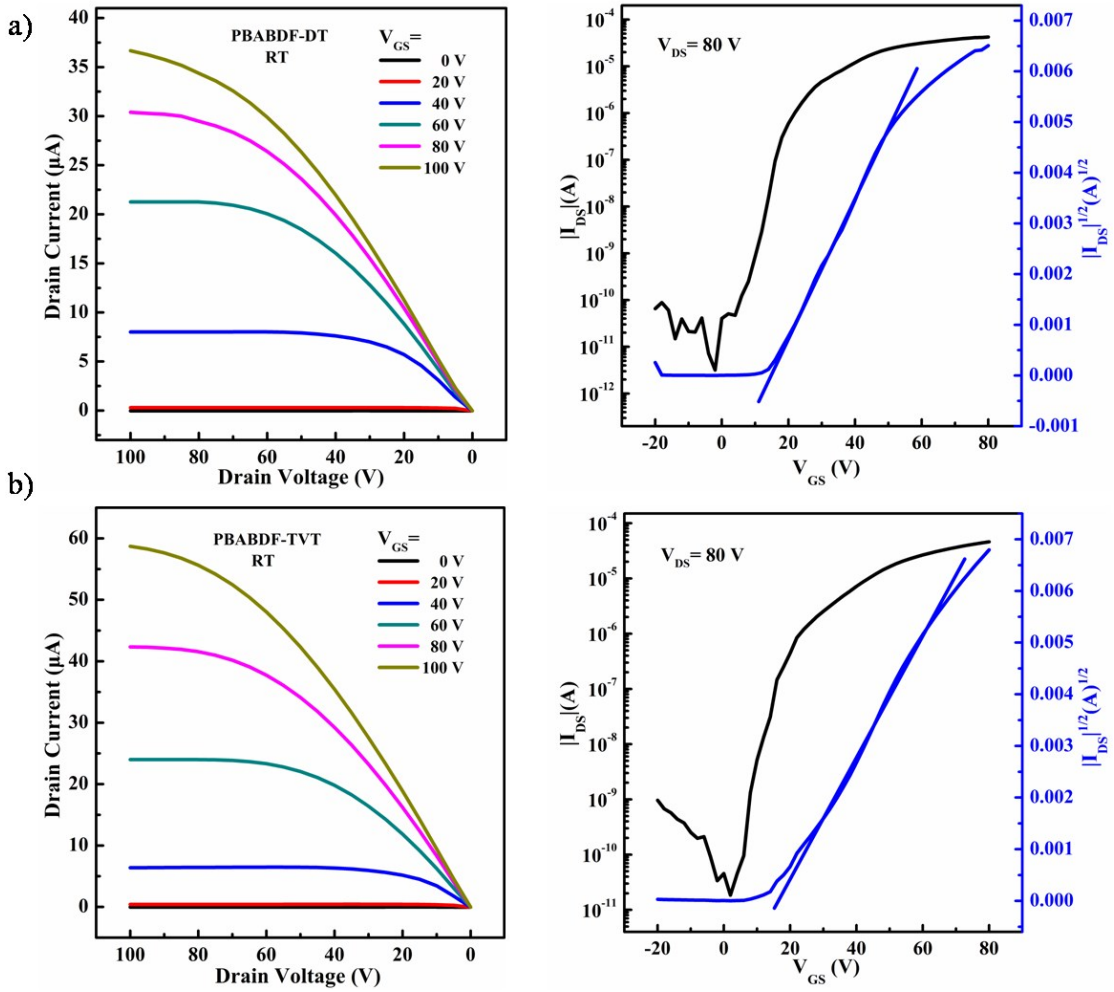


Fig. S4 Transfer and output characteristics of **BABDF**-based polymer films without annealing.

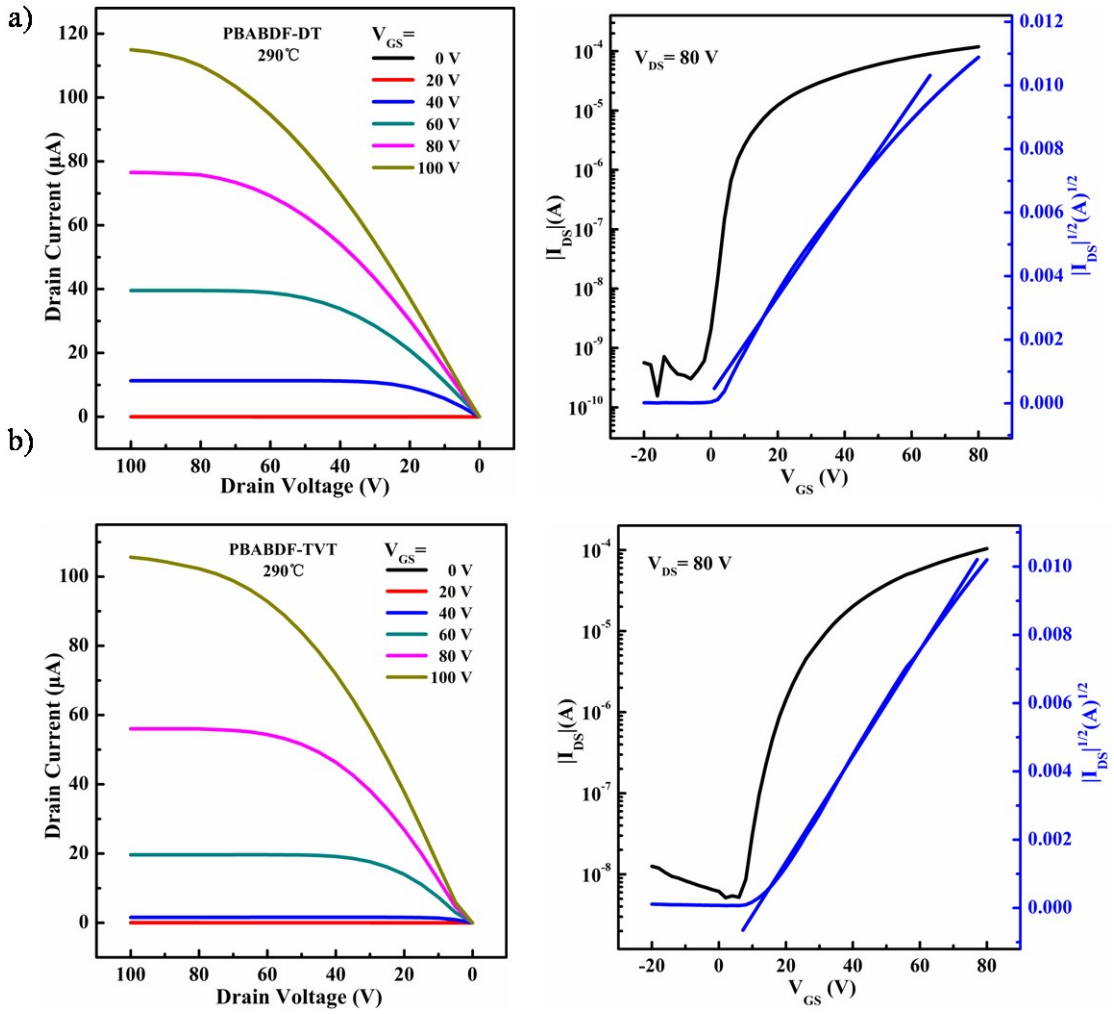


Fig. S5 Transfer and output characteristics of **BABDF**-based polymer films annealed 290 °C in BG/TC devices.

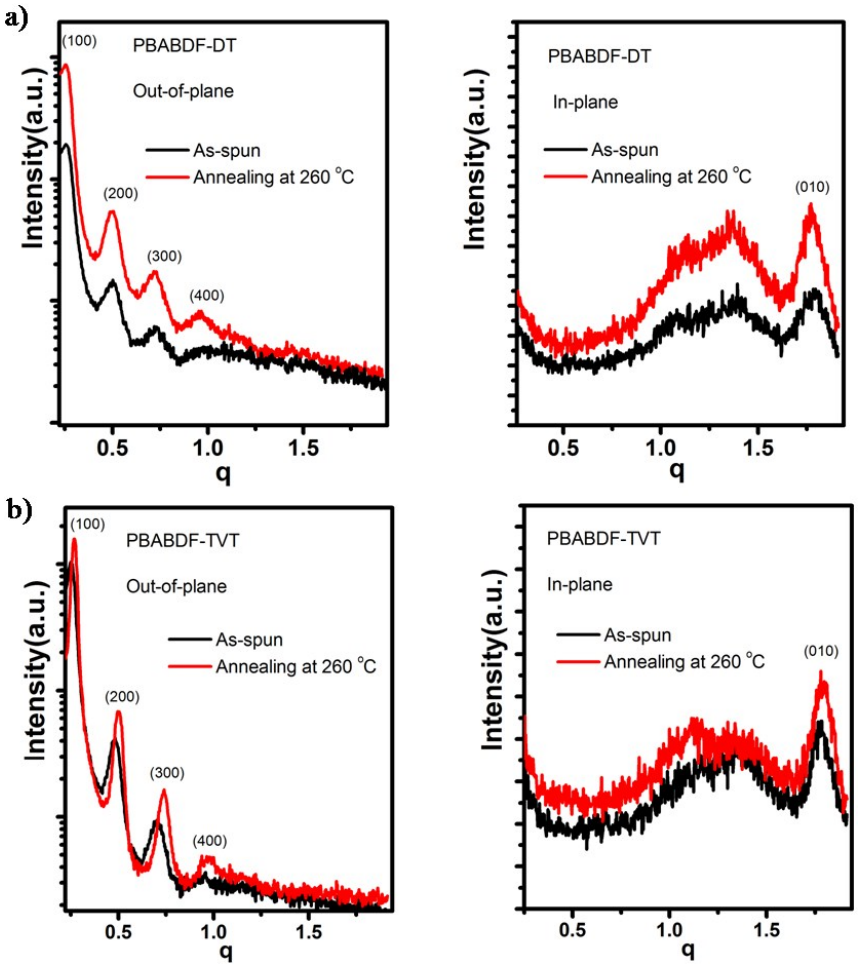


Fig. S6 Out-of-plane and in-plane line cuts of GIXD.

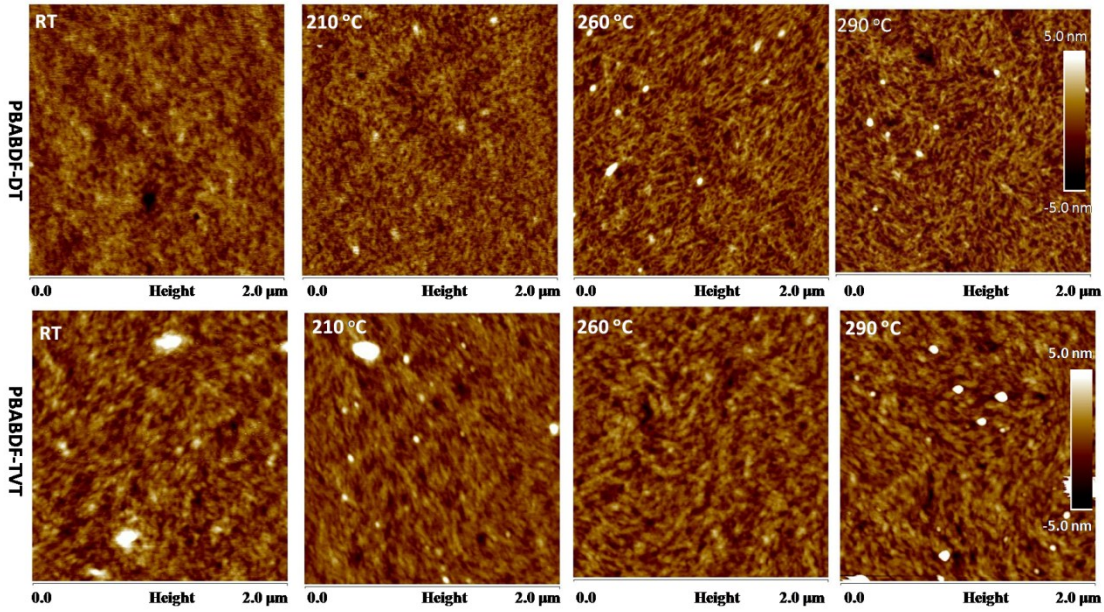


Fig. S7 AFM topography images of polymer films coated on Cytop-modified SiO_2/Si substrate with and without annealing.

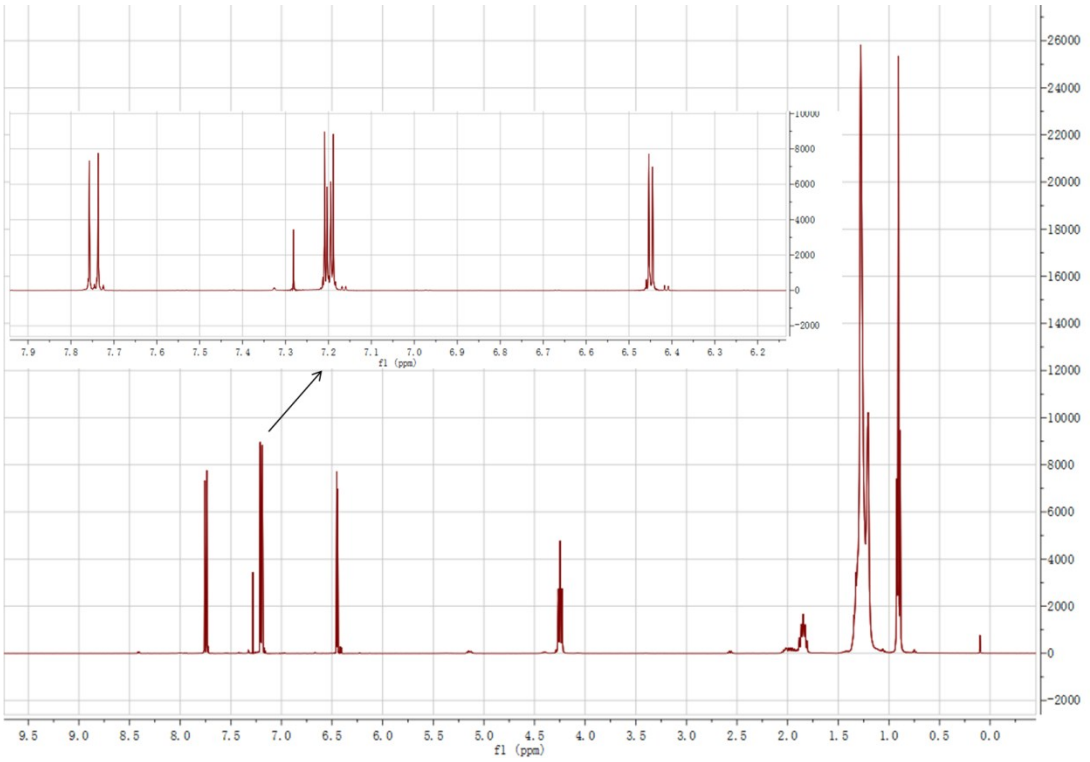


Fig. S8 The ^{1}H of monomer **1**.

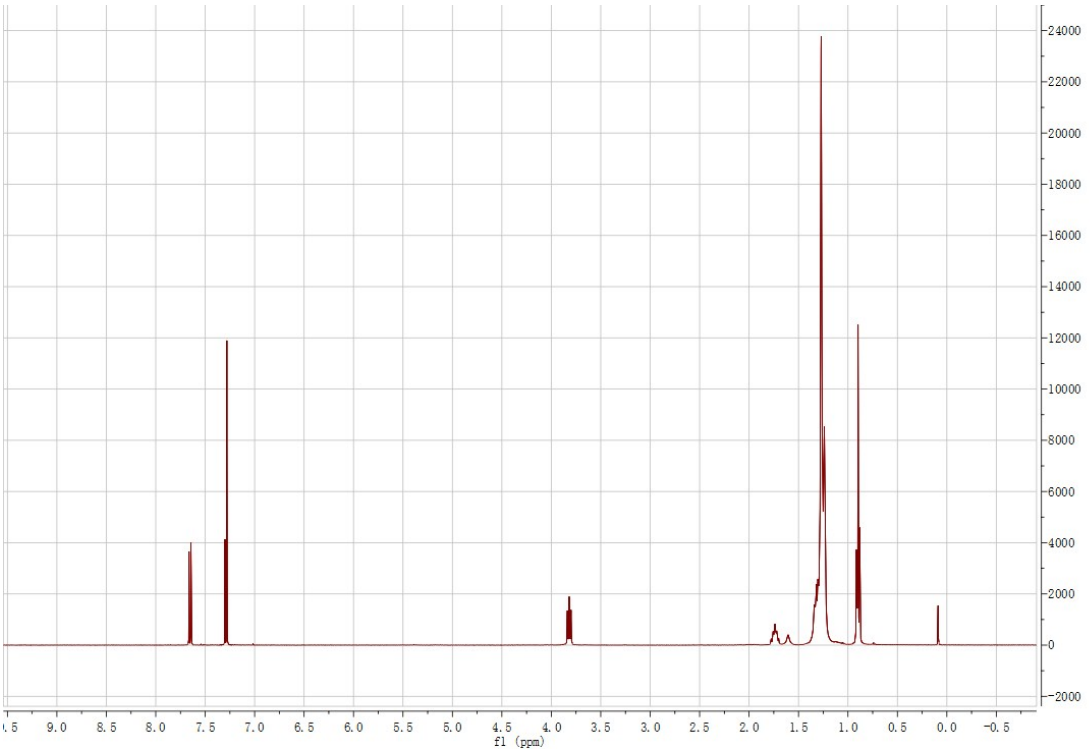


Fig. S9 The ^{1}H of monomer **2**.

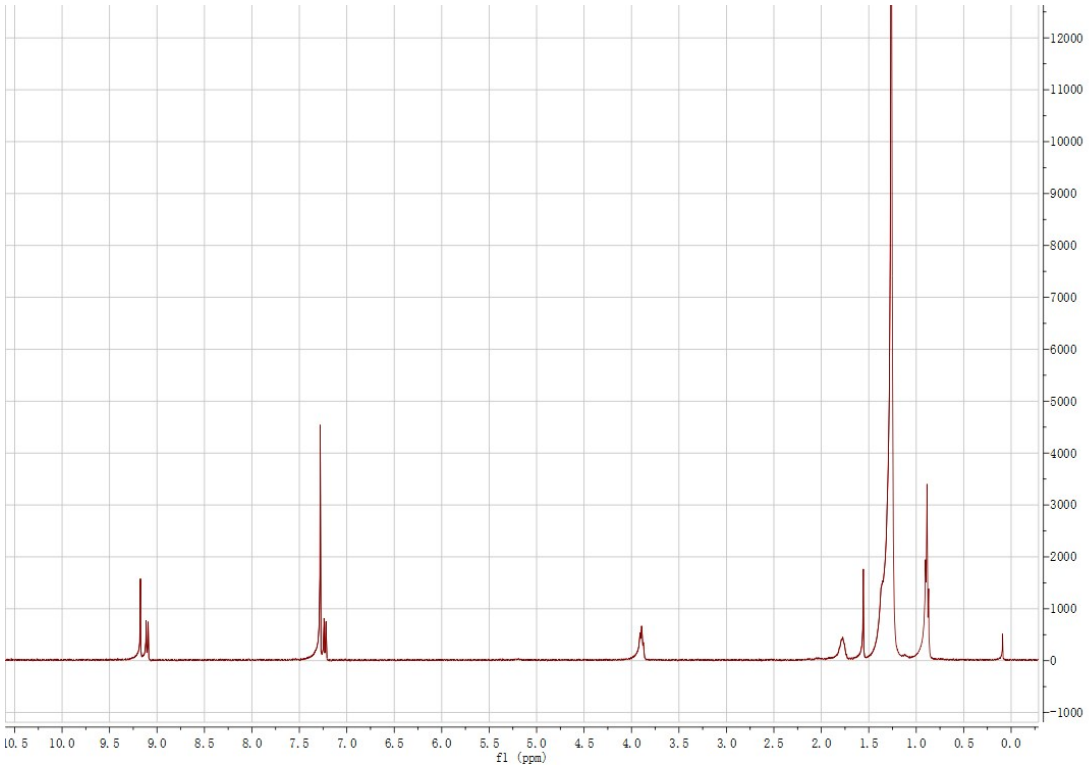


Fig. S10 The ^{1}H of monomer **3**.

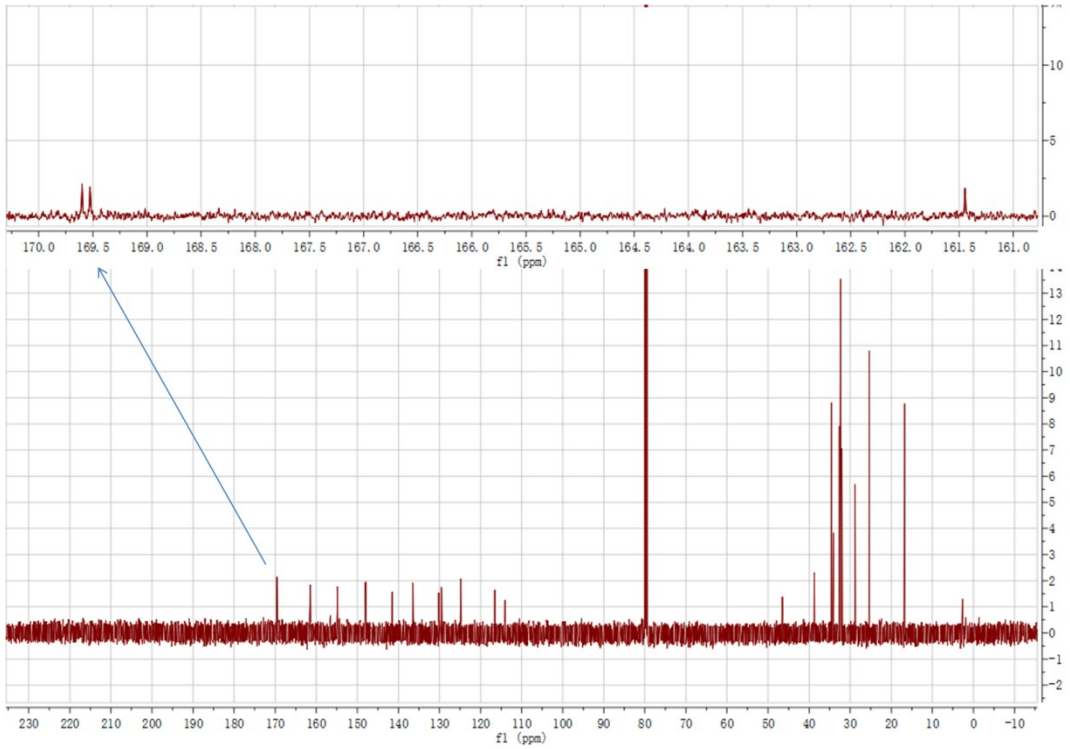


Fig. S11 The ^{13}C of monomer **3**.

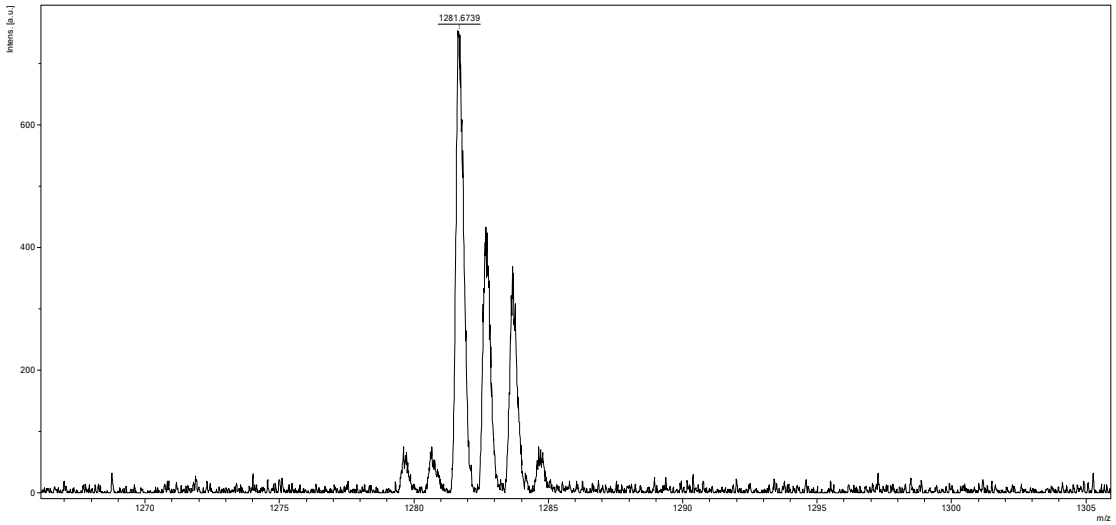


Fig. S12 The mass spectrum (MALDI-TOF) of compound **3.**

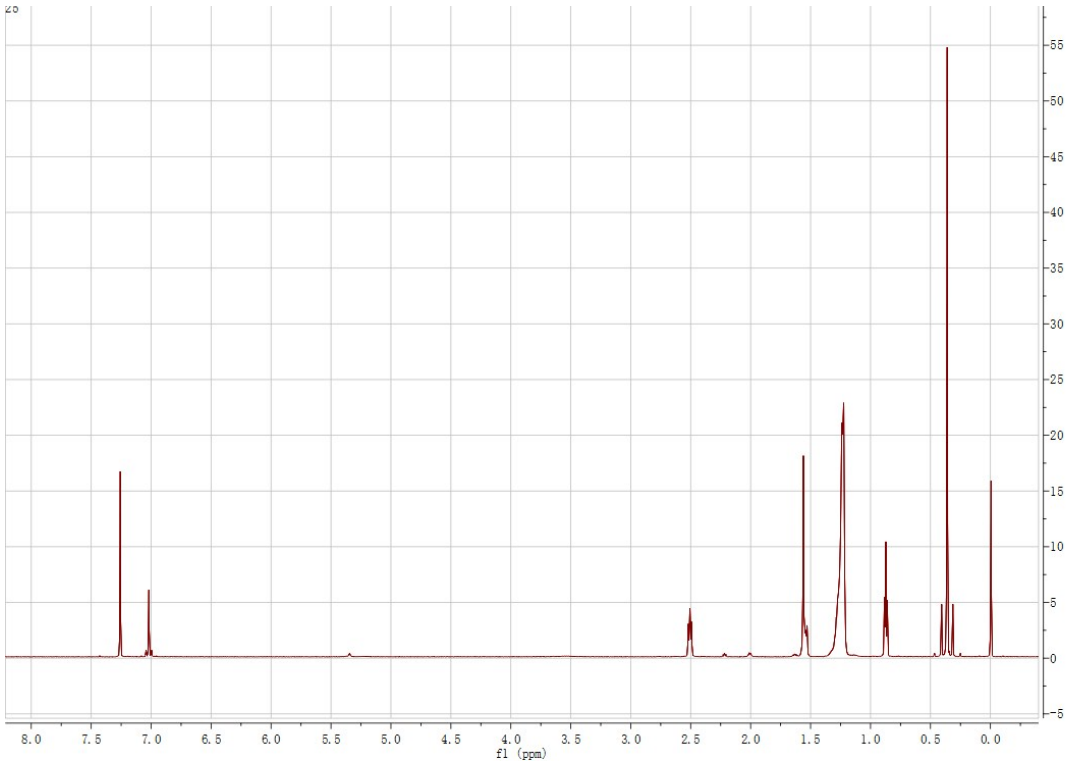


Fig. S13 The ^{1}H of 5,5'-ditrimethylstannyl-3,3'-didodecyl-2,2'-dithiophene.

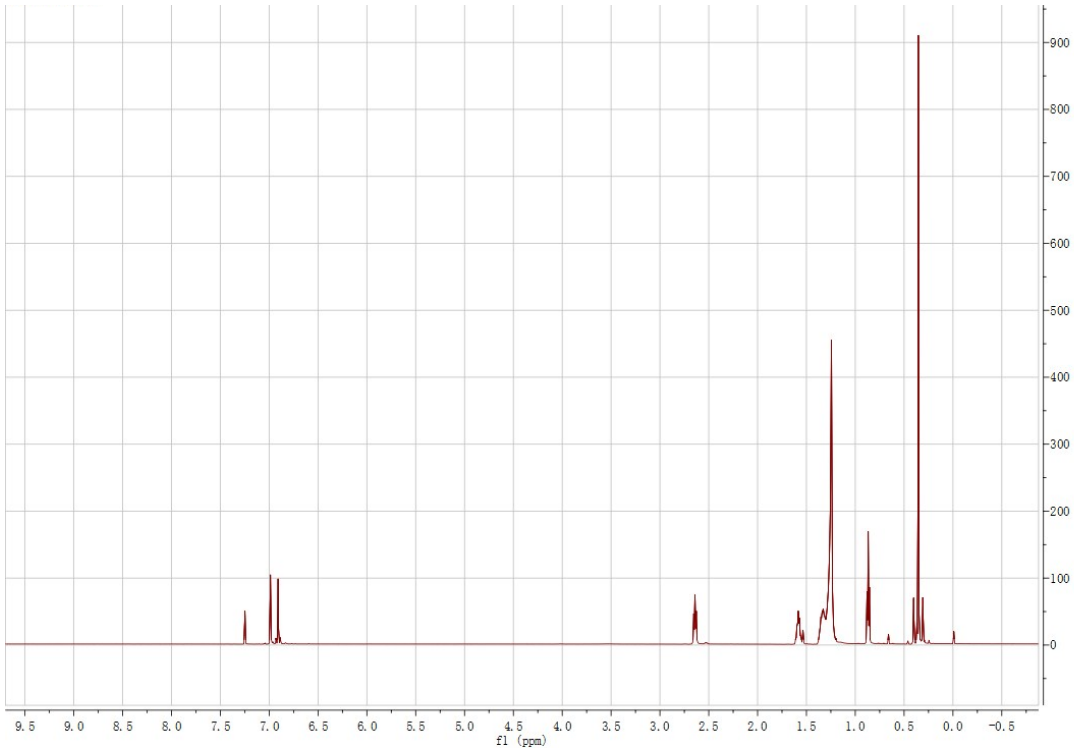
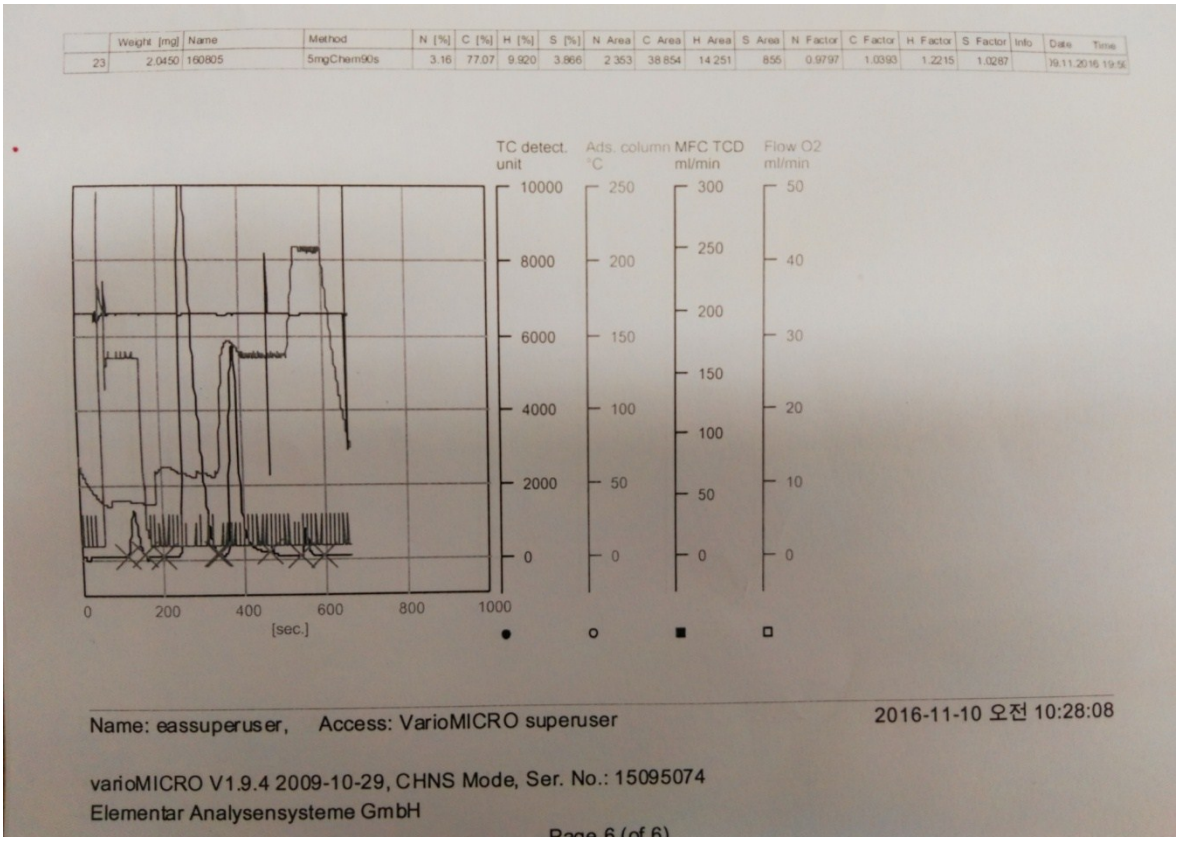


Fig. S14 The ^{1}H of 5,5'-ditrimethylstannyl-*E*- 1,2-(3,3'-didodecyl-2,2'-dithienyl)ethylene.

The element analysis results of polymers



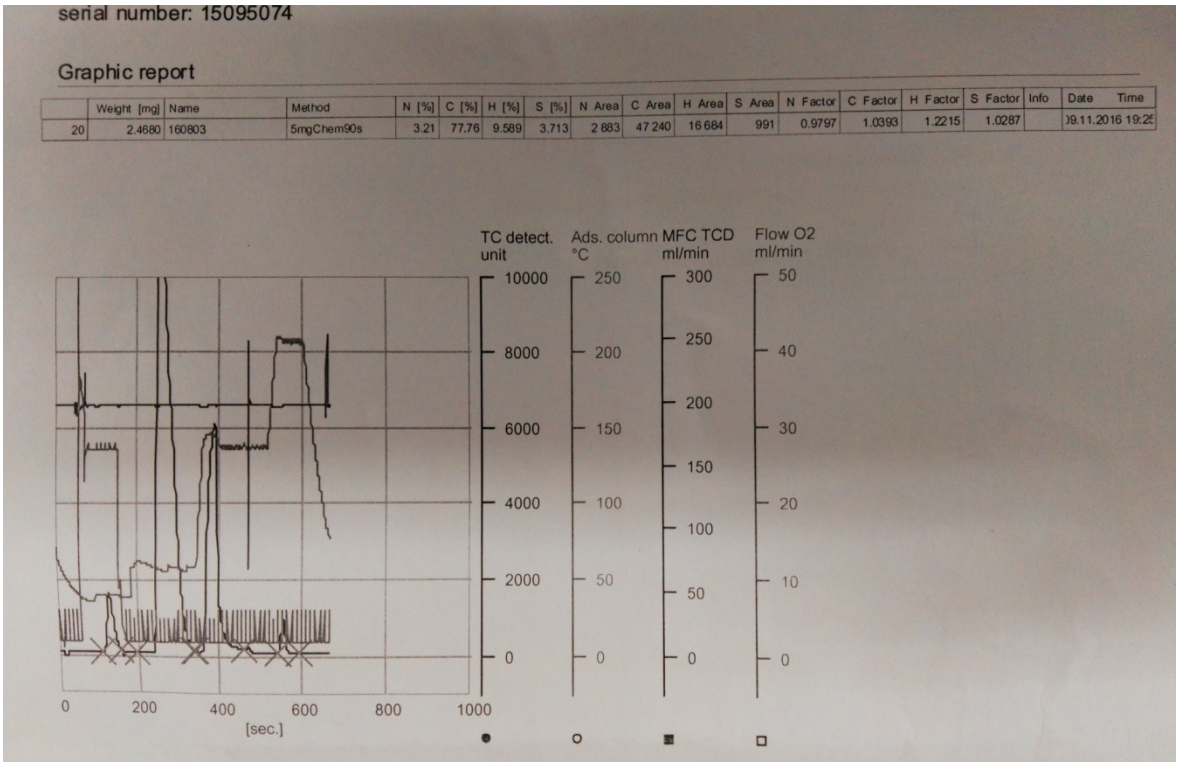
	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	N Factor	C Factor	H Factor	S Factor	Info	Date Time
23	2.0450	160805	5mgChem90s	3.16	77.07	9.920	3.866	2 353	38 854	14 251	855	0.9797	1.0393	1.2215	1.0287		09.11.2016 19:5

Name: eassuperuser, Access: VarioMICRO superuser

2016-11-10 오전 10:28:08

varioMICRO V1.9.4 2009-10-29, CHNS Mode, Ser. No.: 15095074
Elementar Analysensysteme GmbH

The element analysis of PBABDF-DT.



serial number: 15095074

Graphic report

	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	N Area	C Area	H Area	S Area	N Factor	C Factor	H Factor	S Factor	Info	Date Time
20	2.4680	160803	5mgChem90s	3.21	77.76	9.589	3.713	2 883	47 240	16 684	991	0.9797	1.0393	1.2215	1.0287		09.11.2016 19:2

The element analysis of PBABDF-TVT.

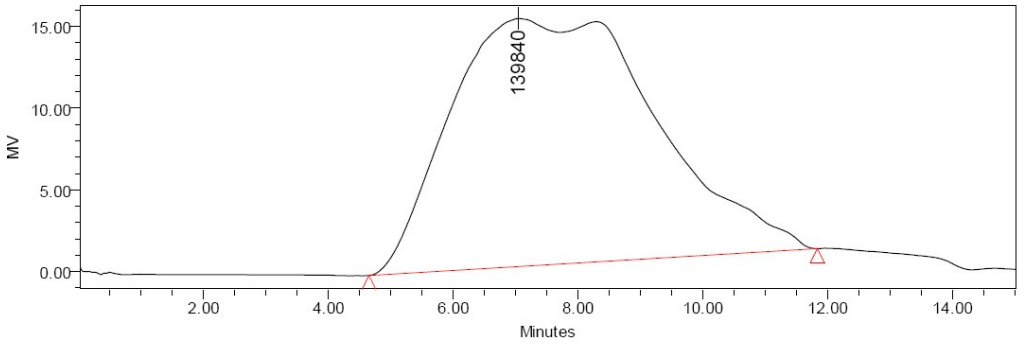
The GPC results of polymers

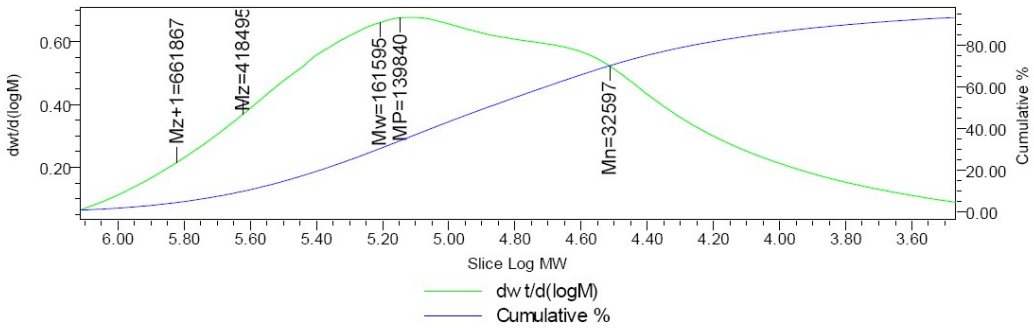
Empower™ 3 SOFTWARE

GPC

SAMPLE INFORMATION

Sample Name:	zgb160805	Acquired By:	System
Sample Type:	Broad Unknown	Sample Set Name:	
Vial:	6	Acq. Method Set:	ljq150918
Injection #:	3	Processing Method:	ljq04
Injection Volume:	25.00 ul	Channel Name:	410
Run Time:	15.0 Minutes	Proc. Chnl. Descr.:	410
Date Acquired:	2016/10/28 19:03:53 HKT		
Date Processed:	2016/10/28 19:23:56 HKT		





GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	7.050	32597	161595	139840	418495	4.957

Reported by User: System
Report Method: GPC
Report Method ID: 16948

Project Name: GPC
Date Printed:
2016/10/28

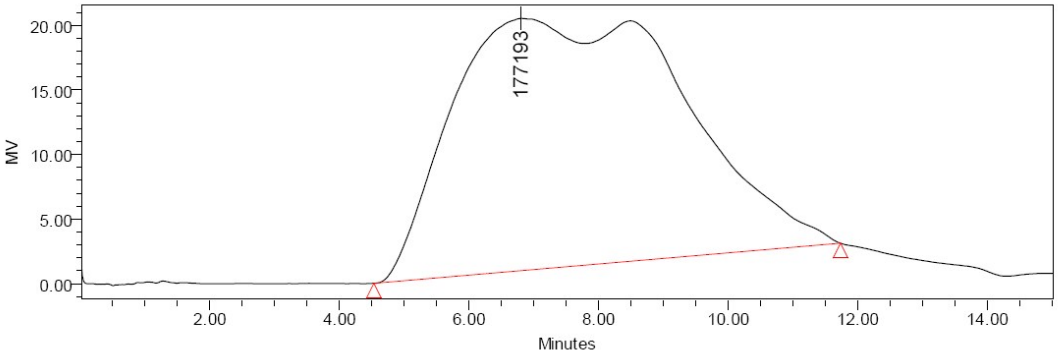
The GPC results of PBABDF-DT.

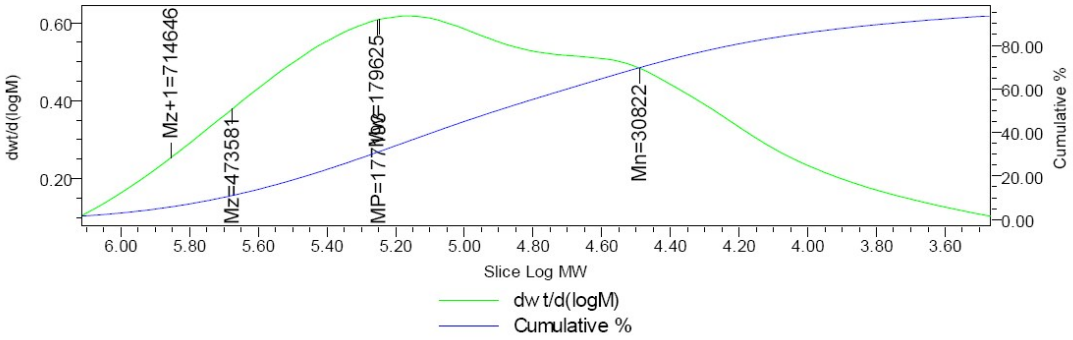
Empower™ 3 SOFTWARE

GPC

SAMPLE INFORMATION

Sample Name:	zgb160803	Acquired By:	System
Sample Type:	Broad Unknown	Sample Set Name:	
Vial:	6	Acq. Method Set:	ljq150918
Injection #:	2	Processing Method:	ljq04
Injection Volume:	25.00 ul	Channel Name:	410
Run Time:	15.0 Minutes	Proc. Chnl. Descr.:	410
Date Acquired:	2016/10/28 18:47:06 HKT		
Date Processed:	2016/10/28 19:14:48 HKT		





GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
1	6.808	30822	179625	177193	473581	5.828

Reported by User: System
Report Method: GPC
Report Method ID: 16948

Project Name: GPC
Date Printed: 2016/10/28

The GPC results of PBABDF-TVT.

S1 G. B. Zhang, Z. W. Ye, P. Li, J. H. Guo, Q. H. Wang, L.X. Tang, H.B. Lu, L.Z. Qiu, *Polymer Chem* **2015**, 6, 3970.

S2 G. B. Zhang, P. Li, L.X. Tang, J. X. Ma, X. H. Wang, H.B. Lu, B. Kang, K. Cho , L.Z. Qiu, *Chem Commun* **2014**, 50, 3180.