Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information for

High-Density and Hetero-Functional Group Engineering of Segmented Hyperbranched Polymers via Click Chemistry

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Table S1 Solvents and Precipitants selected for thiol-epoxy click chemistry.

Code	Solvents	Precipitants
SHP-9	DMF	Dichloromethane
SHP-10	DMF	Ethyl ether
SHP-11	DMF	Acetonitrile
SHP-12	DMF	Ethyl ether
SHP-13	Chloroform	DMF
SHP-14	DMF	Ethyl ehter
SHP-15	DMF	Ethyl ehter

Table S2 Absolute molecular weights of SHP-1.[a]

Code	M_n	M_w	M_z	PDI
30-1-10M[b]	53100	76600	132200	1.443
15-1-3M[c]	38900	66000	128900	1.699
5-1-2M[d]	15100	23400	43100	1.546

[a] Number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), z-averaged molecular weight (M_z), and polydispersity index (PDI) determined by GPC-MALLS system, d*n*/d*c* = 0.051.

[b] The same sample as entry 5 in Table 1.

[c] The same sample as entry 8 in Table 1.

[d] The same sample as entry 11 in Table 1.

Table S3 Synthesis of HPGMAs by RAFT-SCVP of ACDT and GMA at a feed ratio of 5.

Entry	Time(h)	C_{ACDT}(%)[a]	C_{GMA}(%)[a]	C_{total} (%)[b]	m[c]	DB[d]	M_n[e]	M_w[e]	M_p[e]	PDI[e]
1	0	-	-	-	-		-	-	-	-
2	0.33	4.47	11.5	10.32	12.86	0.0721	2200	2700	2500	1.20
3	0.5	5.82	15.76	14.10	13.47	0.0688	2400	3000	2600	1.24
4	0.75	7.72	18.00	16.28	11.65	0.0790	2600	3300	2700	1.27
5	1.5	10.72	36.81	32.46	17.16	0.0550	3000	4000	3000	1.35
6	3	12.92	59.40	51.65	22.98	0.0417	3500	3300	5100	1.43
7	4.5	17.21	64.82	56.88	18.83	0.0504	4100	6100	6000	1.49
8	5.5	21.69	70.15	62.07	16.17	0.0582	4500	6900	6600	1.53
9	6.5	32.58	77.57	70.07	11.90	0.0775	5100	8000	7500	1.56
10	7.5	55.30	87.91	82.47	7.95	0.1117	7300	10500	9200	1.43

[a] Conversions of GMA (C_{GMA}) and ACDT (C_{ACDT}) determined from ^{1}H NMR analysis.

[b] Total conversion of vinyl groups, $C_{total} = (5*C_{GMA} + C_{ACDT})/6$

[c] Unit ratio of GMA to ACDT in polymers, calculated from ^{1}H NMR results.

[d] Degree of branching (DB) calculated from ^{1}H NMR results.

[e] Number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), peak value of M_n (M_p), and polydispersity index (PDI) determined by GPC.

Table S4 Synthesis of HPGMAs by RAFT-SCVP of ACDT and GMA at a feed ratio of 15.

Entry	Time(h)	C_{GMA}(%)[a]	C_{ACDT}(%)[a]	C_{total} (%)[b]	m[c]	DB[d]	M_n[e]	M_w[e]	M_p[e]	PDI[e]
1	0	-	-	-	-		-	-	-	-
2	0.167	11.9	7.1	11.6	25.1	0.0383	5200	5900	6300	1.14
3	0.33	23.2	9.0	22.3	38.6	0.0252	5400	7100	7000	1.31
4	0.5	34.7	22.8	34.0	22.7	0.0420	5700	7600	7500	1.34
5	1	56.6	32.4	55.1	26.2	0.0368	6200	8700	8600	1.40
6	2	84.1	55.0	82.3	36.9	0.0418	7700	11900	11300	1.55
7	3	94.3	67.3	92.6	30.0	0.0454	9200	16200	14700	1.77
8	3.5	96.4	66.4	94.5	31.61	0.0439	12200	20000	17200	1.63
9	4.5	98.8	74.6	97.3	19.87	0.0480	15300	27900	23700	1.81
10	5	99.1	76.8	97.7	19.36	0.0491	20900	37000	28900	1.77

[a] Conversions of GMA (C_{GMA}) and ACDT (C_{ACDT}) determined from ^{1}H NMR analysis.

[b] Total conversion of vinyl groups, $C_{total} = (15*C_{GMA}+ C_{ACDT})/16$

[c] Unit ratio of GMA to ACDT in polymers, calculated from ^{1}H NMR results.

[d] Degree of branching (DB) calculated from ^{1}H NMR results.

[e] Number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), peak value of M_n (M_p), and polydispersity index (PDI) determined by GPC.

Table S5 Solubility of the polymers in common solvents[a].

Code	$CHCl_3$	DMF	H_2O
SHP-1	√	√	×
SHP-2	×	√	×
SHP-3	√	√	√
SHP-4	√	×	×
SHP-5	√	√	×
SHP-6	√	√	×
SHP-7	√	√	×
SHP-8	√	√	×
SHP-9	×	√	√
SHP-10	×	√	×
SHP-11	×	√	×
SHP-12	√	√	×
SHP-13	√	×	×
SHP-14	√	√	×
SHP-14a	×	√	×
SHP-14b	√	√	×
SHP-14c	×	√	×
SHP-14d	√	√	×
SHP-15	√	√	×
SHP-15a	×	√	×
SHP-15b	×	√	√

[a] "√" denotes soluble, "×" denotes insoluble.

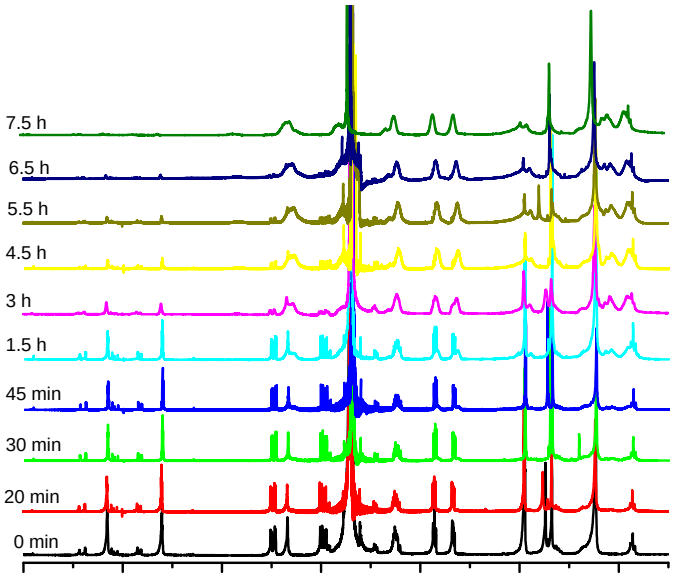

Fig. S1 ^{1}H NMR traces of HPGMAs at different sampling points during copolymerization at feed ratio of 5:1

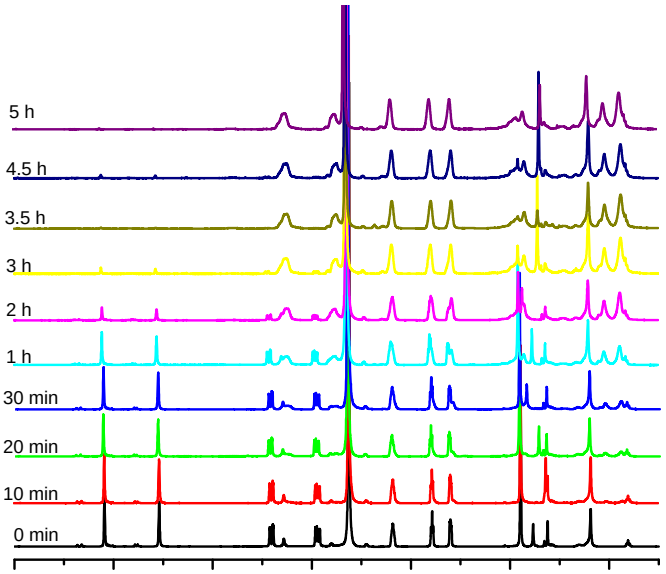

Fig. S2 ^{1}H NMR traces of HPGMAs at different sampling points during copolymerization at feed ratio of 15:1

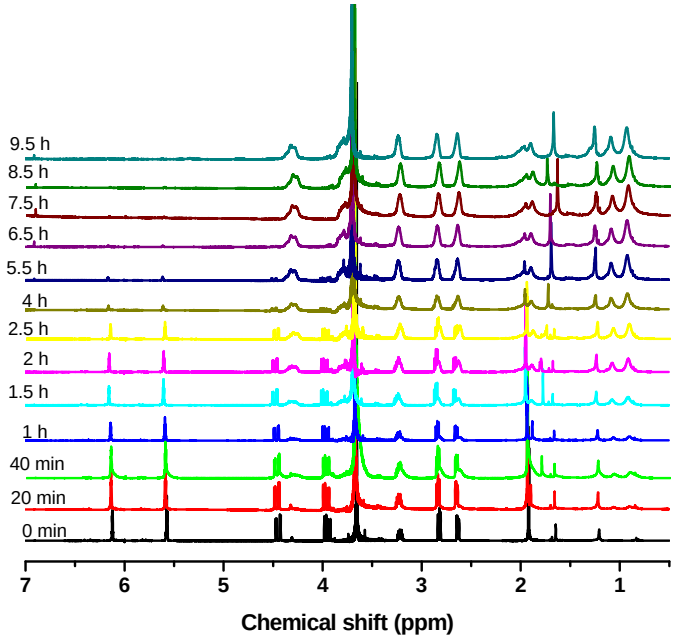

Fig. S3 ^{1}H NMR traces of HPGMAs at different sampling points during copolymerization at feed ratio of 30:1

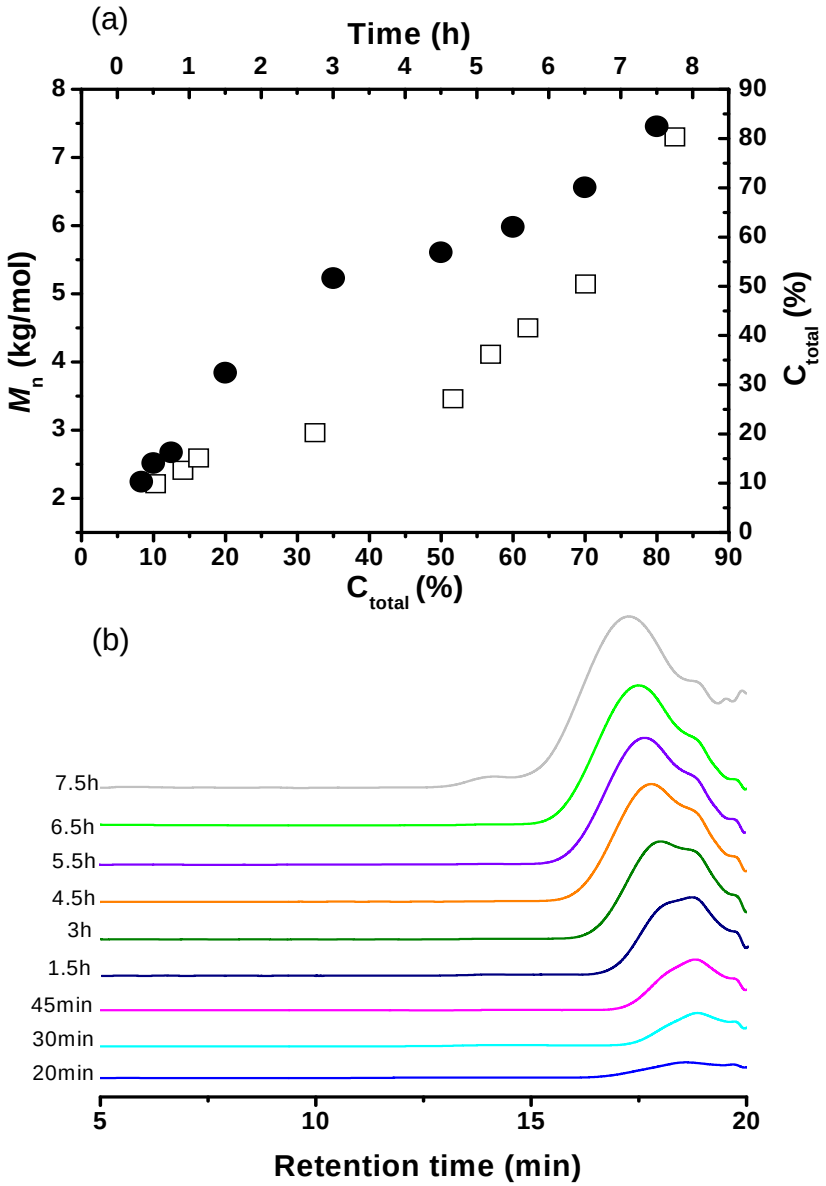

Fig. S4 Polymerization results for RAFT-SCVP of GMA and ACDT at a feed ratio of 5/1. (a) Hollow black squares (□): molecular weight (M_n) as a function of total vinyl group convertion (C_{total}); filled black circles (●): C_{total} as a function of polymerization time. (b) GPC traces of HPGMAs at different reaction time. The samples for ^{1}H NMR and GPC measurements were characterized without purification.

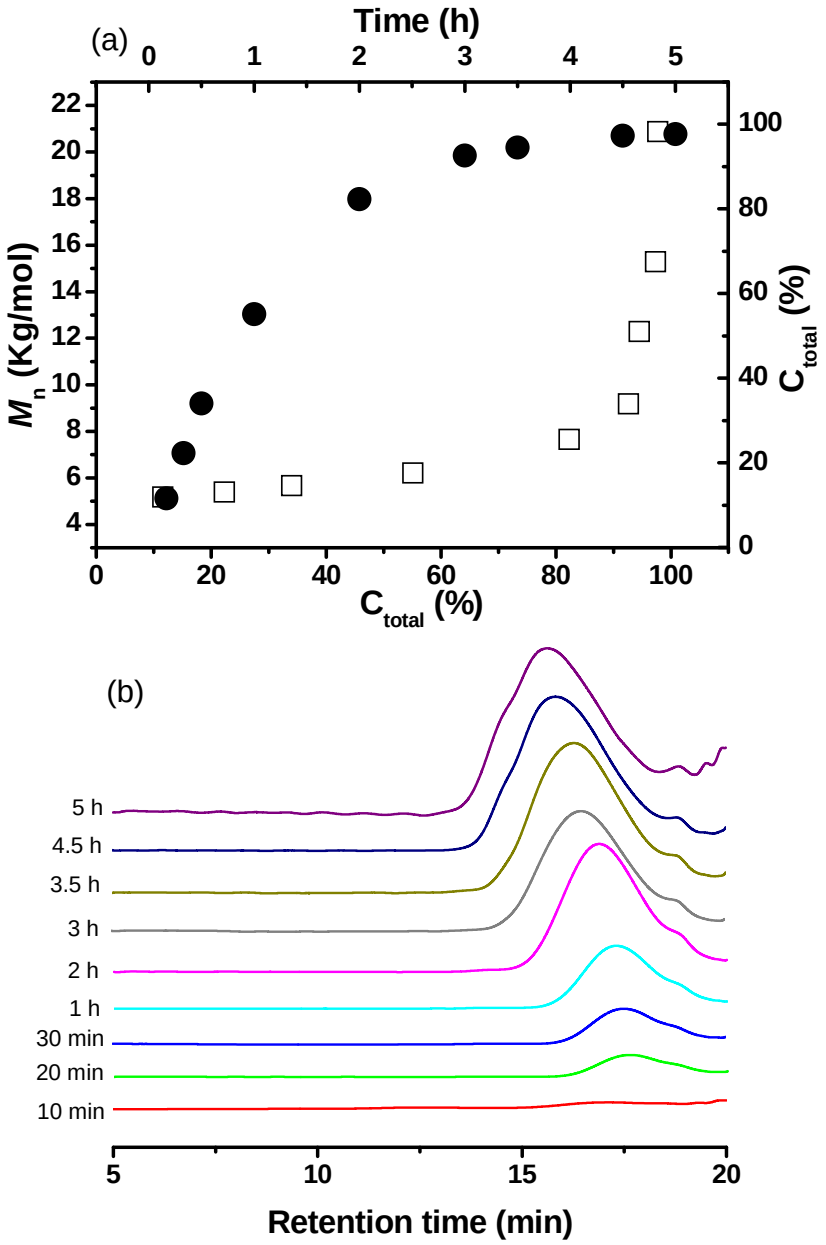

Fig. S5 Polymerization results for RAFT-SCVP of GMA and ACDT at a feed ratio of 15/1. (a) Hollow black squares (□): molecular weight (M_n) as a function of total vinyl group convertion (C_{total}); filled black circles (●): C_{total} as a function of polymerization time. (b) GPC traces of HPGMAs at different reaction time. The samples for ^{1}H NMR and GPC measurements were characterized without purification.

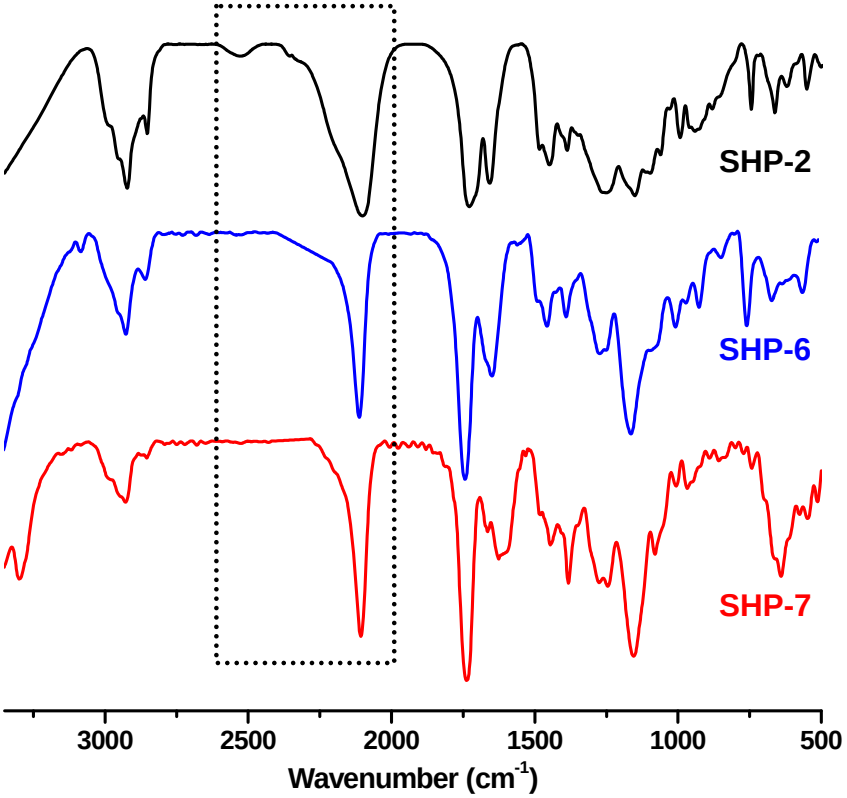

Fig. S6 FTIR spectra of SHP-2, SHP-6 and SHP-7.

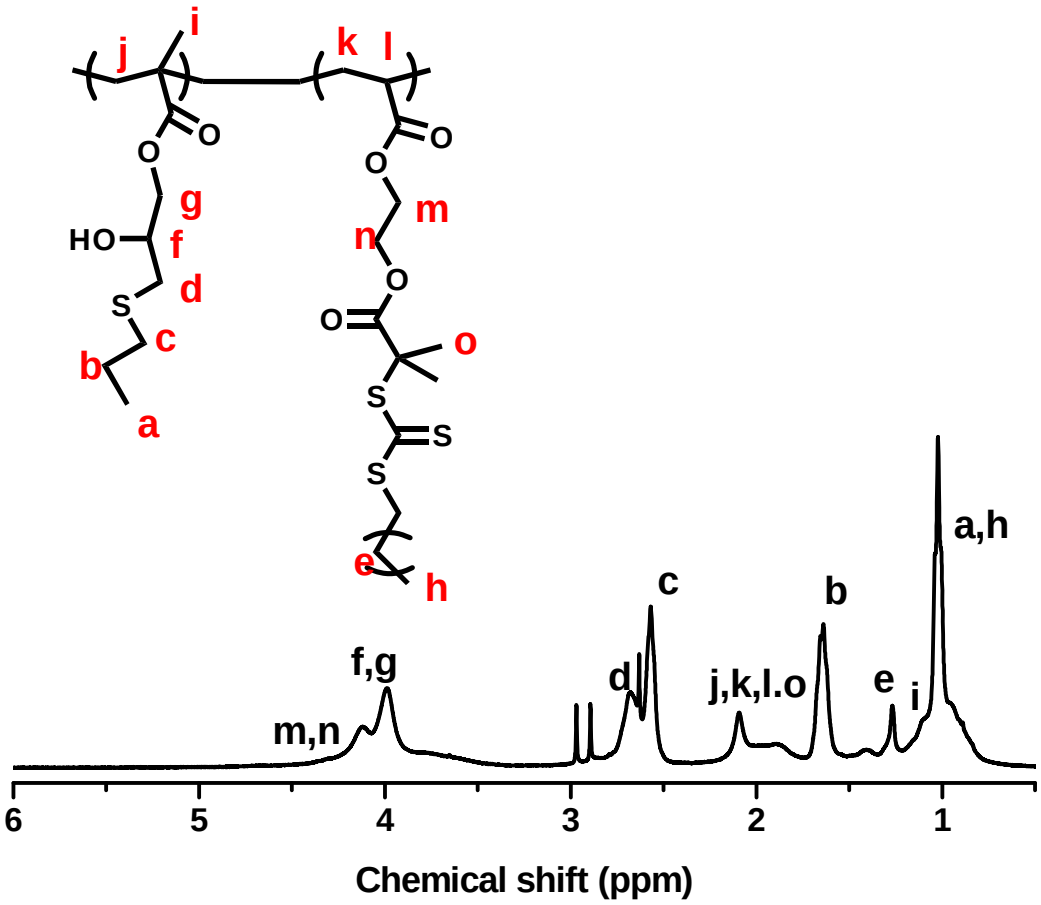

Fig. S7 ^{1}H NMR spectrum of SHP-12.

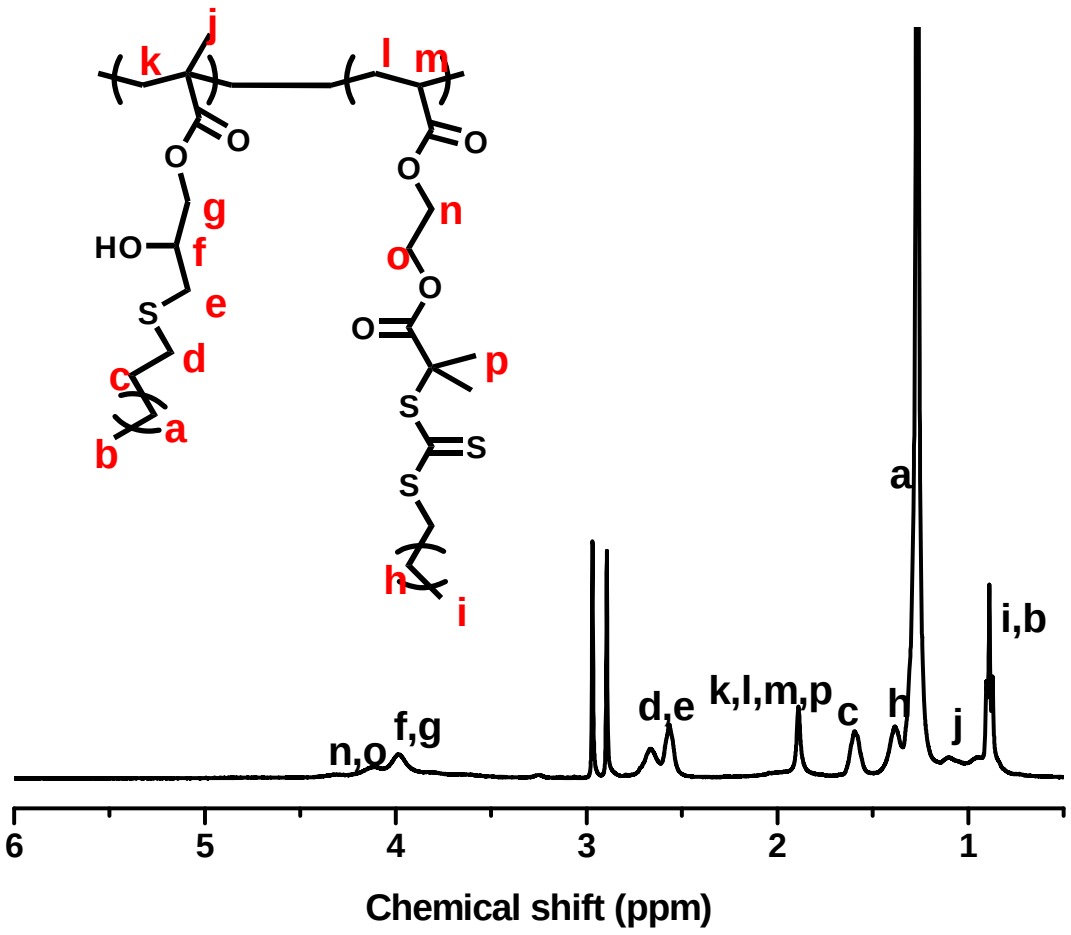

Fig. S8 ^{1}H NMR spectrum of SHP-13.