Highly Efficient Synthesis of Random Isobutylene/Alkenyl Styrene Copolymers with Pendant Vinyl Groups via Cationic Polymerization for Versatile Functionalization

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Electronic Supplementary Information (ESI)

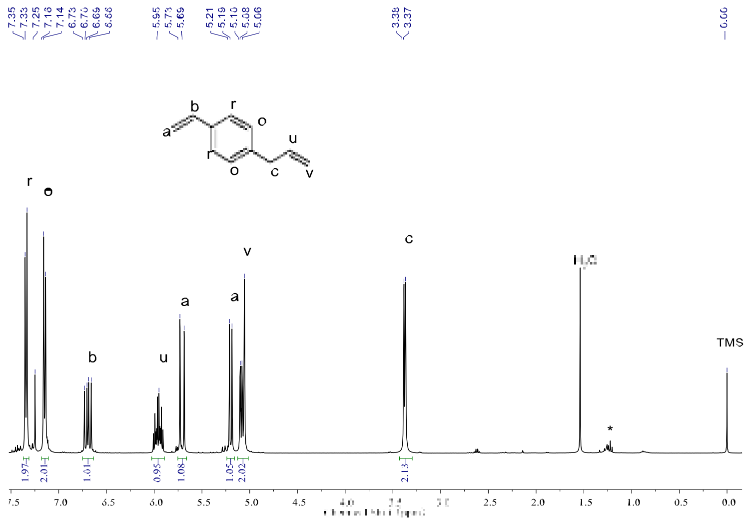

Fig. S1 ^{1}H NMR spectrum of 4-allylstyrene (400 MHz, $CDCl_3$). (* Impurity: *n*-hexane)

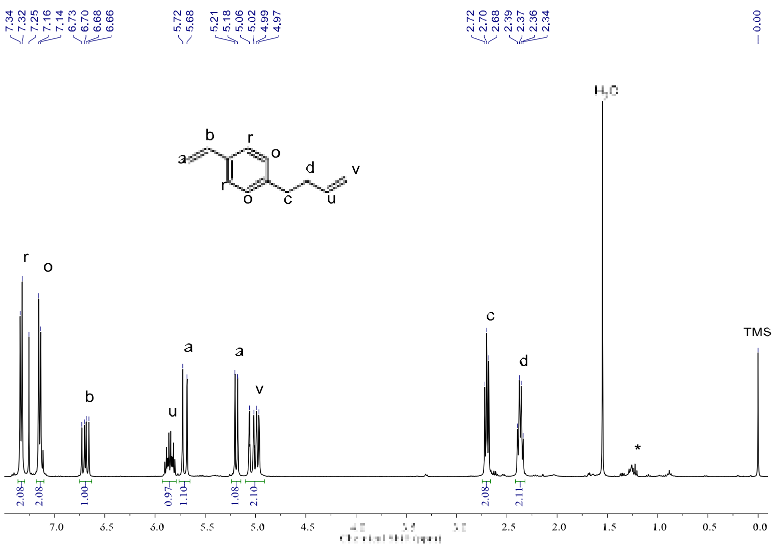

Fig. S2 ^{1}H NMR spectrum of *p*-(3-butenyl)-styrene (400 MHz, $CDCl_3$). (* Impurity: *n*-hexane)

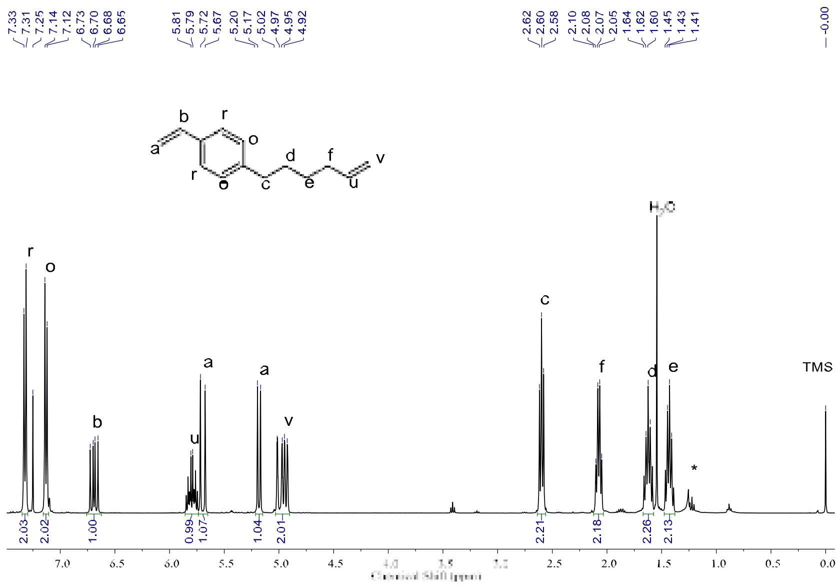

Fig. S3 ^{1}H NMR spectrum of *p*-(5-hexenyl)-styrene (400 MHz, $CDCl_3$). (* Impurity: *n*-hexane)

Table S1 Cationic copolymerization of IB and AS with *t*-BuCl/$FeCl_3$/*i*PrOH initiating system[a]

Samples	[AS]:[IB]	Yield (%)	$M_{n,theo}$ (g/mol)	M_n[c] (g/mol)	M_w/M_n	F_{AS}[d] (%)	BSB[e] (%)	SS[e] (%)	Others[e] (%)	C_{AS}[f] (%)	C_{IB}[f] (%)	T_g (°C)
PIB-13.1k[b]	0:100	92.9	1900	13100	1.37	-	-	-	-	-	-	-65.1
IBAS-12.4k-0.7	1:100	94.6	2000	12400	1.48	0.71	64	7	29	68.1	95.2	-63.6
IBAS-10.2k-2.1	3:100	91.7	2100	10200	1.56	2.15	45	10	45	68.4	93.4	-61.7
IBAS-8.3k-4.2	5:100	85.2	2200	8300	1.52	4.20	42	21	37	75.7	86.4	-60.2
IBAS-7.8k-8.6	10:100	86.4	2400	7800	1.69	8.60	33	47	20	82.2	87.4	-60.7
IBAS-7.8k-14.2	15:100	84.6	2700	7800	1.82	14.23	24	42	34	90.8	82.1	-59.5

[a] Conditions: [IB] = 1 mol/L, 20 mL *n*-hexane/CH_2Cl_2 = 60/40 (v/v), -80°C, polymerization time: 20 min. [b] [*i*PrOH]/[$FeCl_3$] = 1.4 (molar ratio), [*t*-BuCl]/[$FeCl_3$]/[IB] = 1/3/35 (molar ratio). [c] M_n determined by GPC with respect to a polystyrene standard. [d] Incorporation of AS determined by ^{1}H NMR with Eq. (1). [e] Molar ratio of monomer sequence calculated by Eq. (4), (5) and (6). [f] Conversion of AS and IB calculated by Eq. (7) and (8).

Table S2 Cationic copolymerization of IB and BS with *t*-BuCl/$FeCl_3$/*i*PrOH initiating system[a]

NO.	[BS]:[IB]	Yield (%)	$M_{n,theo}$ (g/mol)	M_n[c] (g/mol)	M_w/M_n	F_{BS}[d] (%)	BSB[e] (%)	Others[e] (%)	C_{BS}[f] (%)	C_{IB}[f] (%)
IBBS-5.7k-0.85[b]	1:100	96.8	1000	5700	1.45	0.85	71	29	83.4	97.2
IBBS-4.5k-2.45	3:100	86.1	1000	4500	1.39	2.45	68	32	73.0	87.2
IBBS-4.2k-4.68	5:100	86.3	1100	4200	1.39	4.68	70	30	85.0	86.5
IBBS-4.0k-10.56	10:100	87.9	1200	4000	1.42	10.56	51	49	99.8	84.5
IBBS-4.0k-15.83	15:100	85.5	1400	4000	1.43	15.83	43	57	99.6	79.5

[a] Conditions: [IB] = 1 mol/L, 20 mL *n*-hexane/CH_2Cl_2 = 60/40 (v/v), -80°C, polymerization time: 20 min. [b]

[iPrOH]/[$FeCl_3$] = 1.4 (molar ratio), [t-BuCl]/[$FeCl_3$]/[IB] = 1/3/18 (molar ratio). [c] M_n determined by GPC with respect to a polystyrene standard. [d] Incorporation of BS determined by ^{1}H NMR with Eq. (2). [e] Molar ratio of monomer sequence calculated by Eq. (4). [f] Conversion of BS and IB calculated by Eq. (9) and (10).

Table S3 Cationic copolymerization of IB and HS with t-BuCl/$FeCl_3$/iPrOH initiating system[a]

NO.	[HS]:[IB]	Yield (%)	$M_{n,theo}$ (g/mol)	M_n[c] (g/mol)	M_w/M_n	F_{HS}[d] (%)	BSB[e] (%)	Others[e] (%)	C_{HS}[f] (%)	C_{IB}[f] (%)
IBHS-14.1k-0.79[b]	1:100	99.3	2000	14100	1.43	0.79	65	35	80.1	99.9
IBHS-11.6k-1.86	3:100	86.2	2100	11600	1.49	1.86	53	47	56.5	89.1
IBHS-9.9k-3.42	5:100	81.5	2200	9900	1.46	3.42	58	42	60.3	85.0
IBHS-9.9k-6.45	10:100	86.3	2600	9900	1.48	6.45	49	51	64.5	93.5
IBHS-8.8k-11.39	15:100	74.3	2900	8800	1.48	11.39	36	64	66.9	78.1

[a] Conditions: [IB] = 1 mol/L, 20 mL n-hexane/CH_2Cl_2 = 60/40 (v/v), -80°C, polymerization time: 20 min. [b] [iPrOH]/[$FeCl_3$] = 1.4 (molar ratio), [t-BuCl]/[$FeCl_3$]/[IB] = 1/3/35 (molar ratio). [c] M_n determined by GPC with respect to a polystyrene standard. [d] Incorporation of HS determined by ^{1}H NMR with Eq. (3). [e] Molar ratio of monomer sequence calculated by Eq. (4). [f] Conversion of HS and IB calculated by Eq. (11) and (12).

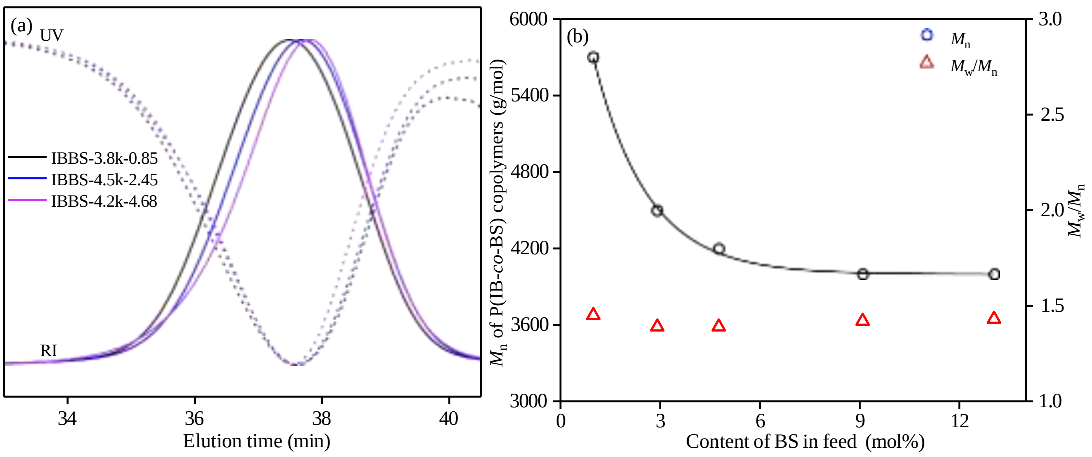

Fig. S4 (a) GPC traces of P(IB-*co*-BS) copolymers with various contents of BS units, (b) M_n and M_w/M_n of P(IB-*co*-BS) copolymers.

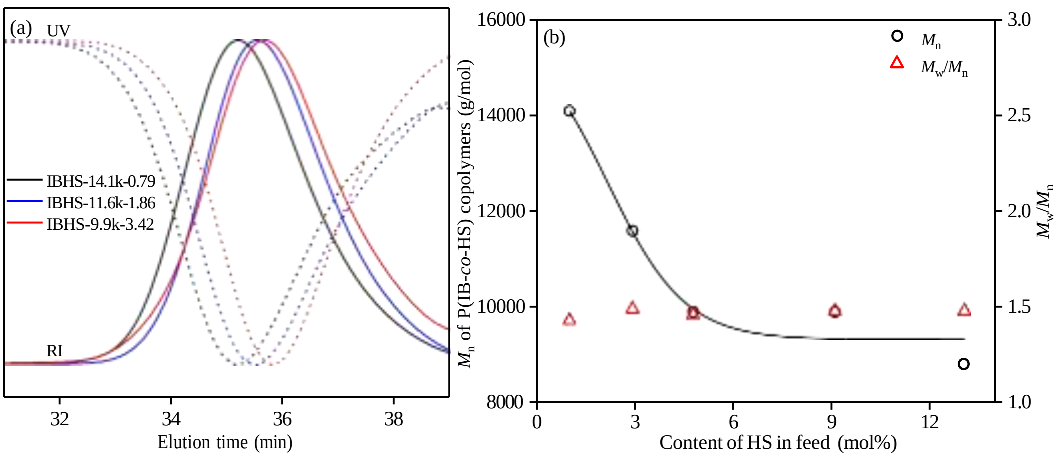

Fig. S5 (a) GPC traces of P(IB-*co*-HS) copolymers with various contents of HS units, (b) M_n and M_w/M_n of P(IB-*co*-HS) copolymers.

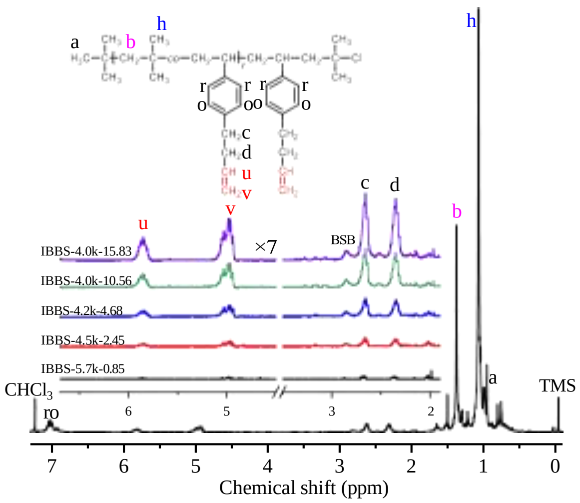

Fig. S6 ^{1}H NMR spectra of P(IB-*co*-BS) copolymers with various contents of BS units.

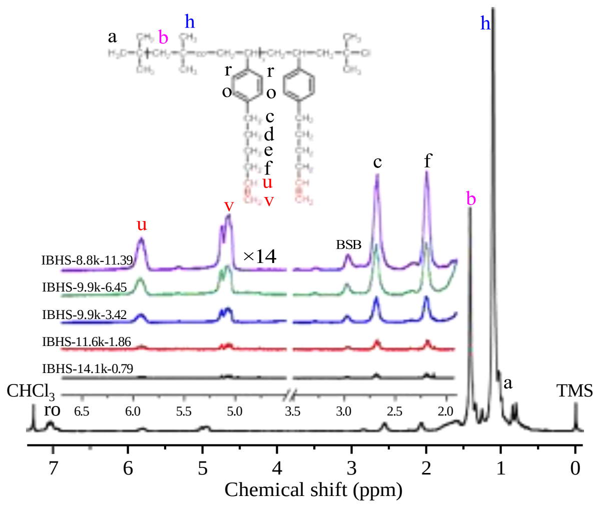

Fig. S7 ^{1}H NMR spectra of P(IB-*co*-HS) copolymers with various contents of HS units.

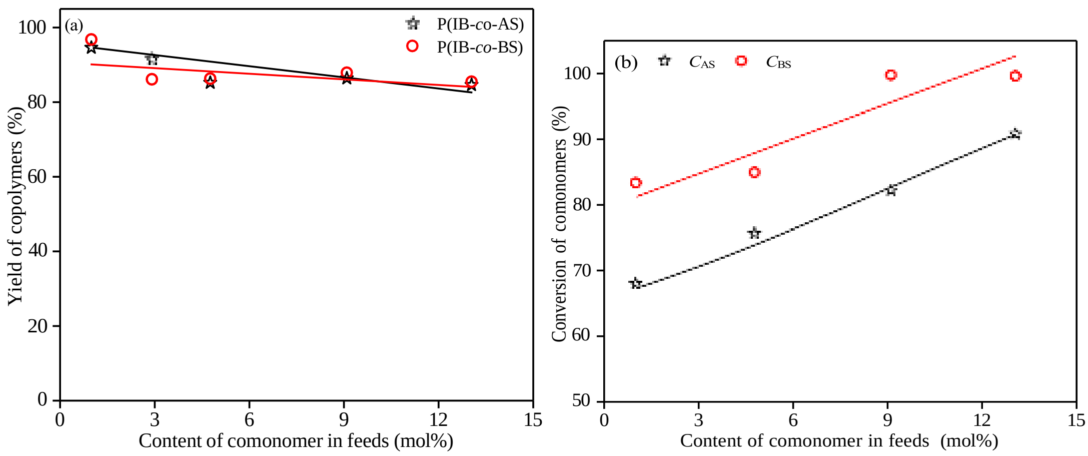

Fig. S8 (a) The P(IB-*co*-AS), P(IB-*co*-BS) and P(IB-*co*-HS) copolymers yields versus various feed ratios, (b) conversions of AS/BS/HS versus various feed ratios.

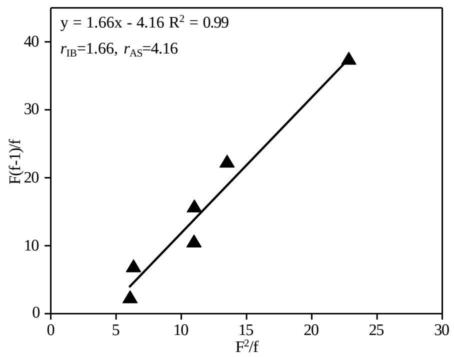

Fig. S9 Fineman-Ross plot for the copolymerization of IB with AS.

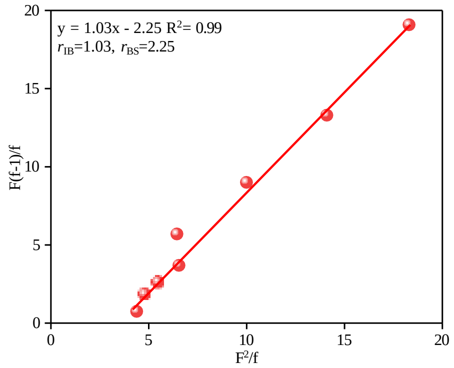

Fig. S10 Fineman-Ross plot for the copolymerization of IB with BS.

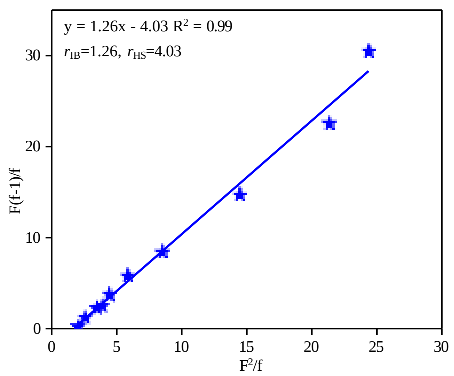

Fig. S11 Fineman-Ross plot for the copolymerization of IB with HS.

Table S4 Copolymerization of IB with AS with *t*-BuCl/$FeCl_3$/*i*PrOH initiating system at different reaction time [a]

NO.	Time (s)	Yield (%)	M_n[c] (g/mol)	M_w/M_n	F_{AS}[d] (%)	C_{AS}[f] (%)	C_{IB}[f] (%)	BSB[e] (%)	SS[e] (%)	Others[e] (%)
20230426-10s	10	4.0	-	-	1.75	2.4	4.1	23	30	47
20230416-30s	30	12.5	-	-	1.20	5.2	13	25	12	63
20230416-50s	50	24.4	-	-	1.30	11.4	25.4	36	23	41
20230416-70s	70	50.0	3500	1.21	1.65	30.3	51.5	36	29	35
20230416-85s	85	53.6	3900	1.33	1.76	30.5	55.4	36	10	54
20230416-100s	100	66.1	3900	1.30	1.83	42.1	68.0	31	16	53
20230416-115s	115	69.0	4000	1.35	1.91	44.1	70.9	41	22	37
20230416-130s	130	72.0	4100	1.41	1.94	47.9	73.8	31	16	53
20230416-165s	165	80.9	4200	1.37	1.96	54.6	82.9	33	29	38
20230416-200s	200	83.7	4200	1.41	2.2	60.8	85.4	30	24	47
20230416-250s	250	84.3	4200	1.56	2.27	63.8	85.8	30	18	52
20230416-300s	300	88.5	4300	2.73	2.29	62.3	90.6	35	21	44
20230416-400s	400	94.0	4700	1.72	2.29	68.8	95.9	33	25	42

[a] Conditions: [IB] = 0.5 mol/L, [AS]/[IB] = 3/100 (molar ratio), 10 mL *n*-hexane/CH_2Cl_2 = 60/40 (v/v), -80 °C. [b] [*i*PrOH]/[$FeCl_3$] = 1.4 (molar ratio), [*t*-BuCl]/[$FeCl_3$]/[IB] = 1/3/18 (molar ratio). [c] M_n determined by GPC with respect to a polystyrene standard. [d] Incorporation of AS determined by ^{1}H NMR with Eq. (1). [e] Molar ratio of monomer sequence calculated by Eq. (4), (5) and (6). [f] Conversion of AS and IB were calculated according to Eq. (7) and Eq. (8).

Table S5 Copolymerization of IB with BS with *t*-BuCl/$FeCl_3$/*i*PrOH initiating system at different reaction time [a]

NO.	Time (s)	Yield (%)	M_n[c] (g/mol)	M_w/M_n	F_{BS}[d] (%)	C_{BS}[f] (%)	C_{IB}[f] (%)	BSB[e] (%)	Others[e] (%)
20231011-5s[b]	5	0.9	-	-	0.72	0.4	0.9	52	48
20231011-10s	10	2.3	-	-	0.86	1.4	2.3	32	68
20231011-15s	15	10.9	-	-	0.88	6.5	11.1	50	50
20231011-20s	20	28.1	-	-	1.04	19.9	28.4	39	61
20231011-25s	25	29.8	3800	1.25	1.03	20.9	30.1	36	64
20231011-30s	30	33.8	3900	1.26	1.08	24.9	34.2	48	52
20231011-35s	35	57.1	4400	1.29	1.12	43.5	57.7	42	58
20231011-40s	40	60.4	4400	1.29	1.19	48.8	60.8	42	58
20231011-45s	45	65.6	4500	1.34	1.09	48.7	66.3	58	42
20231011-50s	50	79.5	4500	1.37	1.20	64.9	80.1	52	48
20231011-60s	60	79.7	4800	1.34	1.25	67.6	80.2	47	53
20231011-100s	100	99.2	4900	1.43	1.22	82.2	99.9	54	46

[a] Conditions: [IB] = 0.5 mol/L, [BS]/[IB] = 1.5/100 (molar ratio), 10 mL *n*-hexane/CH_2Cl_2 = 60/40 (v/v), -80 °C. [b] [*i*PrOH]/[$FeCl_3$] = 1.4 (molar ratio), [*t*-BuCl]/[$FeCl_3$]/[IB] = 1/3/18 (molar ratio). [c] M_n determined by GPC with respect to a polystyrene standard. [d] Incorporation of BS determined by ^{1}H NMR with Eq. (2). [e] Molar ratio of monomer sequence calculated by Eq. (4). [f] Conversion of BS and IB were calculated according to Eq. (9) and Eq. (10).

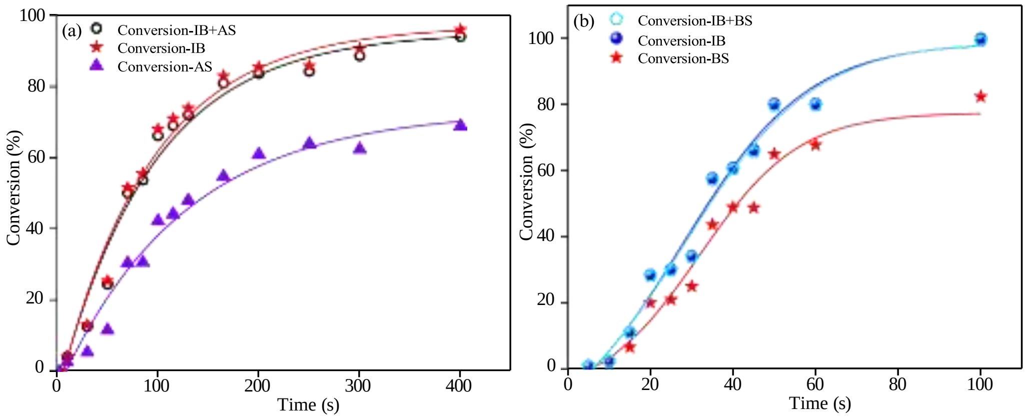

Fig. S12 (a)Plots of P(IB-*co*-AS) yields and conversions of IB and AS versus reaction time and (b)Plots of P(IB-*co*-BS) yields and conversions of IB and BS versus reaction time.

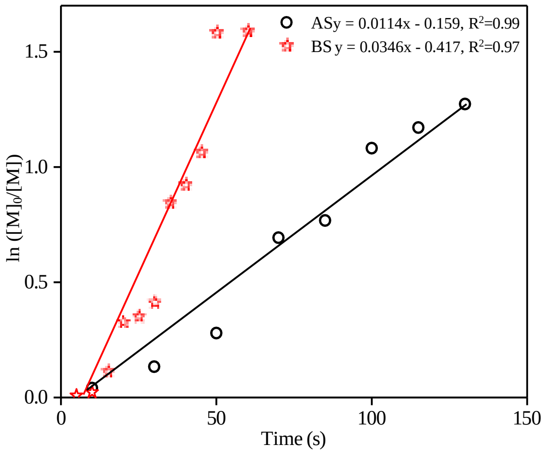

Fig. S13 First order ln $([M]_0/[M])$-time plots for the copolymerization of IB with AS or BS.

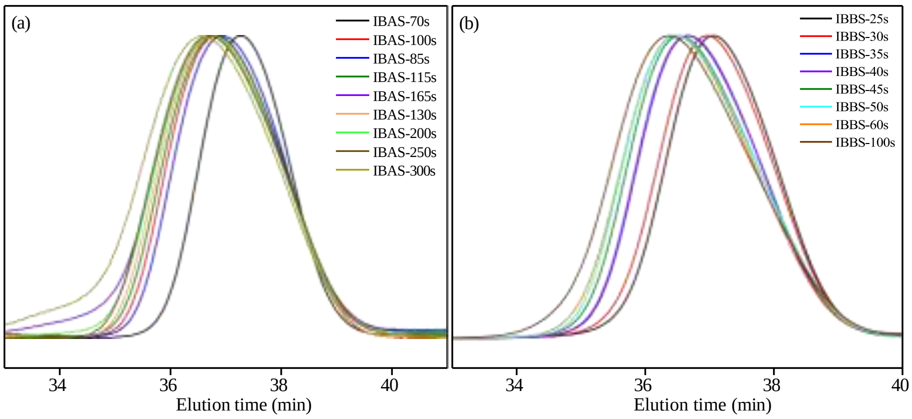

Fig. S14 (a)GPC traces of P(IB-*co*-AS) and (b)GPC traces of P(IB-*co*-BS) obtained with *t*-BuCl/$FeCl_3$/*i*PrOH initiating system at different reaction time

Table S6 AMI and IMA experiments of IB with AS by using *t*-BuCl/$FeCl_3$/*i*PrOH initiating system [a]

j	W_p g	Yield (%)	M_n[c] (g/mol)	M_w/M_n	F_{AS}[d] (%)	BSB[e] (%)	SS[e] (%)	Others[e] (%)	C_{AS}[f] (%)	C_{IB}[f] (%)
1	0.27	74.8	6000	1.43	1.95	51	47	2	50.8	76.7
2	0.61	84.9	8200	1.64	2.59	42	37	21	75.9	85.6
3	0.98	90.9	9900	1.54	2.41	55	40	5	75.8	92.1
4	1.44	99.8	12200	1.49	2.78	55	33	12	95.4	100
5	1.79	99.4	13300	1.51	2.47	54	29	17	84.8	100
6	2.17	99.9	16700	1.48	2.18	64	35	1	75.6	100
7	0.34	92.6	5600	1.51	2.12	67	30	3	68.2	94.5
8	0.64	88.0	6200	1.50	1.87	64	34	2	57.6	90.7
9	0.94	86.9	9500	1.57	2.27	47	30	23	68.4	88.4
10	1.34	92.9	10800	1.53	2.10	60	38	2	67.8	94.9
11	1.74	96.6	12600	1.53	2.15	60	38	2	72.1	98.5
12	2.19	99.9	13100	1.53	2.37	55	18	27	81.9	100

[a] Conditions: [IB] = 1 mol/L, -80 °C, *n*-hexane/CH_2Cl_2 = 60/40 (v/v), [AS]/[IB] = 3/100 (molar ratio). [b] [*i*PrOH]/[$FeCl_3$] = 1.4 (molar ratio), [*t*-BuCl]/[$FeCl_3$] = 1/5 (molar ratio). [c] M_n determined by GPC with respect to a polystyrene standard. [d] Incorporation of AS is determined by ^{1}H NMR with Eq. (1). [e] Molar ratio of monomer sequence calculated by Eq. (4), (5) and (6). [f] Conversion of AS and IB were calculated according to Eq. (7) and Eq. (8).

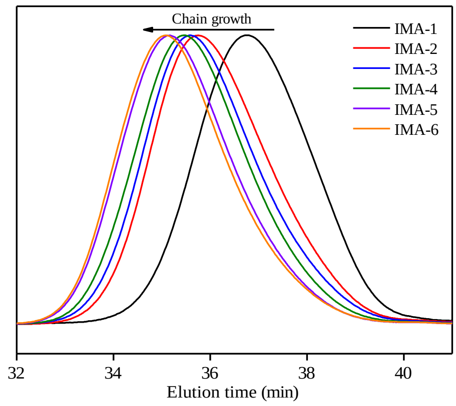

Fig. S15 GPC traces of P(IB-*co*-AS) copolymers obtained in IMA experiments.

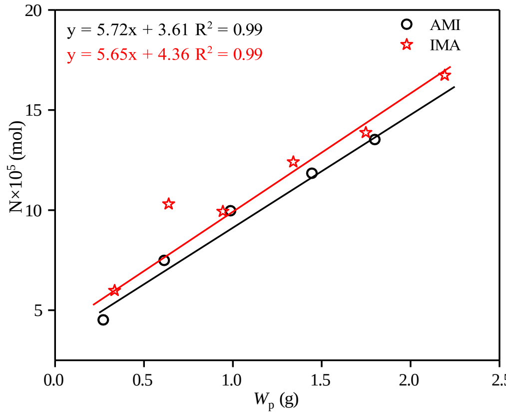

Fig. S16 Number of polymer chains versus W_p in AMI and IMA experiments.

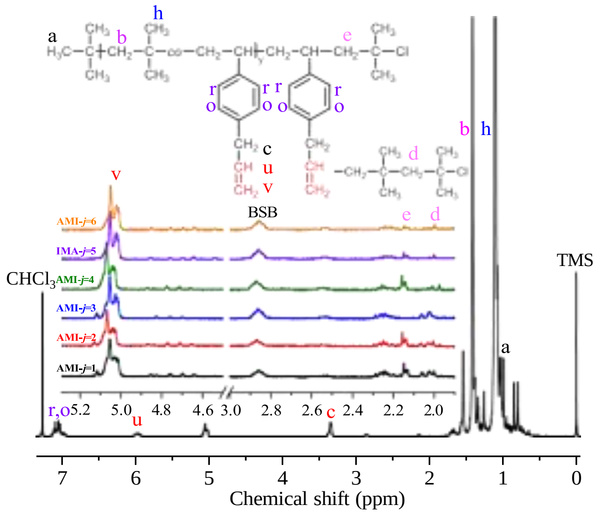

Fig. S17 ^{1}H NMR spectra of P(IB-*co*-AS) copolymers in AMI experiments.

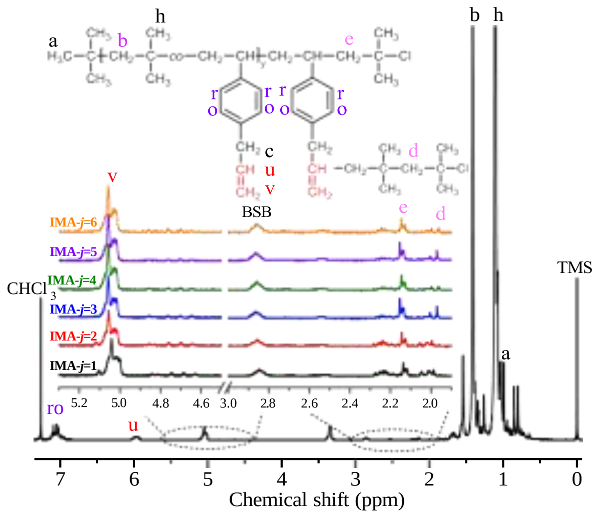

Fig. S18 ^{1}H NMR spectra of P(IB-*co*-AS) copolymers in IMA experiments.

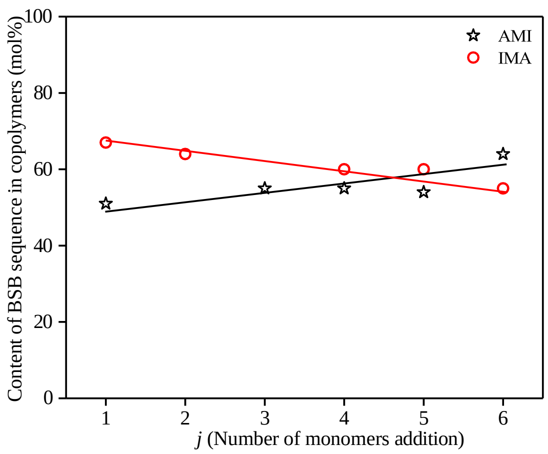

Fig. S19 Evolution content of BSB sequence in P(IB-*co*-AS) copolymers as a function of *j* in AMI and IMA experiments.

Table S7 Effect of temperature on the copolymerization of IB with AS initiated with *t*-BuCl/$FeCl_3$/*i*PrOH system [a]

Samples	T (°C)	Yield (%)	M_n[c] (g/mol)	M_w/M_n	F_{AS}[d] (%)	BSB[e] (%)	SS[e] (%)	Others[e] (%)	C_{AS}[f] (%)	C_{IB}[f] (%)
IBAS-4.7k-2.24[b]	-80	82.6	4700	1.47	2.32	42	29	29	66.4	83.9
IBAS-4.7k-2.18	-75	78.9	4700	1.50	2.25	42	32	26	61.5	80.3
IBAS-4.5k-2.17	-70	82.7	4500	1.47	2.03	47	40	13	58.5	84.6
IBAS-4.3k-2.34	-65	79.9	4300	1.45	2.19	1	35	64	60.9	81.4
IBAS-4.0k-2.08	-60	80.5	4000	1.43	2.12	58	28	14	59.4	82.1
IBAS-3.6k-2.34	-55	75.3	3600	1.40	2.21	69	30	1	57.9	76.7
IBAS-3.2k-2.59	-50	74.7	3200	1.39	2.45	65	27	8	63.2	75.6
IBAS-2.8k-2.64	-45	62.7	2800	1.38	2.46	78	21	1	53.2	63.4
IBAS-2.54k-2.76	-40	60.8	2500	1.34	2.52	75	18	7	52.9	61.5
IBAS-2.2k-2.66	-35	49.3	2200	1.31	2.66	81	18	1	45.3	49.7
IBAS-2.0k-3.31	-30	40.4	2000	1.27	3.32	76	22	2	45.8	40.0

[a] Conditions: [IB] = 1 mol/L, 10 mL *n*-hexane/CH_2Cl_2 = 60/40 (v/v), polymerization time: 20 min, [*i*PrOH]/[$FeCl_3$] = 1.4 (molar ratio). [b] [*t*-BuCl]/[$FeCl_3$]/[IB] = 1/3/18 (molar ratio). [c] M_n determined by GPC with respect to a polystyrene standard. [d] Incorporation of AS is determined by ^{1}H NMR with Eq. (1). [e] Molar ratio of monomer sequence calculated by Eq. (4), (5) and (6). [f] Conversion of AS and IB were calculated according to Eq. (7) and Eq. (8).

Table S8 Effect of temperature on the copolymerization of IB with BS initiated with *t*-BuCl/$FeCl_3$/*i*PrOH system [a]

NO.	T (°C)	Yield (%)	M_n[c] (g/mol)	M_w/M_n	F_{BS}[d] (%)	BSB[e] (%)	Others[e] (%)	C_{BS}[f] (%)	C_{IB}[f] (%)
IBBS-5.7k-2.07[b]	-80	88.3	5700	1.49	2.07	54	46	63.6	90.3
IBBS-5.9k-2.49	-75	76.4	5900	1.45	2.49	54	46	65.8	77.3
IBBS-5.0k-2.43	-70	77.9	5000	1.41	2.43	44	56	65.5	78.9
IBBS-4.6k-2.29	-65	79.7	4600	1.48	2.29	58	42	63.3	81. 1
IBBS-4.7k-2.28	-60	78.3	4700	1.45	2.28	72	28	61.9	79.7
IBBS-4.3k-2.48	-55	77.2	4300	1.41	2.48	79	21	66.2	78.1
IBBS-3.9k-2.37	-50	75.2	3900	1.37	2.37	72	28	61.7	76.3
IBBS-3.6k-2.46	-45	70.3	3600	1.38	2.46	58	42	59.8	71.2
IBBS-2.7k-2.65	-40	68.8	2700	1.38	2.65	63	37	62.9	69.3
IBBS-2.3k-2.63	-35	62.9	2300	1.34	2.63	80	20	57.1	63.4

[a] Conditions: [IB] = 1 mol/L, 10 mL *n*-hexane/CH_2Cl_2 = 60/40 (v/v). [b] [*i*PrOH]/[$FeCl_3$] = 1.4 (molar ratio), polymerization time: 20 min, [*t*-BuCl]/[$FeCl_3$]/[IB] = 1/3/18 (molar ratio). [c] M_n determined by GPC with respect to a polystyrene standard. [d] Incorporation of BS is determined by ^{1}H NMR with Eq. (2). [e] Molar ratio of monomer sequence calculated by Eq. (4). [f] Conversion of BS and IB were calculated according to Eq. (9) and Eq. (10).

Table S9 Effect of temperature on the copolymerization of IB with HS initiated with *t*-BuCl/$FeCl_3$/*i*PrOH system [a]

NO.	T (°C)	Yield (%)	M_n[c] (g/mol)	M_w/M_n	F_{HS}[d] (%)	BSB[e] (%)	Others[e] (%)	C_{HS}[f] (%)	C_{IB}[f] (%)
IBHS-7.3k-2.12[b]	-80	86.7	7300	1.52	2.12	46	54	64.2	88.9
IBHS-7.1k-2.04	-75	90.7	7100	1.51	2.04	50	50	64.7	93.2
IBHS-6.7k-1.84	-70	96.3	6700	1.53	1.84	54	46	62.3	99.7
IBHS-6.3k-2.08	-65	95.3	6300	1.48	2.08	71	29	69.3	97.9
IBHS-5.4k-1.92	-60	78.9	5400	1.47	1.92	72	28	53.1	81.4
IBHS-5.0k-2.03	-55	69.7	5000	1.46	2.03	67	33	49.5	71.7
IBHS-4.3k-2.15	-50	74.7	4300	1.46	2.15	64	36	56.0	76.5
IBHS-3.4k-2.3	-45	70.7	3400	1.53	2.3	71	29	56.6	72.1
IBHS-3.2k-2.26	-40	68.3	3200	1.50	2.26	69	31	53.8	69.8
IBHS-2.8k-2.47	-35	63.2	2800	1.41	2.47	67	33	54.1	64.1
IBHS-2.1k-2.41	-30	55.1	2100	1.40	2.41	76	24	46.1	55.9

[a] Conditions: [IB] = 1 mol/L, 10 mL *n*-hexane/CH_2Cl_2 = 60/40 (v/v), polymerization time: 20 min, [*i*PrOH]/[$FeCl_3$] = 1.4 (molar ratio). [b] [*t*-BuCl]/[$FeCl_3$]/[IB] = 1/3/18 (molar ratio). [c] M_n determined by GPC with respect to a polystyrene standard. [d] Incorporation of HS is determined by ^1H NMR with Eq. (3). [e] Molar ratio of monomer sequence calculated by Eq. (4). [f] Conversion of HS and IB were calculated according to Eq. (11) and Eq. (12).

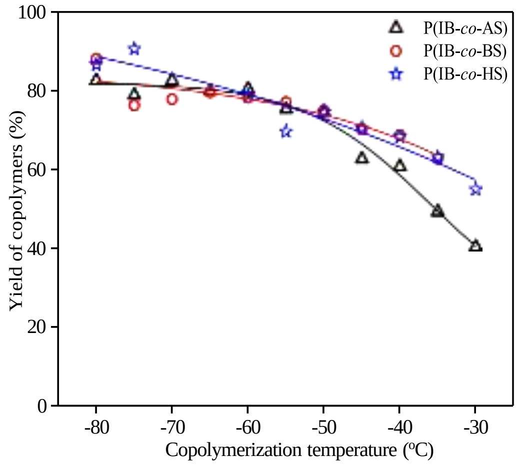

Fig. S20 P(IB-*co*-AS), P(IB-*co*-BS) and P(IB-*co*-HS) copolymer yields at different copolymerization temperatures.

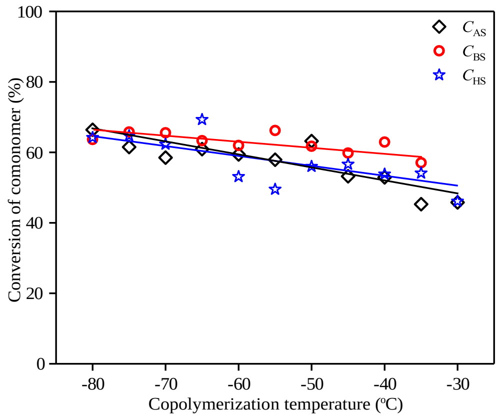

Fig. S21 Conversions of AS, BS and HS as a function of copolymerization temperature.

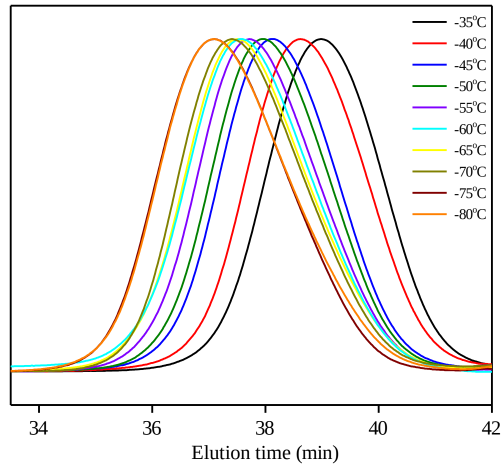

Fig. S22 GPC curves of P(IB-*co*-BS) obtained at different copolymerization temperatures with *t*-BuCl/$FeCl_3$/*i*PrOH initiating system.

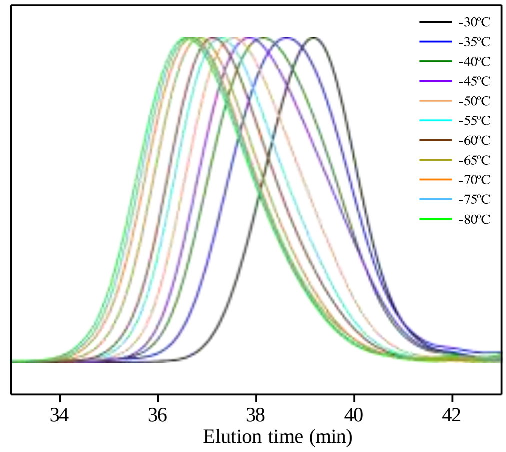

Fig. S23 GPC curves of P(IB-*co*-HS) copolymers obtained at different copolymerization temperatures with *t*-BuCl/$FeCl_3$/*i*PrOH initiating system.

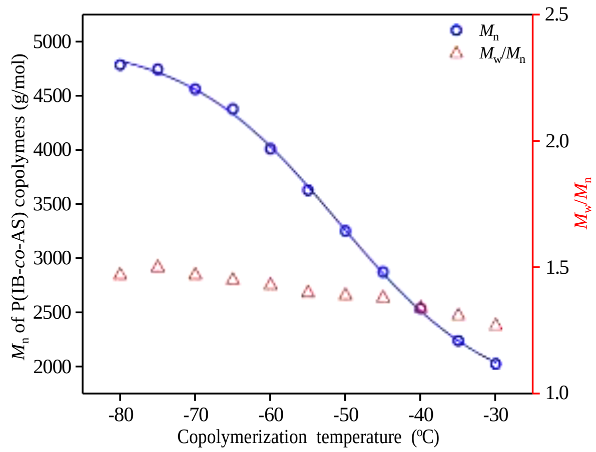

Fig. S24 M_n and M_w/M_n of P(IB-*co*-AS) copolymers obtained at different copolymerization temperatures.

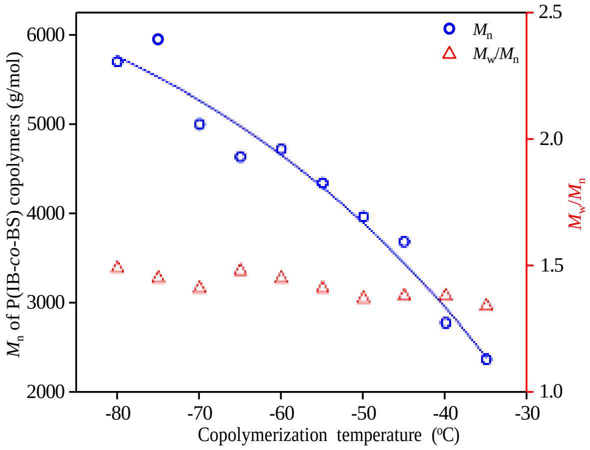

Fig. S25 M_n and M_w/M_n of P(IB-*co*-BS) copolymers obtained at different copolymerization temperatures.

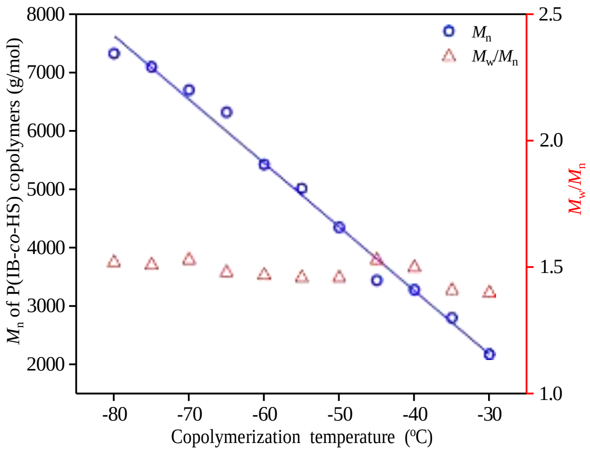

Fig. S26 M_n and M_w/M_n of P(IB-*co*-HS) copolymers obtained at different copolymerization temperatures.

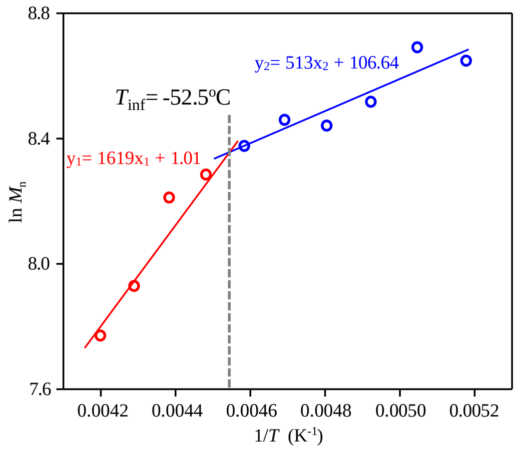

Fig. S27 Arrhenius plots of ln M_n versus 1/T for the copolymerization of IB with BS by using *t*-BuCl/$FeCl_3$/*i*PrOH initiating system.

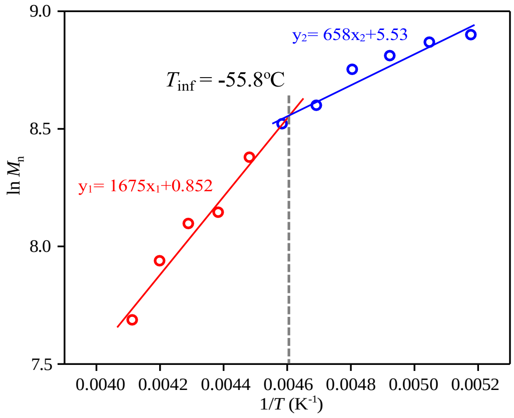

Fig. S28 Arrhenius plots of ln M_n versus 1/*T* for the copolymerization of IB with HS by using *t*-BuCl/$FeCl_3$/*i*PrOH initiating system

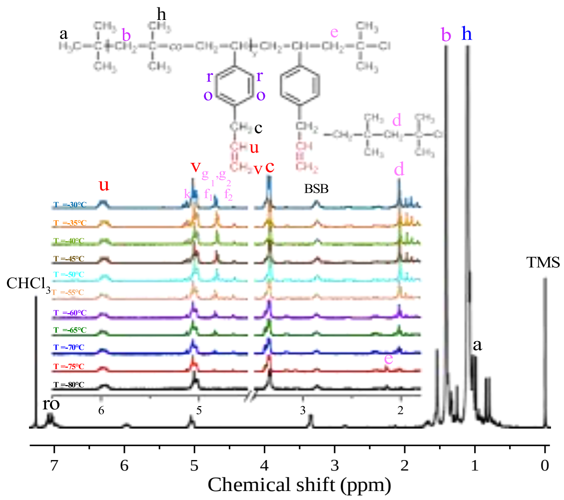

Fig. S29 [1]H NMR spectra of P(IB-*co*-AS) copolymers at different copolymerization temperatures.

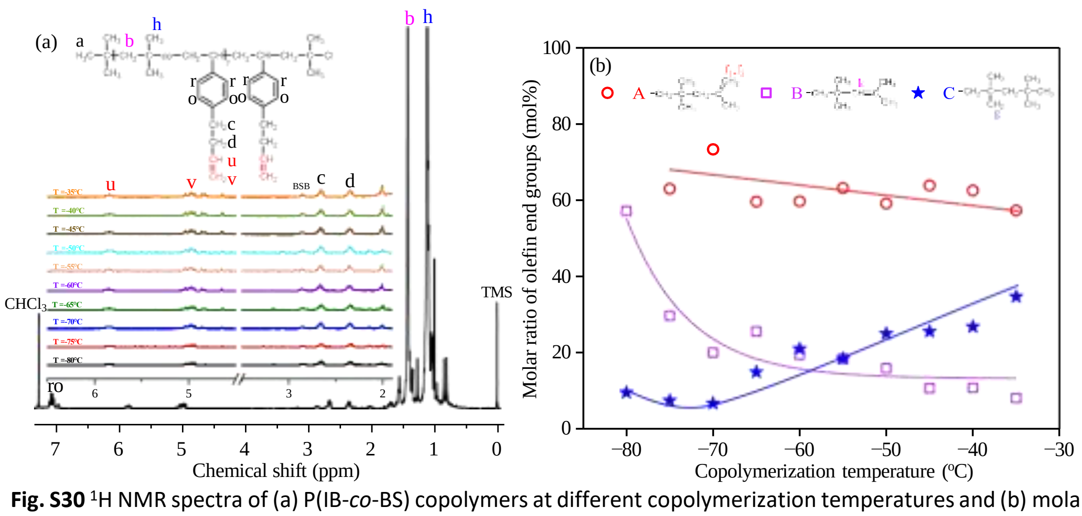

Fig. S30 [1]H NMR spectra of (a) P(IB-*co*-BS) copolymers at different copolymerization temperatures and (b) molar ratio of olefin end groups in P(IB-*co*-BS) copolymers at different copolymerization temperatures.

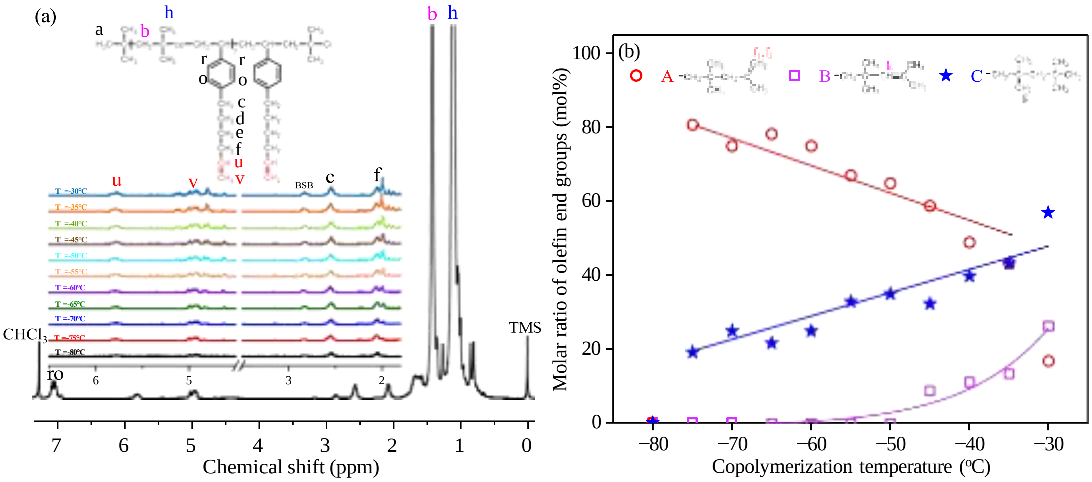

Fig. S31 [1]H NMR spectra of (a) P(IB-*co*-HS) copolymers at different copolymerization temperatures and (b) molar ratio of olefin end groups in P(IB-*co*-HS) copolymers at different copolymerization temperatures.

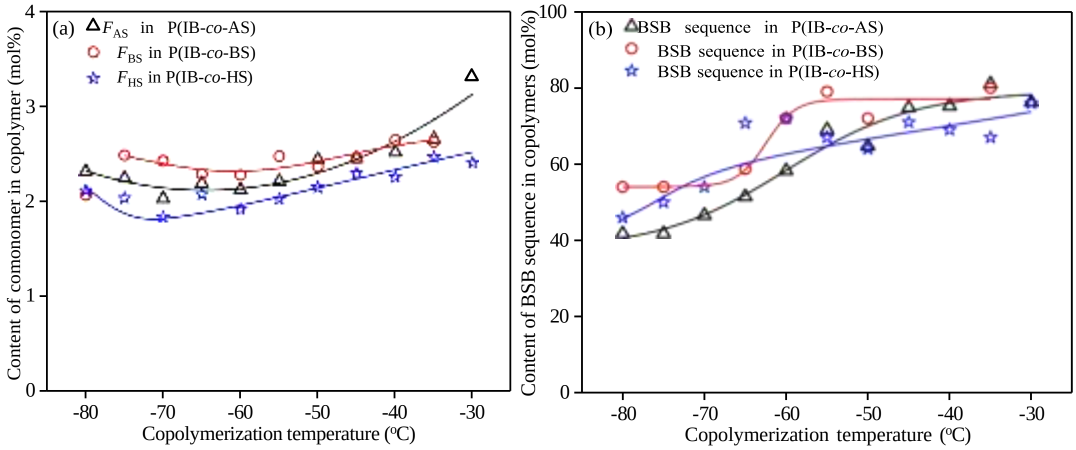

Fig. S32 (a) Content of AS/BS/HS units and (b) content of BSB sequence in copolymers as a function of copolymerization temperature.

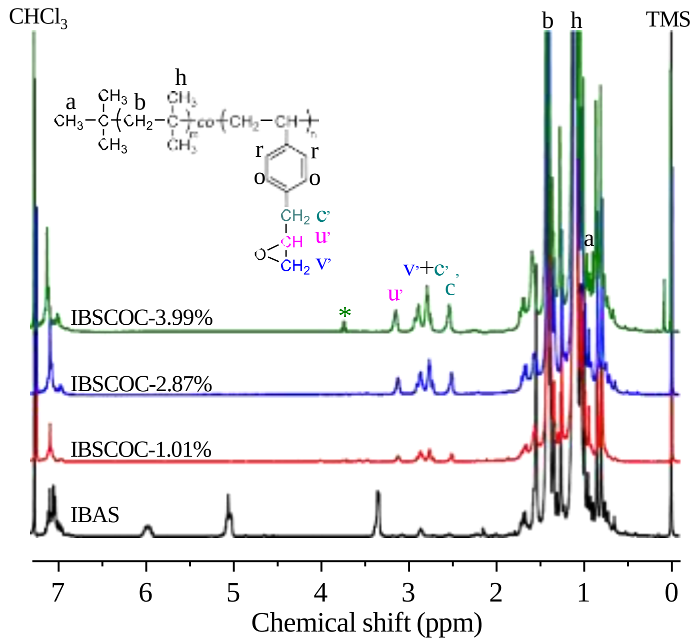

Fig. S33 [1]H NMR spectra of epoxy functionalized P(IB-*co*-AS) with various contents of epoxy groups. (* Impurity: ethanol)