Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Highly Syndioselective Coordination (Co)Polymerization of Vinyl Heteroaromatic Monomers by Rare-Earth-Metal Complexes

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Fig. S23 DSC curve of the syndiotactic VDBT-St copolymer (Table 3, entry 6).

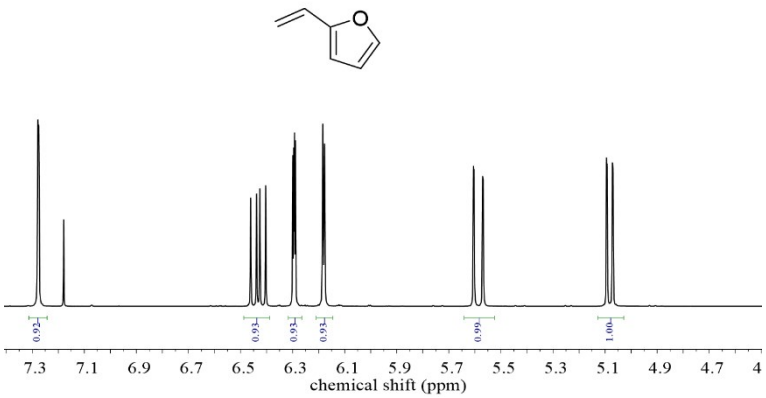

Fig. S1 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of VF.

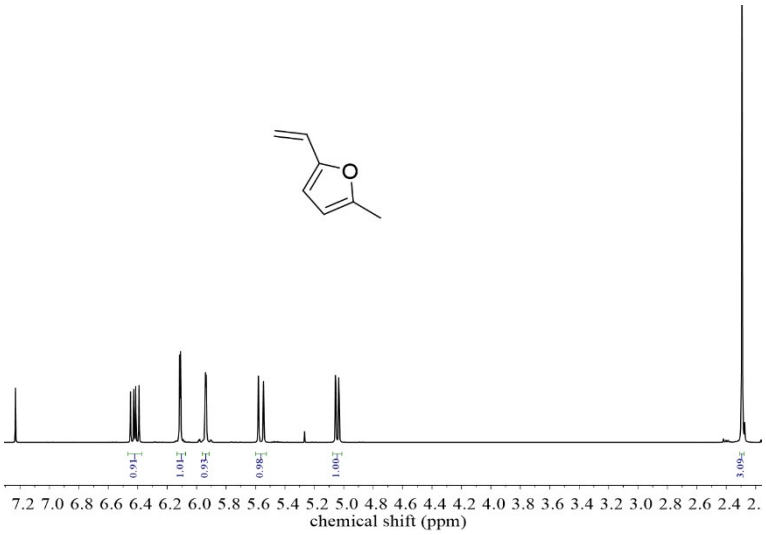

Fig. S2 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of MVF.

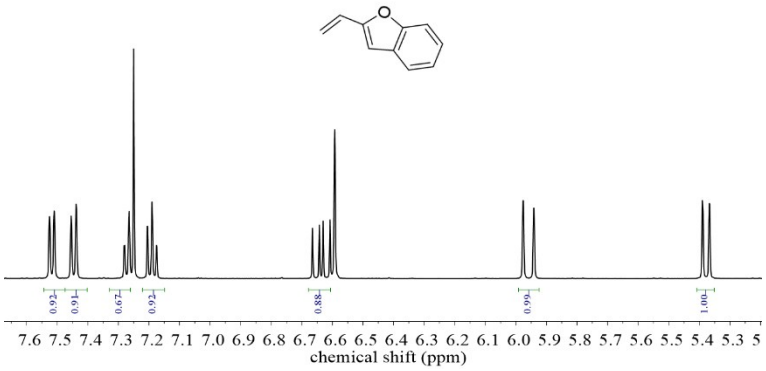

Fig. S3 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of VBF.

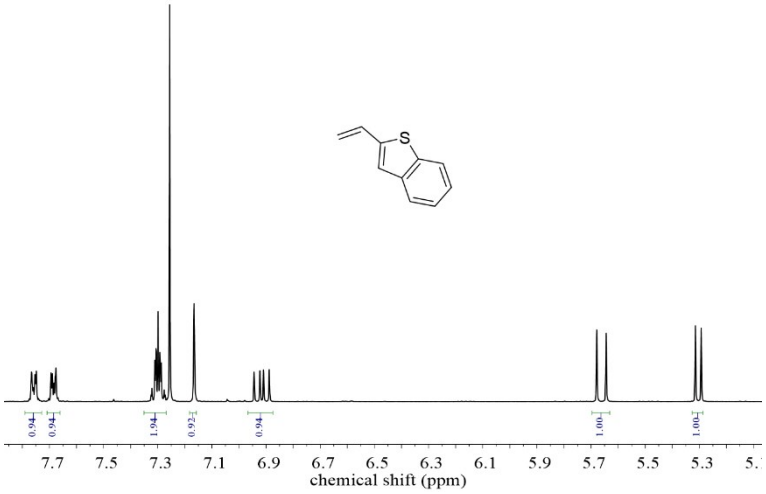

Fig. S4 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of VBT.

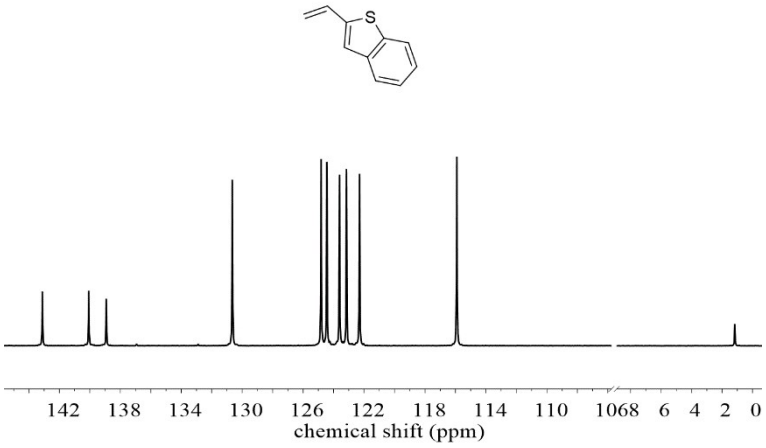

Fig. S5 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 25 ℃) of VBT.

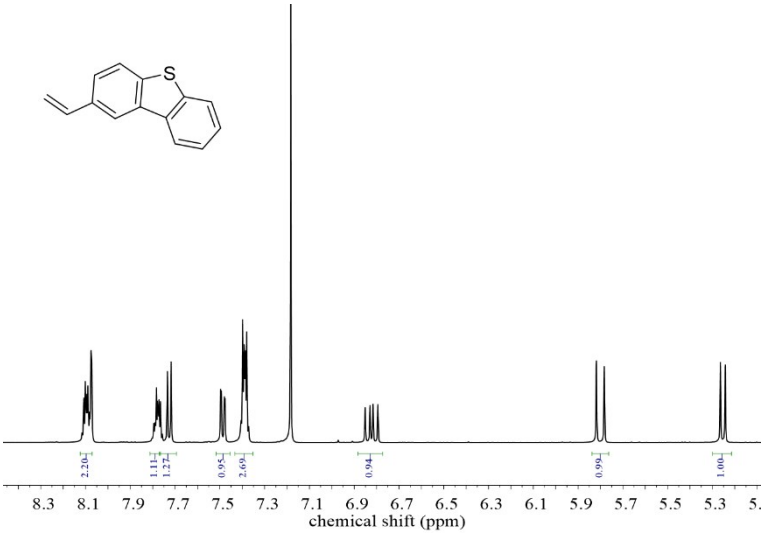

Fig. S6 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of VDBT.

Table S1. Homopolymerization of Vinyl Heteroaromatic Monomers by Complexes **1-4** [a]

Entry	Monomer	Cat.	[M] / [Cat.]	t (h)	Conv. (%)	M_n [b] (10^4)	M_w/M_n [b]	T_g [c] (℃)
1	VF/MVF/VBF	**1**	100/1	24	---			
2	VF	**2**	100/1	24	5	n.d. [d]	n.d.	n.d.
3	MVF	**2**	100/1	24	13.5	0.3	1.6	88
4	VBF	**2**	100/1	24	15.1	1.0	1.4	101
5	VF/MVF/VBF	**3**	100/1	24	---			
6	VF/MVF/VBF	**4**	100/1	24	---			
7	VT	**1**	100/1	24	---			
8	VT	**2**	100/1	24	16.9	n.d. [d]	n.d.	105
9	VT	**3**	100/1	24	24.1	n.d. [d]	n.d.	105
10	VT	**4**	100/1	24	23.2	n.d. [d]	n.d.	105

[a] General conditions: rare-earth metal complex (10 μmol), [Cat.]/[Ph_3C][$B(C_6F_5)_4$]/[Al^{i}Bu$_3$] = 1/1/10 (mol/mol), toluene 1 mL, polymerization temperature T_p = 25 ℃, unless otherwise noted. [b] Determined by GPC in trichlorobenzene at 150 ℃ against polystyrene standard. [c] Determined by DSC. [d] Not determined because of the insolubility in common solvents.

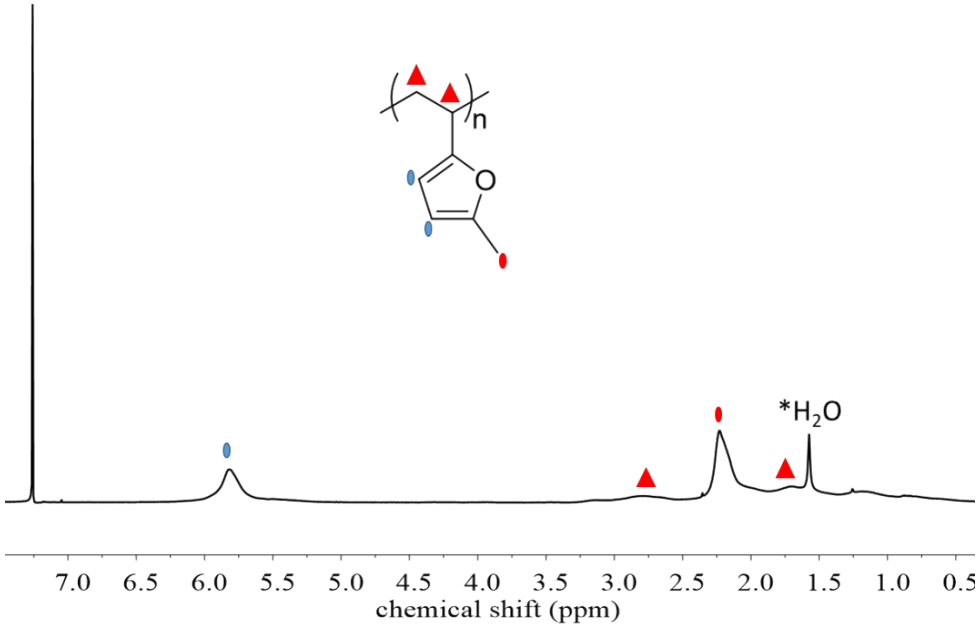

Fig. S7 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 ℃) of PMVF.

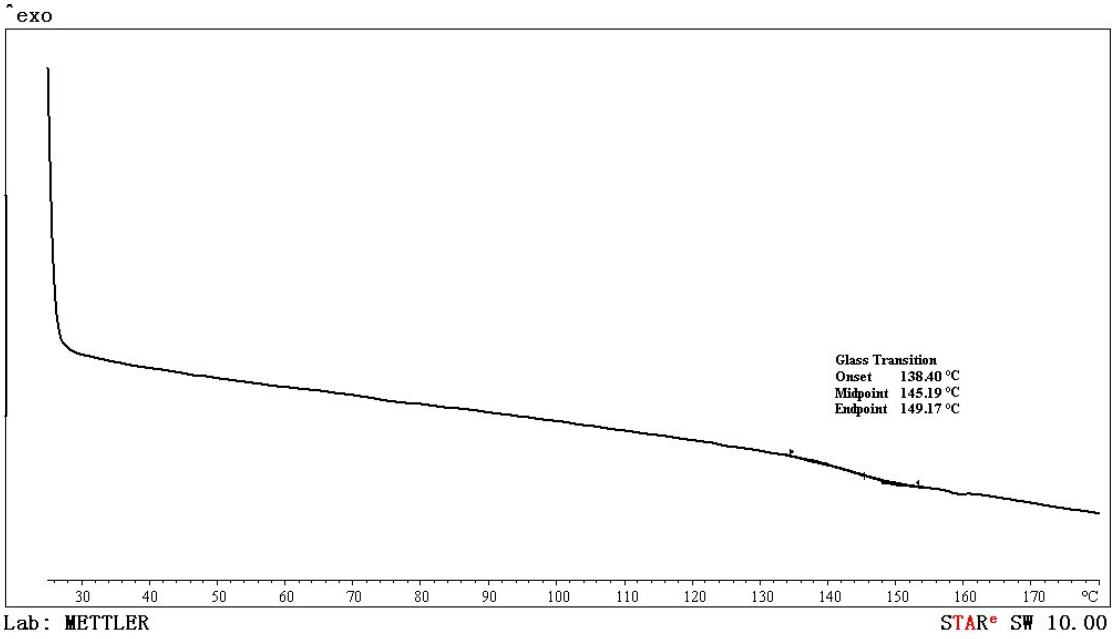

Fig. S8 DSC curve of PVBT (Table 1, entry 4).

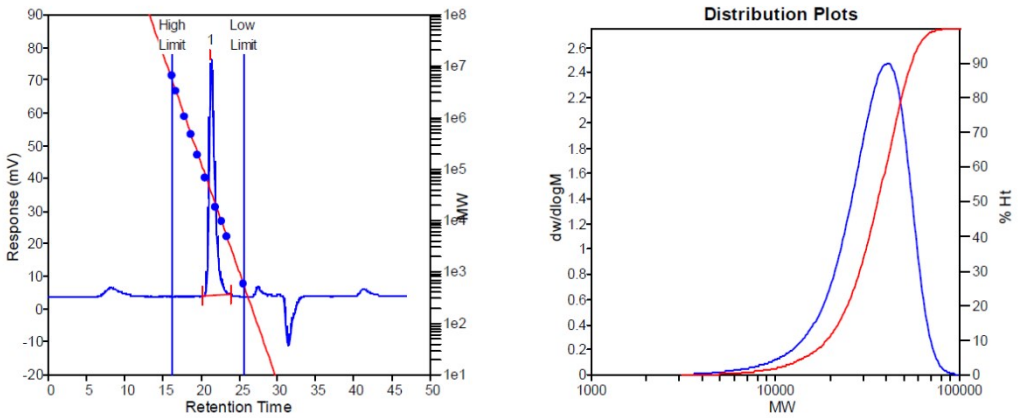

Fig. S9 GPC curve of PVBT (Table 1, entry 4).

Table S2. Syndioselective Copolymerization of St and VBT under different reaction time.

Entry	t (min)	VBT in copolymer [b] (%)	M_n[c] (10^4)	M_w/M_n[c]
1	0.3	96.6	3.9	1.10
2	0.5	95.2	8.4	1.12
3	1	91.7	8.7	1.12
4	2	87.3	9.3	1.14
5	3	84.7	9.8	1.15
6	4	77.5	10.5	1.15
7	5	71.4	10.9	1.21
8	6	61.2	11.7	1.21
9	7	58.8	11.9	1.21
10	9	55.2	12.0	1.20
11	11	54.1	12.1	1.20
12	13	50.0	12.3	1.22

[a] General conditions: rare-earth-metal complex (20 μmol), [Cat.]/[Ph_3C][$B(C_6F_5)_4$]/[Al^{i}Bu$_3$] = 1/1/10 (mol/mol), [St]/[VBT]/[**Y**] = 500/500/1; toluene 10 mL, polymerization temperature T_p = 25 ℃, unless otherwise noted [b] Determined by ^{1}H NMR. [c] Determined by GPC in 1,2,4-trichlorobenzene at 150 ℃ against polystyrene standard.

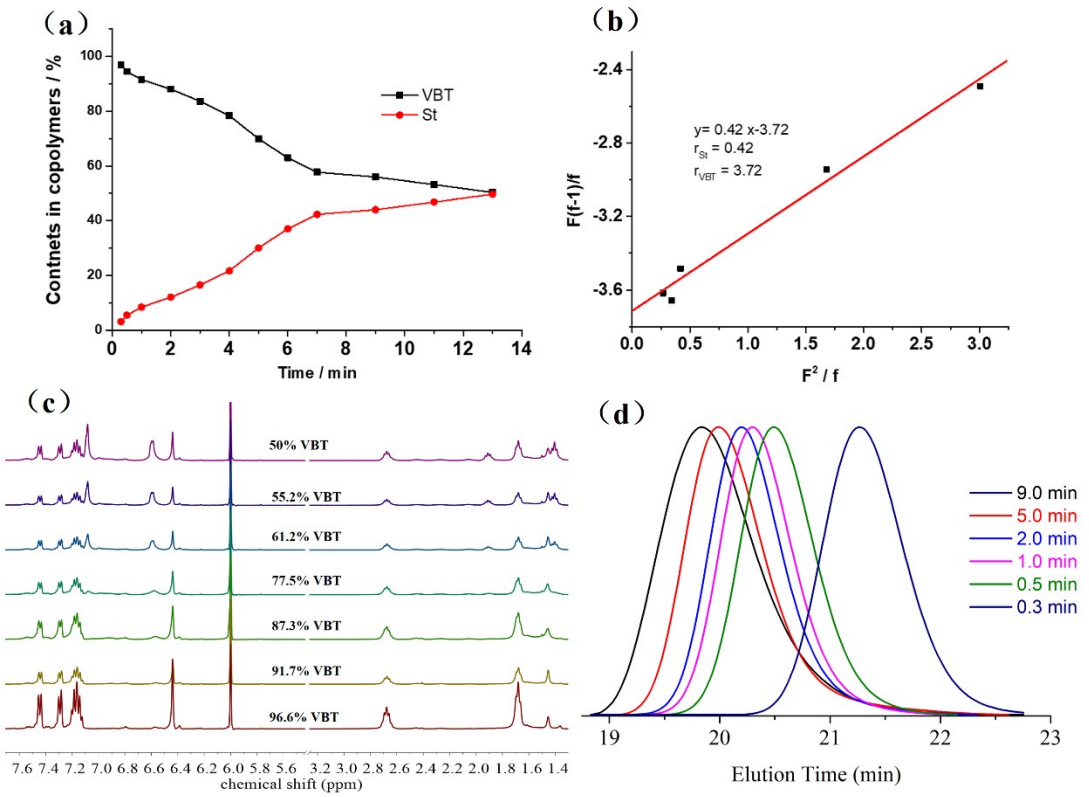

Fig. S10 VBT-St copolymers isolated at different polymerization times**:** (a) Plots of the contents of St (red point) and VBT units (black point) in the copolymers versus time;(b) Fineman-Ross plots for copolymerizations of St with VBT; (c) ^{1}H NMR spectra; (d) GPC curves.

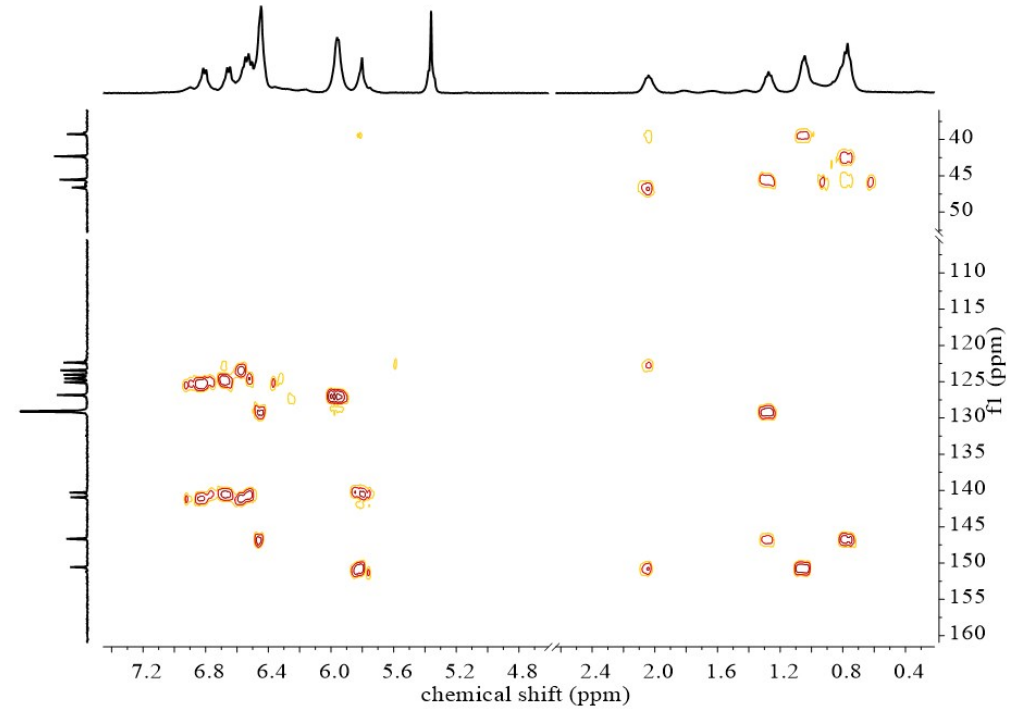

Fig. S11 HMBC spectrum (1,1,2,2-$C_2D_2Cl_4$, 110 ℃) of the syndiotactic VBT-St copolymer (Table 2, entry 3).

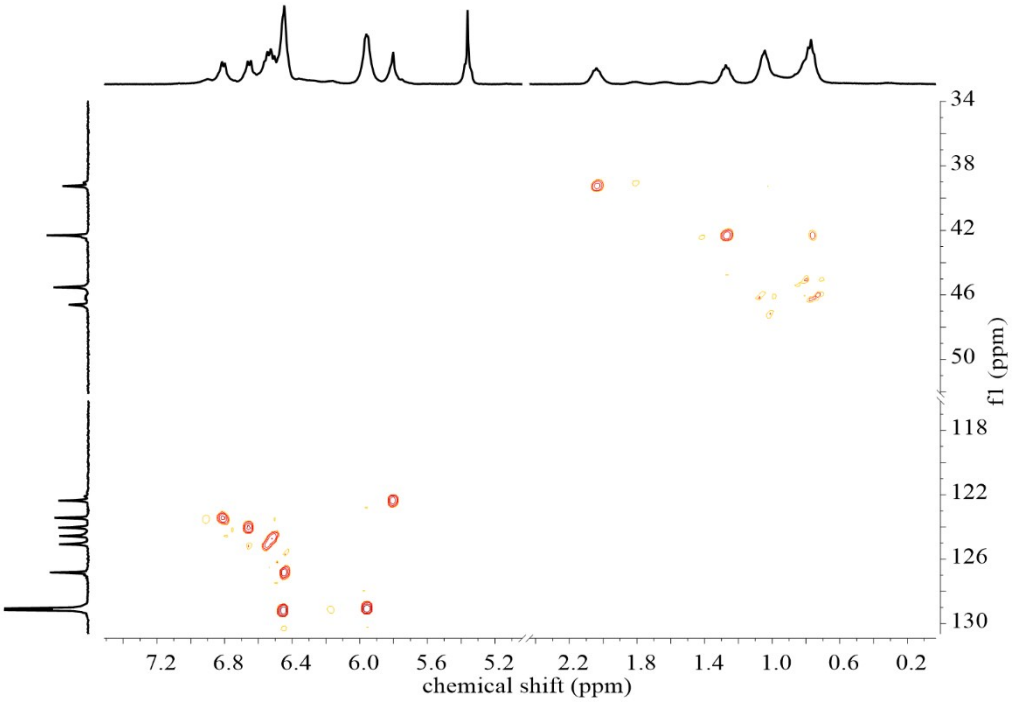

Fig. S12 HSQC spectrum (1,1,2,2-$C_2D_2Cl_4$, 110 ℃) of the syndiotactic VBT-St copolymer (Table 2, entry 3).

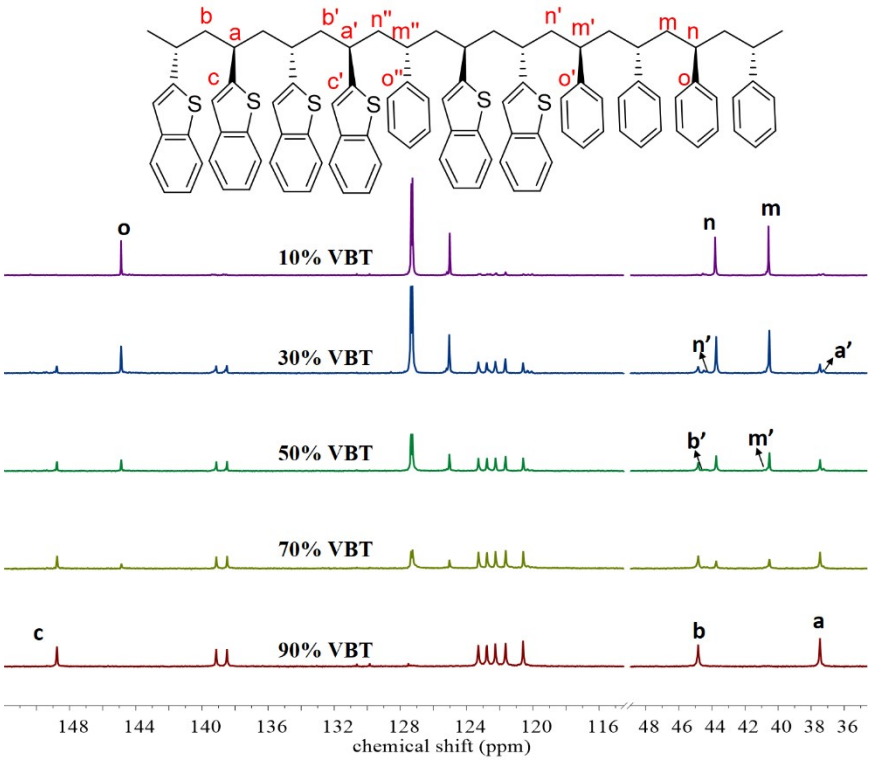

Fig. S13 ^{13}C NMR spectra (100 MHz, 1,1,2,2-$C_2D_2Cl_4$, 110 ℃) of the syndiotactic VBT-St copolymers (Table 2, entries 1-5).

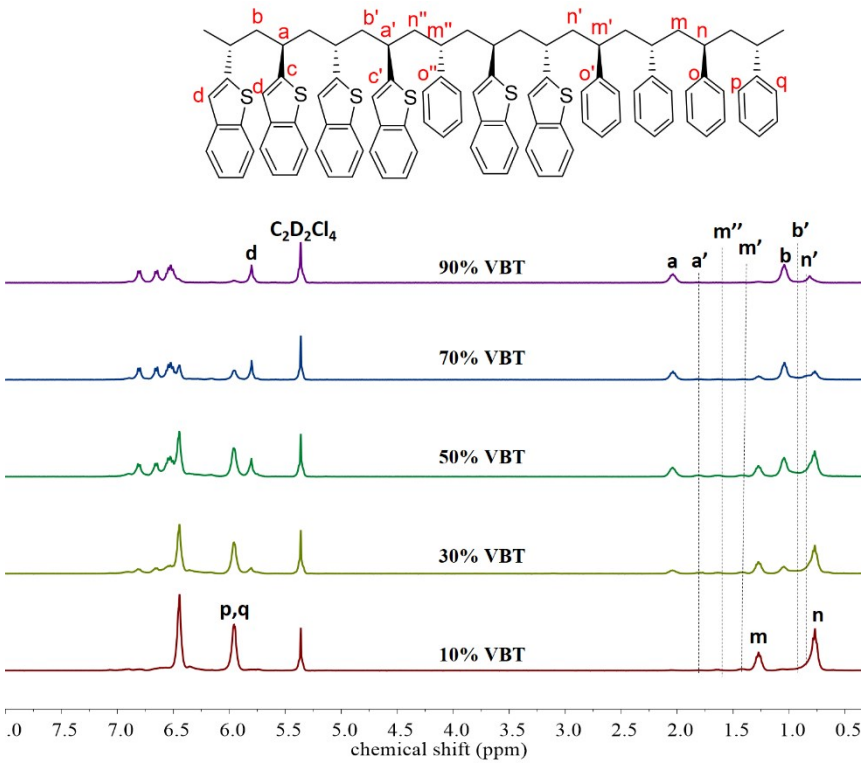

Fig. S14 ^{1}H NMR spectra (400 MHz, 1,1,2,2-$C_2D_2Cl_4$, 110 ℃) of the syndiotactic VBT-St copolymers (Table 2, entries 1-5).

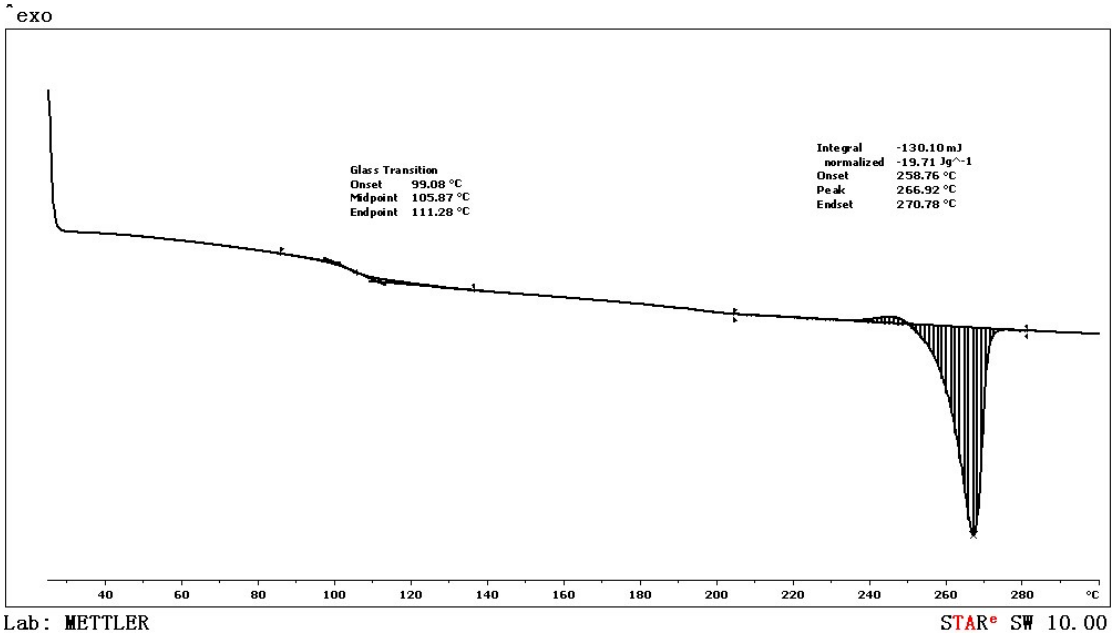

Fig. S15 DSC curve of the syndiotactic VBT-St copolymer (Table 2, entry 1).

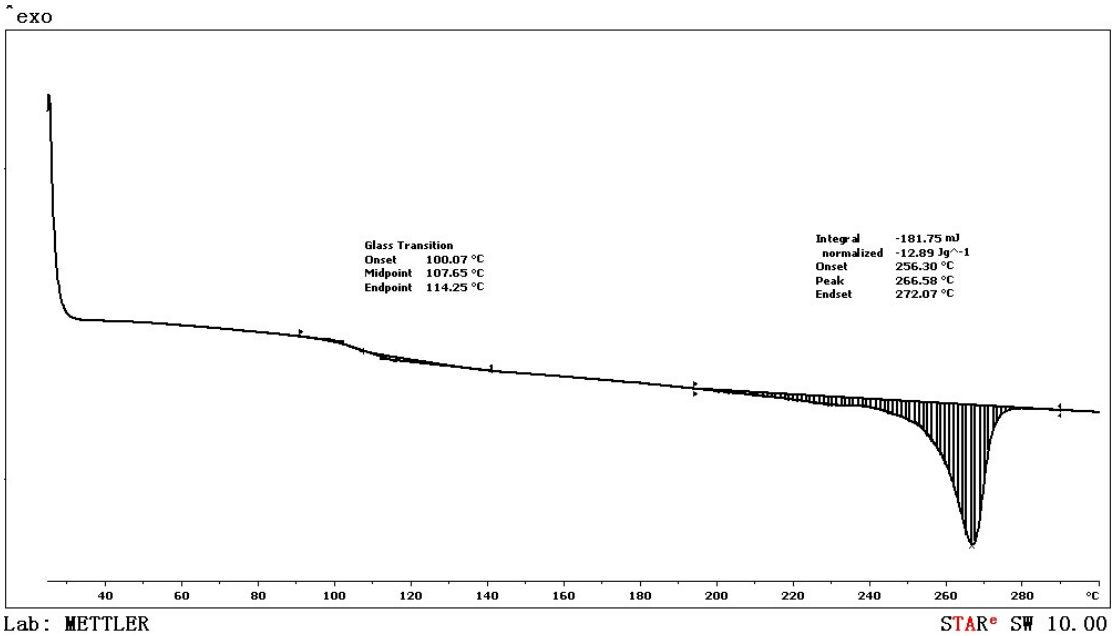

Fig. S16 DSC curve of the syndiotactic VBT-St copolymer (Table 2, entry 2).

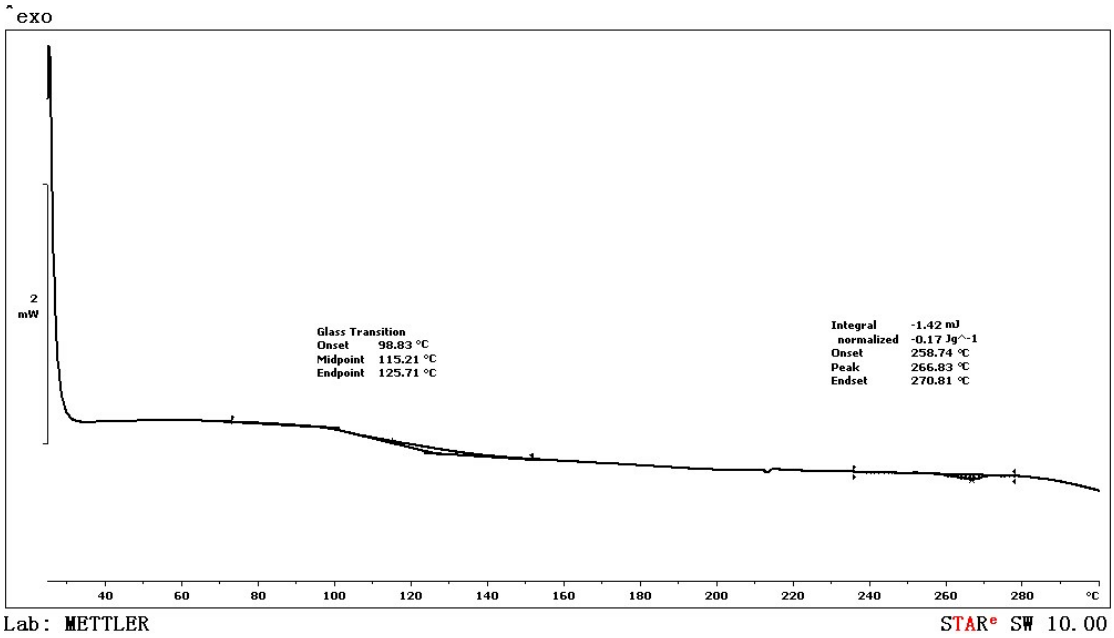

Fig. S17 DSC curve of the syndiotactic VBT-St copolymer (Table 2, entry 3).

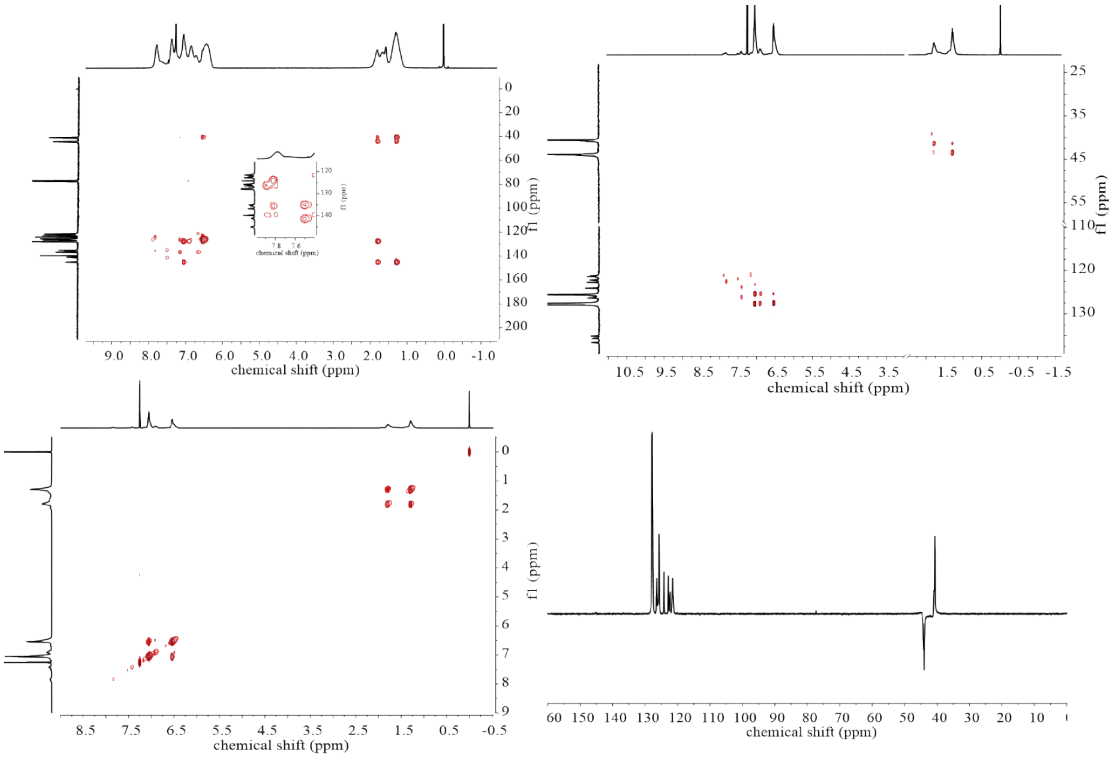

Fig. S18 HSQC, HMBC, H-H COSY and DEPT-135 NMR spectrum (1,1,2,2-$C_2D_2Cl_4$, 110 ℃) of the syndiotactic VDBT-St copolymers (Table 3, entry 4).

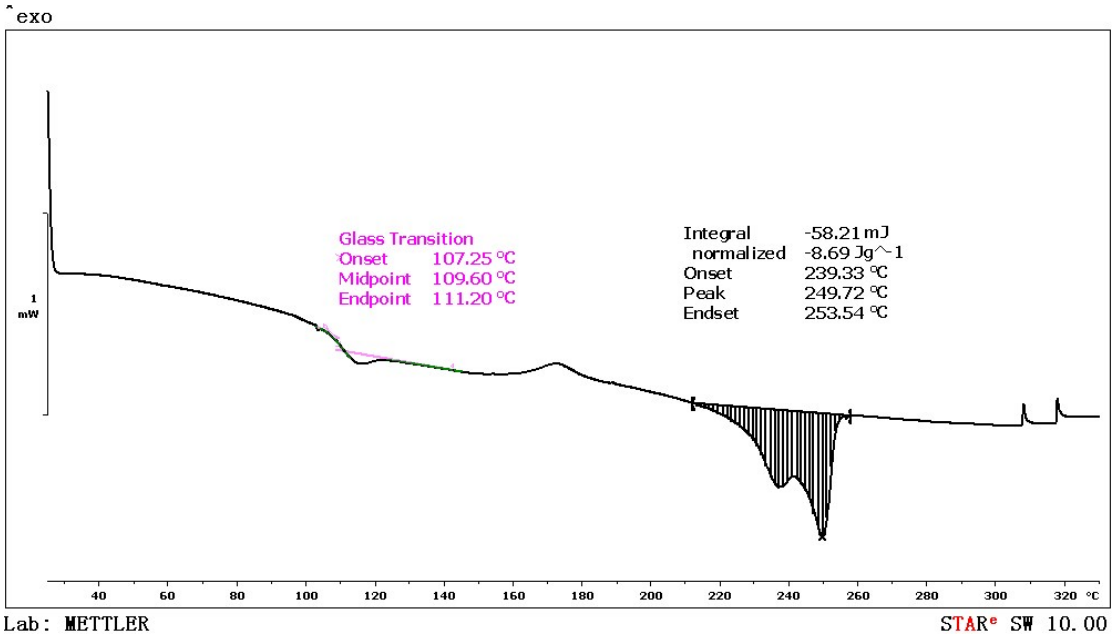

Fig. S19 DSC curve of the syndiotactic VDBT-St copolymer (Table 3, entry 2).

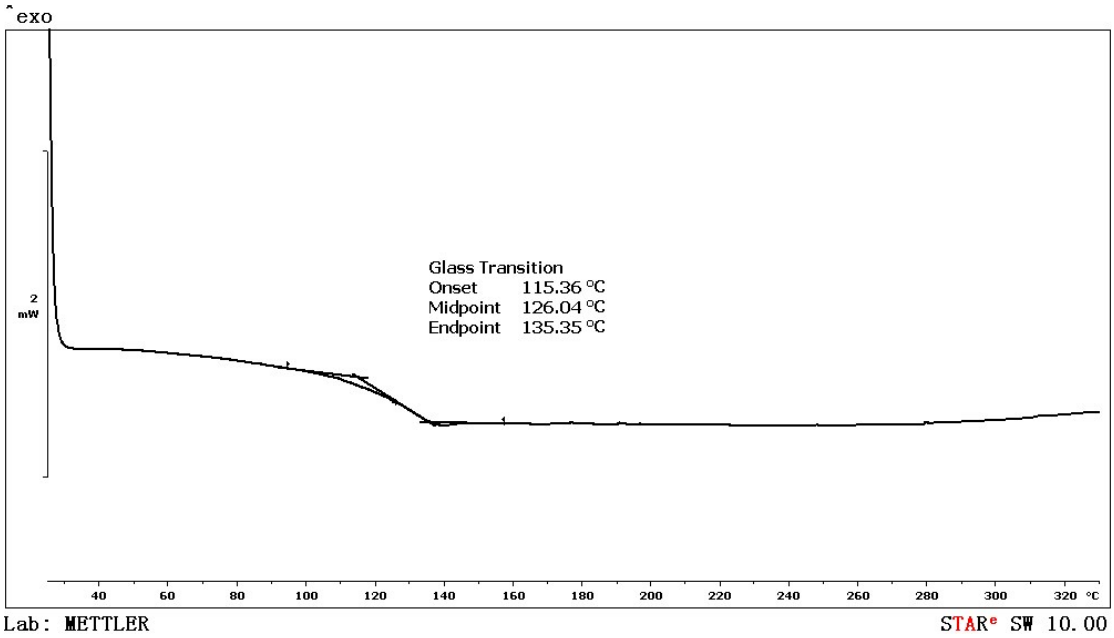

Fig. S20 DSC curve of the syndiotactic VDBT-St copolymer (Table 3, entry 3).

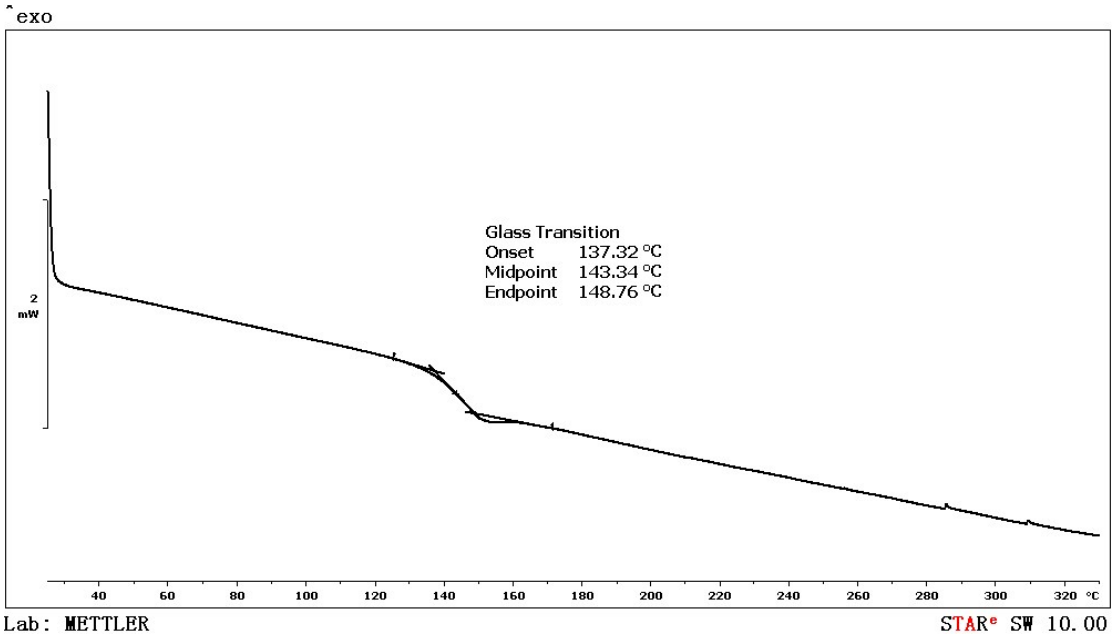

Fig. S21 DSC curve of the syndiotactic VDBT-St copolymer (Table 3, entry 4).

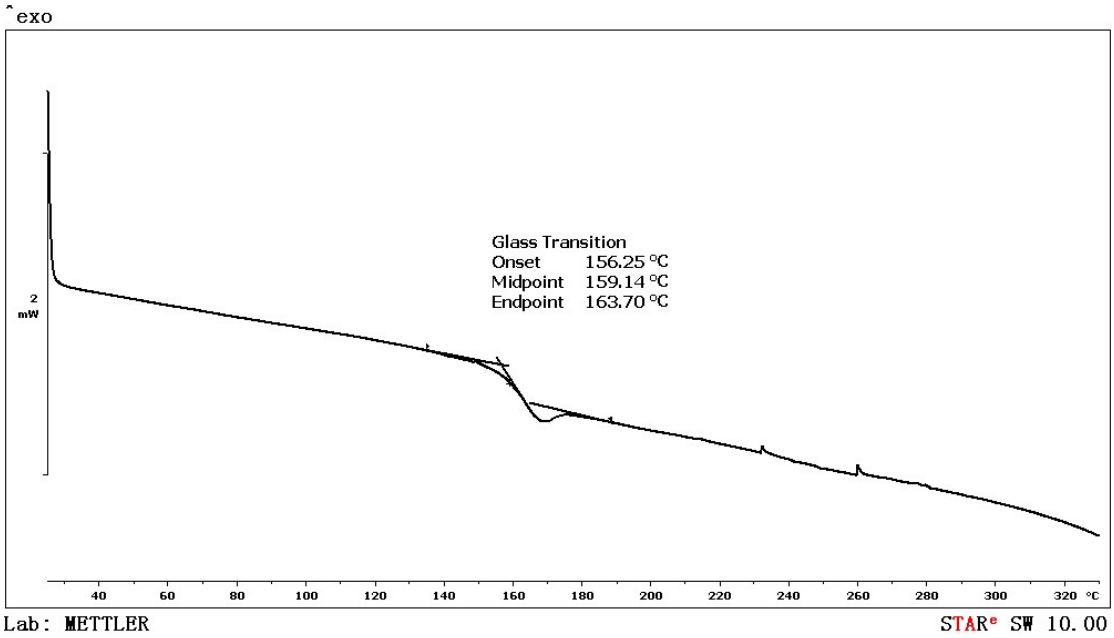

Fig. S22 DSC curve of the syndiotactic VDBT-St copolymer (Table 3, entry 5).

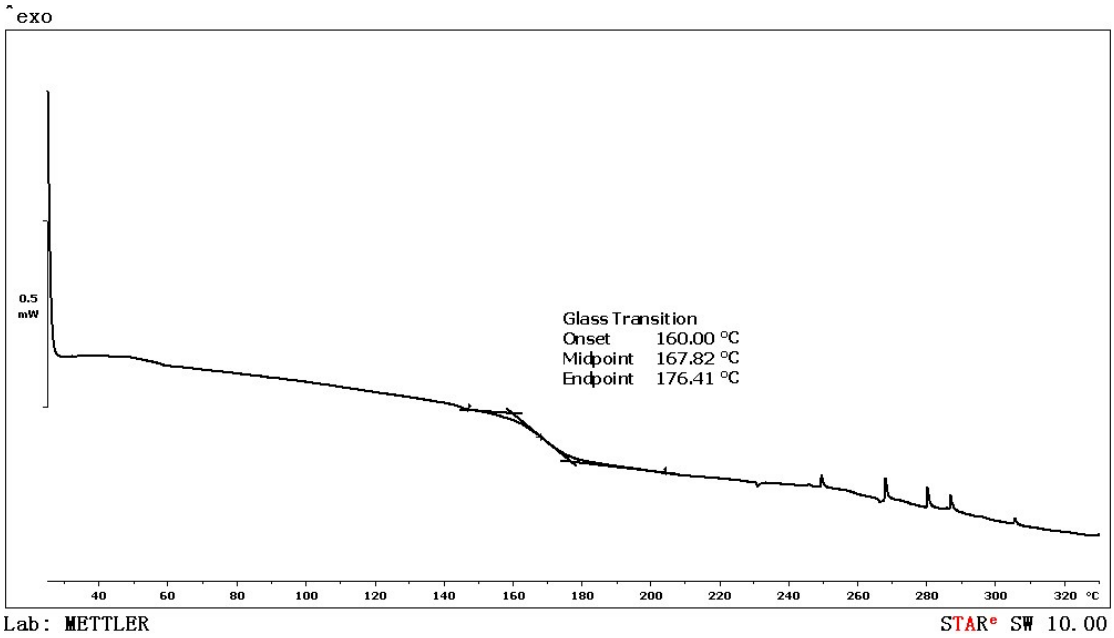

Fig. S23 DSC curve of the syndiotactic VDBT-St copolymer (Table 3, entry 6).