Electronic Supplementary Information

Ultrafast and Green Ionic Liquid-Mediated Controlled Cationic Polymerization Towards Amphiphilic Diblock Copolymers

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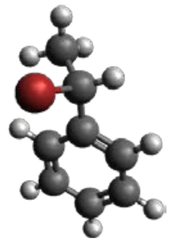
A. Computational details

The optimized coordinates, geometries, and energy of all the systems are given below.

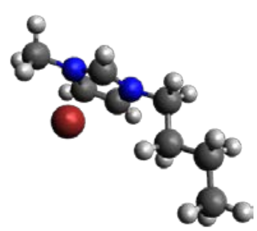
1. Optimized coordinates, energy, and optimized geometries of all the systems

   a. Initiator (Energy: -2884.81 a.u.)



C	2.860723	-0.7153291	0.893120
C	1.541988	-0.3958184	1.224941
C	0.713814	0.2773295	0.314302
C	1.234294	0.6169067	-0.945110
C	2.549335	0.2958854	-1.279701
C	3.368297	-0.3695798	-0.360979
H	3.490777	-1.2367692	1.615456
H	1.145934	-0.6715560	2.205149
H	0.599553	1.1203848	-1.676164
H	2.938191	0.5636686	-2.263499
H	4.396924	-0.6199711	-0.624857
C	-0.687803	0.6363226	0.716292
H	-0.848398	0.3753872	1.768443
C	-1.110139	2.0714677	0.446823
H	-2.137131	2.2478716	0.790342
H	-0.435028	2.7527713	0.989211
H	-1.057550	2.3182265	-0.621292
Br	-1.996573	-0.6014845	-0.213666

   b. $[BMIM]^+[Br]^-$ (energy: -2997.98 a.u.)



C	1.123855	0.715876	-0.793814
C	0.519523	2.281917	0.664592
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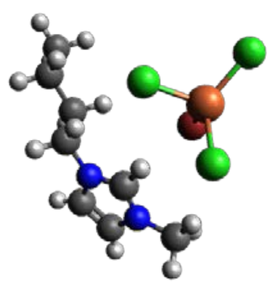
N	2.215947	1.064511	-0.077829

H	1.111862	0.036600	-1.633576
H	-0.146593	2.964125	1.176867
H	2.541290	2.400474	1.591437
C	3.461966	0.306097	-0.105220
H	4.141906	0.716603	0.648280
H	3.210001	-0.744726	0.121175
H	3.930180	0.376527	-1.095121
C	-1.288333	1.346730	-0.866942
C	-2.158741	0.587369	0.138445
H	-1.241033	0.799382	-1.818480
H	-1.688312	2.350623	-1.078280
C	-3.562957	0.319659	-0.413276
H	-1.648076	-0.360733	0.380189
H	-2.229965	1.168517	1.073832
C	-4.454710	-0.416103	0.590601
H	-4.041530	1.270966	-0.706684
H	-3.477928	-0.280485	-1.334866
H	-5.451084	-0.612617	0.169885
H	-4.011270	-1.381040	0.875383
H	-4.589858	0.173494	1.510121
N	0.096962	1.500326	-0.402636
Br	0.696226	-1.957025	0.108424

c. $[BMIM]^+[FeCl_3Br]^-$ (energy: -5642.84 a.u.)



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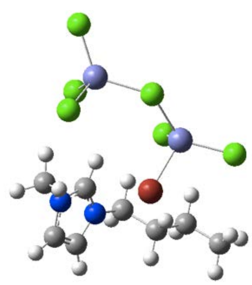
C	3.534235	1.525058	-0.118880
C	2.915517	2.708176	-0.408813
N	1.628989	2.626584	0.094947
H	0.546845	1.071186	1.138537
H	4.539673	1.182235	-0.328523
H	3.277293	3.591180	-0.920766
C	0.577527	3.636708	-0.052652
H	0.948271	4.603066	0.309945
H	0.292104	3.709448	-1.109323
H	-0.293883	3.315188	0.531499
C	2.823993	-0.654622	0.992698
C	2.757774	-1.639184	-0.176436

H	2.032623	-0.877464	1.720828
H	3.796446	-0.695757	1.505438
C	2.948874	-3.085147	0.295161
H	1.777211	-1.531506	-0.666952
H	3.527695	-1.383321	-0.924733
C	2.871548	-4.090368	-0.856704
H	3.920581	-3.183180	0.809875
H	2.173603	-3.320738	1.042232
H	3.007935	-5.118655	-0.493925
H	1.895035	-4.039409	-1.359317
H	3.648859	-3.895906	-1.611534
N	2.616338	0.740622	0.559000
Fe	-2.008978	-0.237548	0.445195
Cl	-3.744822	-1.328202	-0.163530
Cl	-0.652638	-1.484201	1.549045
Cl	-1.916290	1.630985	1.603222
Br	-0.840149	0.200019	-1.497419

d. $[BMIM]^+[Fe_2Cl_6Br]^-$ (energy: -3445.03 a.u.)



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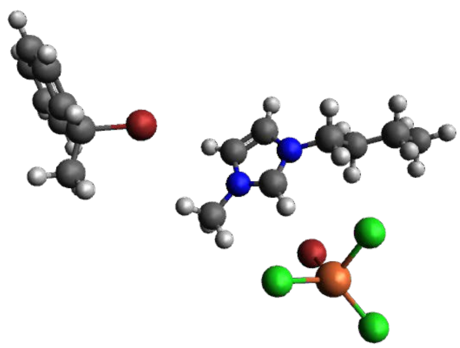
C	-2.931274	-3.446397	-0.218807
C	-1.856054	-3.887840	-0.938022
N	-0.778628	-3.095786	-0.586871
H	-0.565844	-1.422363	0.773457
H	-3.954934	-3.797435	-0.188643
H	-1.765049	-4.692752	-1.656558
C	0.565219	-3.158707	-1.171250
H	0.792618	-4.200560	-1.420914
H	0.603292	-2.533276	-2.071823
H	1.291879	-2.785679	-0.441256
C	-3.332387	-1.565612	1.451013
C	-4.276655	-0.646180	0.674595
H	-2.644498	-0.972386	2.066939
H	-3.884187	-2.252521	2.109636
C	-5.096638	0.242763	1.617772
H	-3.676589	-0.019944	-0.004404
H	-4.953433	-1.250134	0.046404

C	-6.054226	1.168718	0.863413
H	-5.666481	-0.388739	2.321300
H	-4.405584	0.846188	2.228360
H	-6.624270	1.798907	1.559880
H	-5.504494	1.834589	0.182791
H	-6.776610	0.595180	0.263000
N	-2.492825	-2.389859	0.559235
Fe	-0.259967	1.869242	-0.295965
Cl	1.830147	1.383989	-0.172972
Cl	-1.095253	3.735445	-0.783507
Cl	-1.034123	1.236984	1.582894
Br	-1.109271	0.475225	-1.898890
Fe	3.195579	-0.183841	0.427112
Cl	2.065345	-1.410160	1.749218
Cl	3.808667	-1.368527	-1.203743
Cl	4.937238	0.390096	1.439965

e. Species 1 (energy: -8527.66 a.u.)
Have two imaginary frequencies: *i*7.06 cm^{-1}, *i*4.96 cm^{-1}



C	1.464788156	0.397762385	0.821063896
C	3.584394603	0.034928680	0.269284530
C	3.383871499	1.387040497	0.293962897
N	2.057458265	1.591200658	0.641977433
H	0.419541409	0.246619442	1.095517415
H	4.474165986	-0.543676150	0.049635394
H	4.064804081	2.211528368	0.109189825
C	1.384737527	2.888872373	0.748435749
H	1.877670204	3.486729001	1.527968109
H	1.443941102	3.402552302	-0.219946631
H	0.329941169	2.711818345	1.000938735
C	2.102422327	-2.014667021	0.624529918
C	1.965583022	-2.596251647	-0.789197453
H	1.162253634	-2.150428777	1.183163359
H	2.920311627	-2.493268210	1.186147237
C	1.653661024	-4.098675312	-0.753223513

H	1.154709979	-2.061162258	-1.311367939
H	2.897588638	-2.417375531	-1.359843065
C	1.516881503	-4.702801776	-2.158944748
H	2.448316663	-4.626835443	-0.195106282
H	0.714993766	-4.255725338	-0.190053386
H	1.287626529	-5.777676504	-2.107953770
H	0.704534190	-4.216812146	-2.721314561
H	2.448630446	-4.583654932	-2.740493305
N	2.378725947	-0.563855663	0.607324273
Fe	-2.257401655	-0.089193804	-0.076571897
Cl	-4.142216985	-0.579552252	-0.980753718
Cl	-1.512496136	-1.936217561	0.803121366
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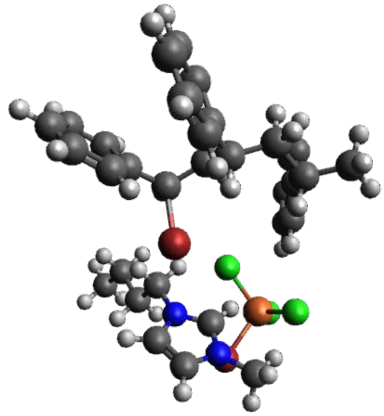
Br	-0.776971822	0.518561958	-1.789639315
C	8.807382692	6.041846599	4.311981170
C	7.526035021	5.525306972	4.635187649
C	6.413308700	5.745583667	3.777864741
C	6.614463646	6.490683814	2.580770620
C	7.894347045	7.004727773	2.254785795
C	8.994686041	6.783630209	3.120043452
H	9.659714703	5.865084436	4.992909242
H	7.382985031	4.943130895	5.566722912
H	5.766776185	6.662657323	1.892333998
H	8.034999733	7.582258740	1.321724936
H	9.994612996	7.188378767	2.863993866
C	5.047021060	5.203006452	4.175115983
H	5.077744404	4.816239990	5.217661254
C	3.853474229	6.127282546	3.976583332
H	2.908358161	5.644621147	4.317779851
H	4.024368950	7.042207652	4.583315095
H	3.731516007	6.428453316	2.910863358
Br	4.665662086	3.467351879	3.125380000

f. Species 2 (energy: -9147.20 a.u.)
Have five imaginary frequencies: *i*18.48 cm^{-1}, *i*9.74 cm^{-1}, *i*8.28 cm^{-1}, *i*6.36 cm^{-1}, *i*4.84 cm^{-1}. All these imaginary frequencies corresponds to the wagging of the whole system and hence represent the floppy structure of the system.



C	1.113903859	1.180886456	-0.863204027
C	2.708806297	0.308318784	-2.136195440
C	1.909740871	1.081298922	-2.931737894
N	0.922875232	1.618992862	-2.118638089
H	0.489189361	1.429124585	-0.006223097
H	3.595018974	-0.272161380	-2.370177495
H	1.959461954	1.293862585	-3.992596841
C	-0.192654584	2.464290070	-2.554740917
H	0.195482437	3.409868094	-2.956087961
H	-0.767245003	1.933631992	-3.324362139
H	-0.841701439	2.656254467	-1.691149359
C	2.705906648	-0.343043003	0.324232918
C	2.303122995	-1.820238865	0.306075803
H	2.285566709	0.155295530	1.208450626
H	3.798261556	-0.212128082	0.334122879
C	2.815493935	-2.557211311	1.548839734
H	1.203546389	-1.883685744	0.259478481
H	2.696675132	-2.304005164	-0.604915596
C	2.426294750	-4.038569404	1.553548863
H	3.913924891	-2.461248072	1.609850625
H	2.406646903	-2.066035403	2.446991903
H	2.799929652	-4.543423757	2.455409106
H	1.333161152	-4.159092582	1.530971994
H	2.840760917	-4.564843425	0.679879106
N	2.198182548	0.387031283	-0.851553407
Fe	-1.957626846	0.525824428	1.386783827
Cl	-3.594707736	-0.410081538	2.406054648
Cl	-0.137521906	0.242424116	2.546159143
Cl	-1.780658208	2.617564569	0.722872135
Br	-1.715252853	-0.646188104	-0.616879918
C	9.047194608	1.255114954	2.585711002
C	7.689598875	1.590542798	2.547621394
C	7.192144049	2.469895661	1.571366443
C	8.082905876	2.987903741	0.618228589

C	9.438085795	2.648655215	0.650829280
C	9.926610109	1.784511414	1.635429451
H	9.413205041	0.570206072	3.352540984
H	7.005068103	1.163749291	3.288061414
H	7.709903611	3.651608615	-0.161406660
H	10.116910136	3.062314948	-0.099197825
H	10.986269943	1.518628133	1.655895948
C	5.723013406	2.817880718	1.644761863
H	5.193639375	1.969786997	2.099560839
C	5.297921282	4.078188158	2.419352943
H	4.214463893	3.989399840	2.588968183
H	5.765449648	3.988190126	3.416333322
Br	4.891724745	2.845018387	-0.200650662
C	5.579497259	5.477548249	1.834881963
H	5.270919080	5.453781604	0.773834236
C	7.043837965	5.916880038	1.869892717
C	7.618658812	6.524922791	0.741421088
C	7.833893478	5.803948899	3.025781849
C	8.939523701	6.990652250	0.757195381
H	7.018733926	6.628733982	-0.167849950
C	9.155726726	6.266317588	3.048115355
H	7.418277980	5.343027882	3.925220717
C	9.715963168	6.859685815	1.912680997
H	9.362908388	7.455347962	-0.136019127
H	9.751503565	6.160750337	3.957641223
H	10.749040355	7.218572943	1.929539189
C	4.702433138	6.567154754	2.531346191
H	5.091819320	7.548065901	2.204687084
H	4.873021077	6.536411381	3.622336967
C	3.174740793	6.542936670	2.223989533
H	3.060655085	6.323951802	1.144631268
C	2.575068749	7.950387175	2.483673282
H	1.493178282	7.965254263	2.262246135
H	3.072588093	8.710378379	1.858816165
H	2.702699347	8.247274034	3.538907746
C	2.354108106	5.494566399	2.976650114
C	1.450032896	4.662350760	2.297442129
C	2.421495955	5.392291272	4.376825009
C	0.645538735	3.746663637	2.985289125
H	1.374048276	4.736051937	1.209096964
C	1.623439329	4.477464839	5.070443912
H	3.104701035	6.037549364	4.936956047
C	0.733138186	3.650723958	4.376584619
H	-0.055741285	3.114022418	2.435269611
H	1.693443242	4.415108315	6.158643246
H	0.108675207	2.933659429	4.913295916

B. Supporting tables, schemes and figures

Table S1 Reaction conditions and results for the IL-mediated cationic polymerization of St at 25 ^{o}C using BEB as the initiator.[a]

Entry	IL	Time	Conv.[b] (%)	$M_{n,theo.}$[c] (g mol^{-1})	$M_{n,SEC}$[d] (g mol^{-1})	*Đ*[d]
P1	BMIMBr	<1 min	100	5400	4900	1.17
P2	HMIMBr	<1 min	100	5400	4500	1.33
P3	OMIMBr	<1 min	100	5400	5800	1.36
P4	DMIMBr	<1 min	100	5400	5400	1.45

[a]Reaction Conditions: $[St]_0/[BEB]_0/[FeCl_3]_0/[IL]_0$ = 50/1/5/2. [b]Determined gravimetrically based on monomer feed. [c]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([St]_0/[BEB]_0 \times \text{yield} \times M_{St}) + M_{BEB}$, where M_{St} (= 104.15 g mol^{-1}) and M_{BEB} (= 185.06 g mol^{-1}) are the molecular weight of St and BEB, respectively. [d]Obtained from SEC measurements.

Table S2 Reaction conditions and results for the blank experiments: cationic polymerization of St at 25 ^{o}C using BEB as the initiator in absence of ionic liquid using $FeCl_3$ as co-initiator .[a]

Entry	Solvent	Time	Conv.[b] (%)	$M_{n,theo.}$[c] (g mol^{-1})	$M_{n,SEC}$[d] (g mol^{-1})	*Đ*[d]
P5	-	<1 min	100	5400	7200	2.35
P6	dichloromethane	<1 min	100	5400	8100	2.63
P7	toulene	48 h	100	5400	2600	1.94

[a]Reaction Conditions: $[St]_0/[BEB]_0/[FeCl_3]_0$ = 50/1/5. [b]Determined gravimetrically based on monomer feed. [c]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([St]_0/[BEB]_0 \times \text{yield} \times M_{St}) + M_{BEB}$, where M_{St} (= 104.15 g mol^{-1}) and M_{BEB} (= 185.06 g mol^{-1}) are the molecular weight of St and BEB, respectively. [d]Obtained from SEC measurements.

Table S3. Effect of concentration of BMIMBr on the IL-mediated Cationic Polymerization of St at 25 °C using BEB as the initiator.[a]

Entry	$[St]_0/[BMIMBr]_0$	Time	Conv.[b] (%)	$M_{n,theo.}$[c] (g mol^{-1})	$M_{n,SEC}$[d] (g mol^{-1})	$Đ$[d]
P8	25.00	<1 min	100	5400	5000	1.17
P9	10.00	1 h	100	5400	4700	1.17
P10	5.00	2 h	100	5400	5100	1.19
P11	2.50	6 h	100	5400	5200	1.18
P12	1.67	6 h	51	2800	2200	1.21
P13	1.25	24 h	<3%	-	1400	3.17

[a]Reaction Conditions: $[St]_0/[BEB]_0/[FeCl_3]_0$ = 50/1/5. [b]Determined gravimetrically based on monomer feed. [c]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([St]_0/[BEB]_0 \times \text{yield} \times M_{St}) + M_{BEB}$, where M_{St} (= 104.15 g mol^{-1}) and M_{BEB} (= 185.06 g mol^{-1}) are the molecular weight of St and BEB, respectively. [d]Obtained from SEC measurements.

Table S4. Reaction conditions and results for the effect of varying $[St]_0/[BEB]_0$ on the IL-mediated Cationic Polymerization of St at 25 °C using BEB as the initiator.[a]

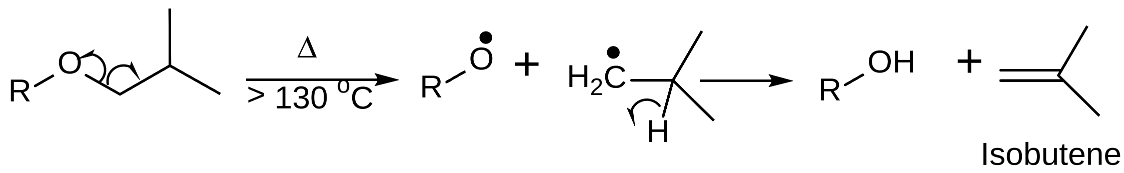
Entry	$[St]_0/[BEB]_0$	Conv.[b] (%)	$M_{n,theo.}$[c] (g mol^{-1})	$M_{n,NMR}$[d] (g mol^{-1})	$M_{n,SEC}$[e] (g mol^{-1})	$Đ$[e]	ω-end Br per chain[f]
P14	25	100	2800	2100	2500	1.18	0.91
P15	50	100	5400	4400	4900	1.17	0.89
P16	100	100	10600	9500	10300	1.19	0.85
P17	150	100	15800	14800	15200	1.20	0.84
P18	200	100	21000	19900	20400	1.19	0.85

[a]Reaction Conditions: reaction time < 1 min. $[BEB]_0/[FeCl_3]_0/[BMIMBr]_0$ = 1/5/2. [b]Determined gravimetrically based on monomer feed. [c]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([St]_0/[BEB]_0 \times \text{yield} \times M_{St}) + M_{BEB}$, where M_{St} (= 104.15 g mol^{-1}) and M_{BEB} (= 185.06 g mol^{-1}) are the molecular weight of St and BEB, respectively. [d]Determined by ^{1}HNMR (see equations 1-2 in the Experimental Section for details). [e]Obtained from SEC measurements. [f]Calculated as the ratio of integrals (normalized to one hydrogen) as 5I(e)/I(c) (where signal "c" and "e" refer to phenylic protons and end group CH(Br), respectively. please refer to Fig. 1)

Table S5. Molecular characterization data of PSt-*b*-PIBVE diblock copolymers prepared by IL-mediated Cationic Polymerization at 25 ^{o}C.

Entry	Polymer	$M_{n,SEC}$[a] (g mol^{-1})	$Đ$[a]	$T_{d,10\%}$[b] (°C)
P19	PSt_{50}-*b*-$PIBVE_{50}$	9400	1.18	204
P20	PSt_{50}-*b*-$PIBVE_{100}$	14500	1.21	194
P21	PSt_{50}-*b*-$PIBVE_{150}$	19000	1.19	183
P22	PSt_{50}-*b*-$PIBVE_{200}$	24700	1.20	168
P23	PSt_{50}-*b*-$PIBVE_{250}$	29100	1.19	165

[a]Obtained from SEC measurements. [b]Assessed by thermogravimetric analysis (TGA), under air; 10 °C/min. *$T_{d,10\%}$ of a PSt_{50}-Br samples was estimated to be 369 °C.



Scheme S1. Degradation of *iso*-butyl ether groups of the PSt-*b*-PIBVE copolymers upon heating above 130 °C.

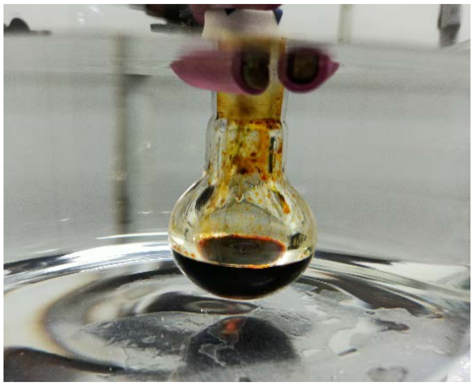


Fig. S1 Representative image of BMIMBr (ionic liquid)-mediated controlled cationic polymerization of styrene.

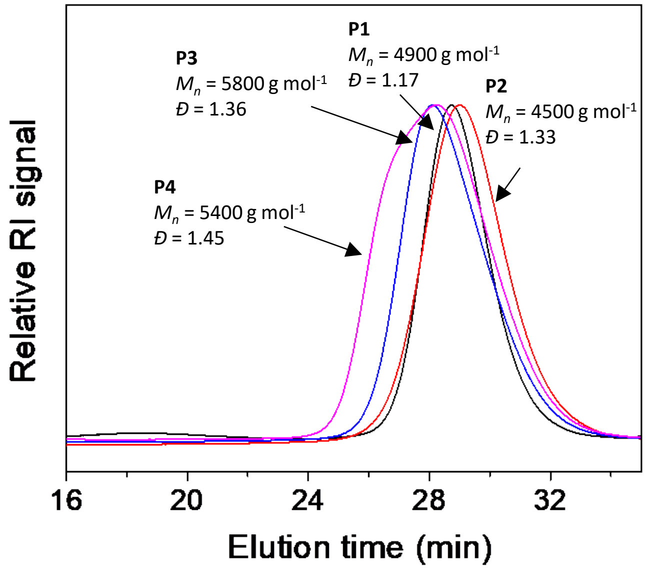


Fig. S2 SEC traces of PSts prepared by IL-mediated cationic polymerization at 25 °C (P1-P4, Table S1) in presence of different ILs.

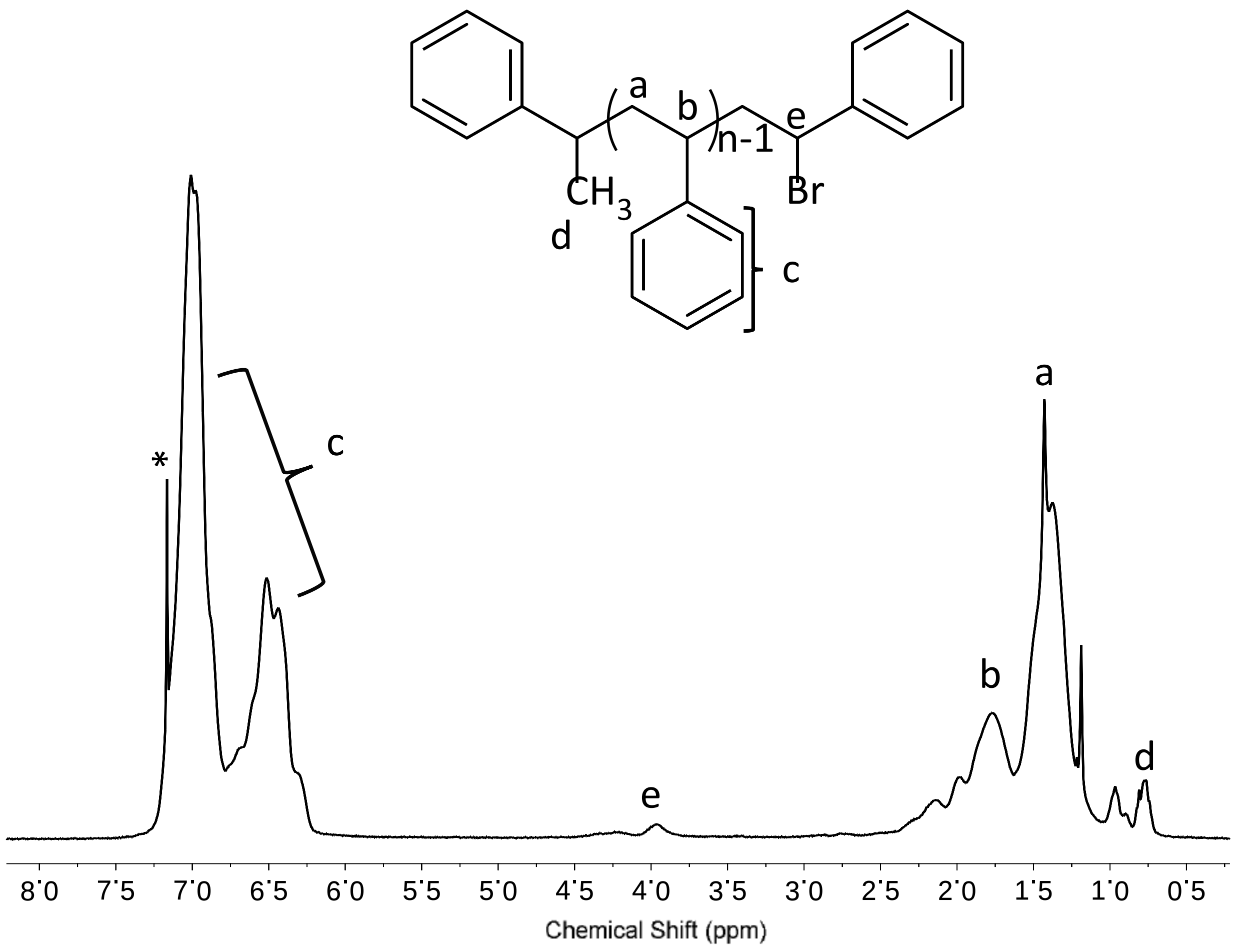


Fig. S3 ^{1}H NMR spectrum ($CDCl_3$, 20 °C) of PSt (P14, Table S4) prepared by IL-mediated Cationic Polymerization of St at 25 ^{o}C using BEB as the initiator. (*) Solvent ($CDCl_3$) peak.

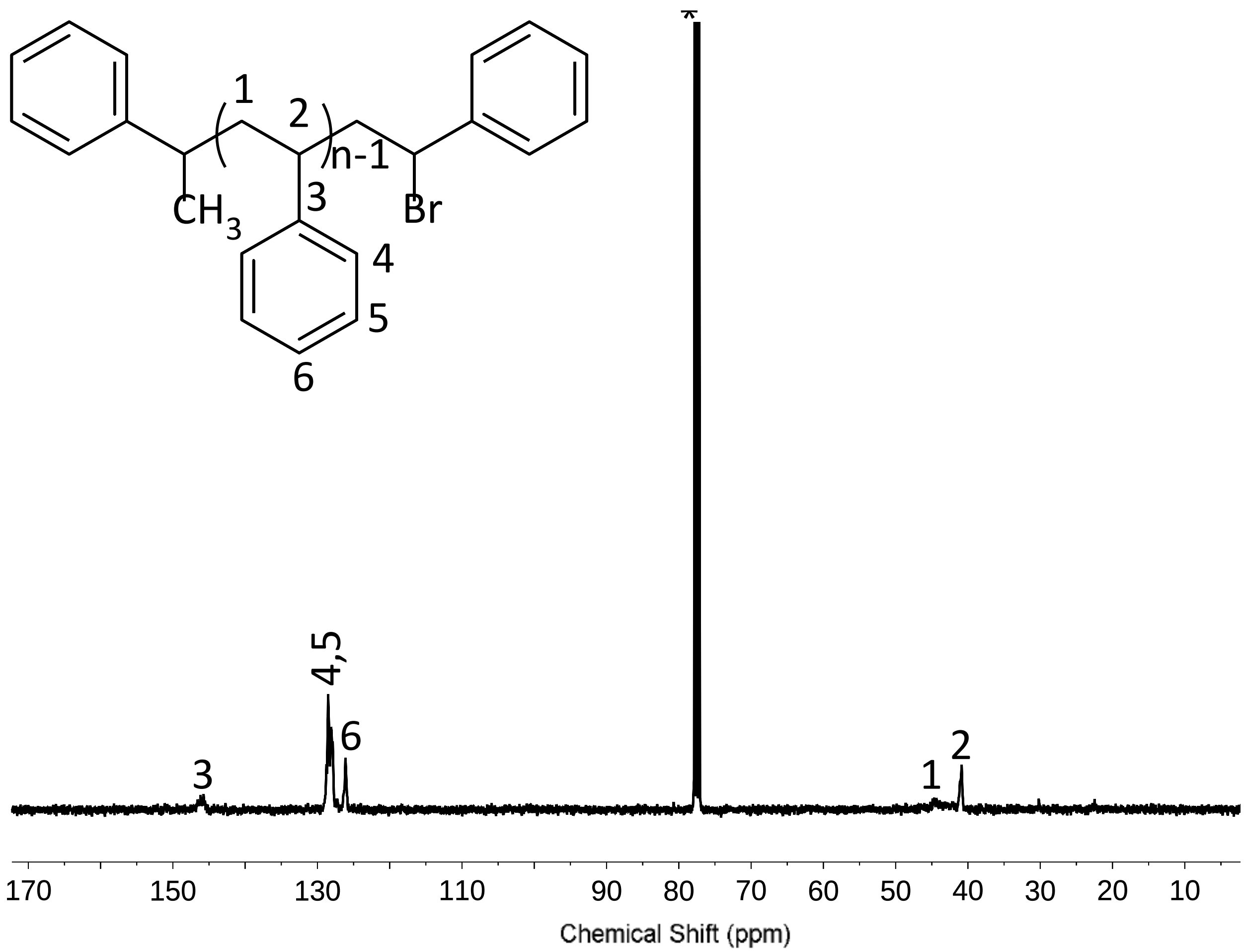


Fig. S4 ^{13}C NMR spectrum ($CDCl_3$, 20 °C) of PSt (P14, Table S4) prepared by IL-mediated Cationic Polymerization of St at 25 ^{o}C using BEB as the initiator. (*) Solvent ($CDCl_3$) peak.

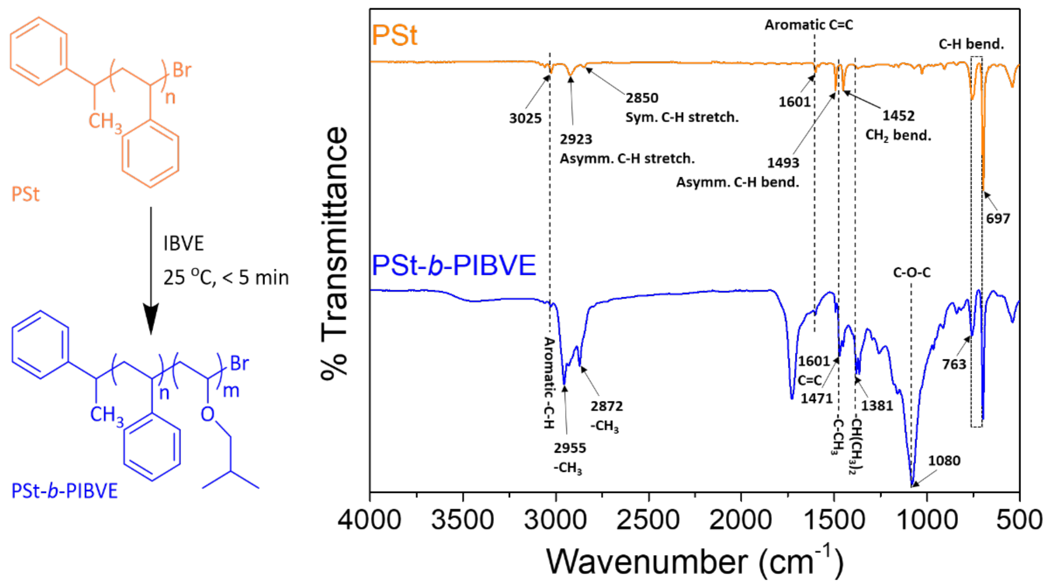


Fig. S5 ATR-IR spectra of PSt-Br (P1, Table S1). and PSt-*b*-PIBVE (P19, Table S5).

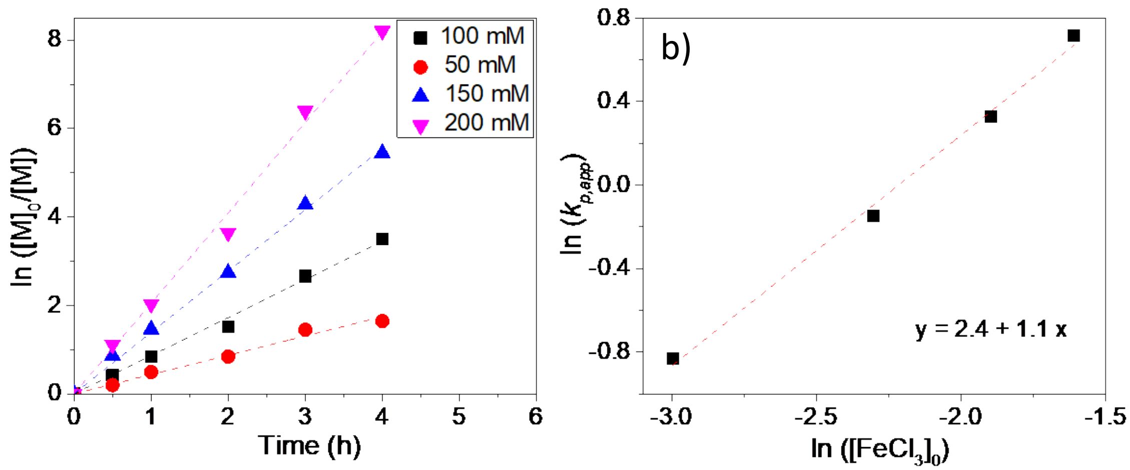


Fig. S6 Plot of a) ln([M]$_0$/[M]) vs. time, and b) ln($k_{p,app}$) vs. ln([FeCl$_3$]$_0$) for IL-mediated cationic polymerization of St.

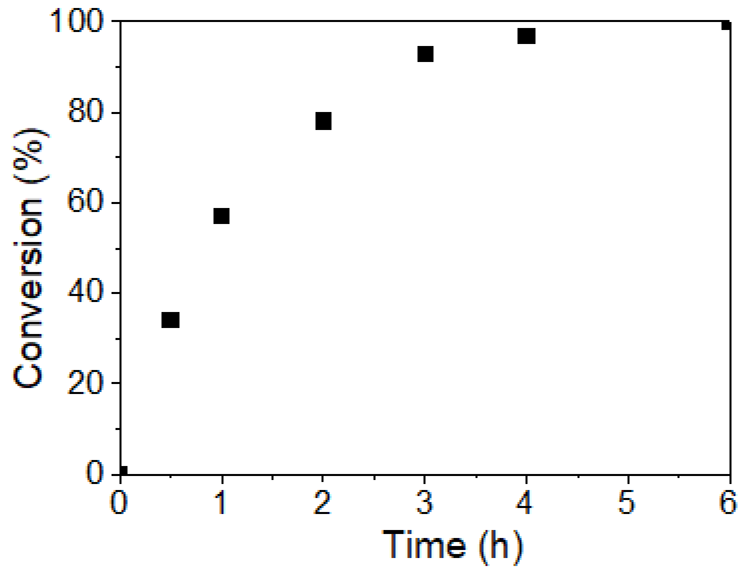


Fig. S7 Plot of conversion vs. time for IL-mediated cationic polymerization of St at 25 °C using BEB as the initiator. $[St]_0/[BEB]_0 = 200$.

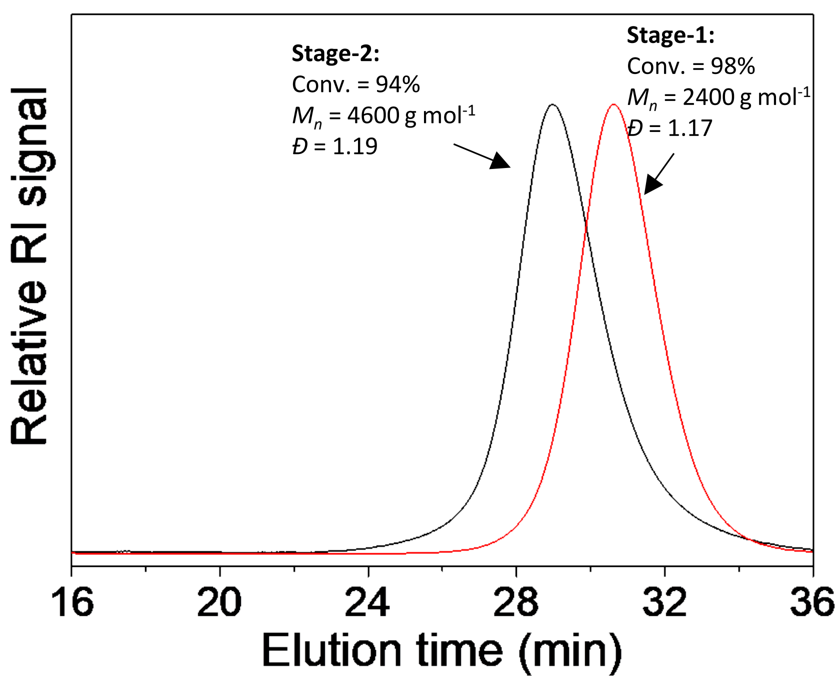


Fig. S8 Evolution of SEC traces along with M_n and $Đ$ values during *in situ* chain extension for IL-mediated cationic polymerization of St at 25 °C using BEB as the initiator. $[St]_0/[BEB]_0/[FeCl_3]_0/[IL]_0 = 25/1/2.5/1$.

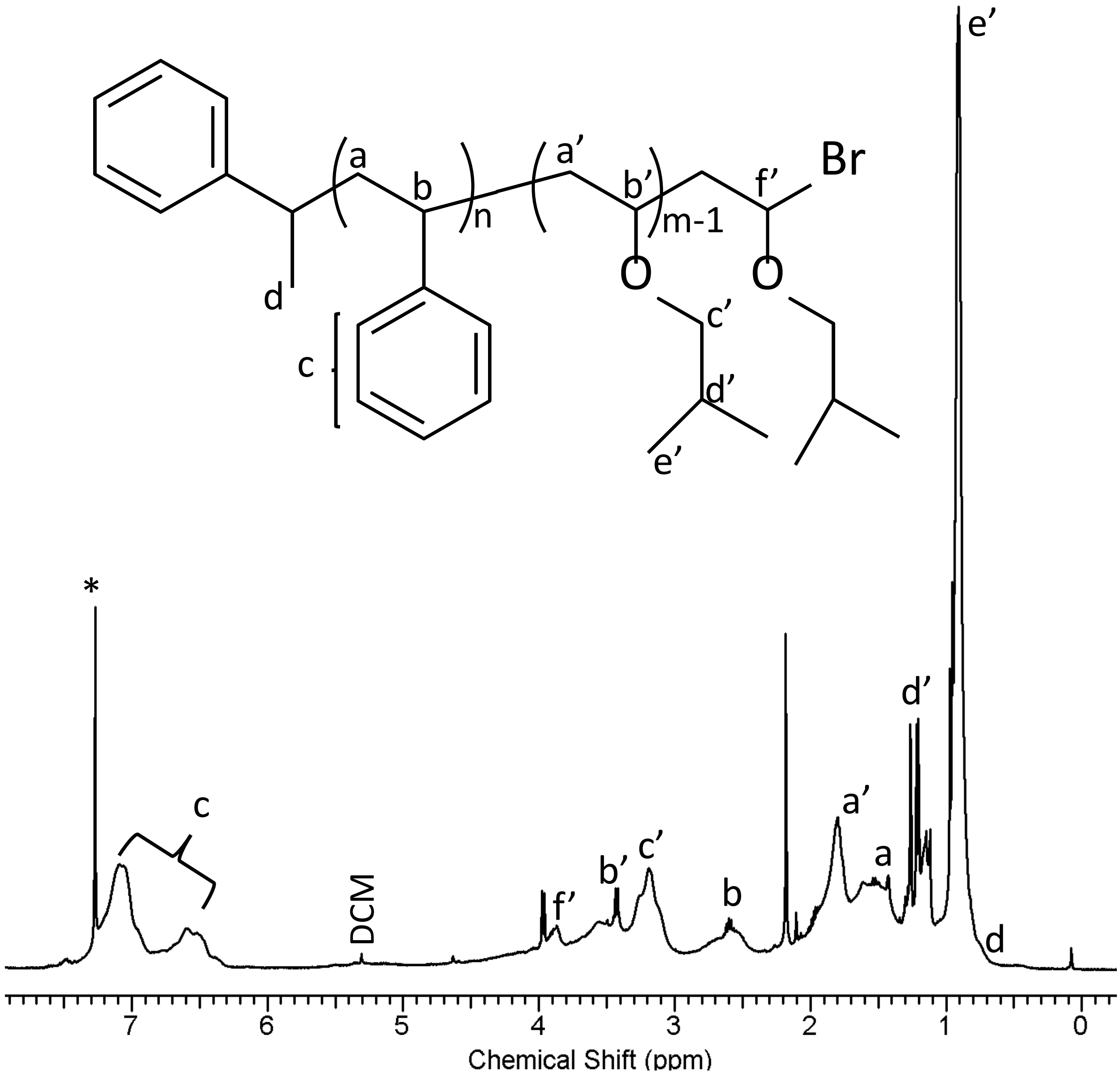


Fig. S9 [1]H NMR spectrum ($CDCl_3$, 20 °C) of PSt-*b*-PIBVE (P19, Table S5) prepared by IL-mediated cationic polymerization of St at 25 °C using BEB as the initiator. (*) Solvent ($CDCl_3$) peak.

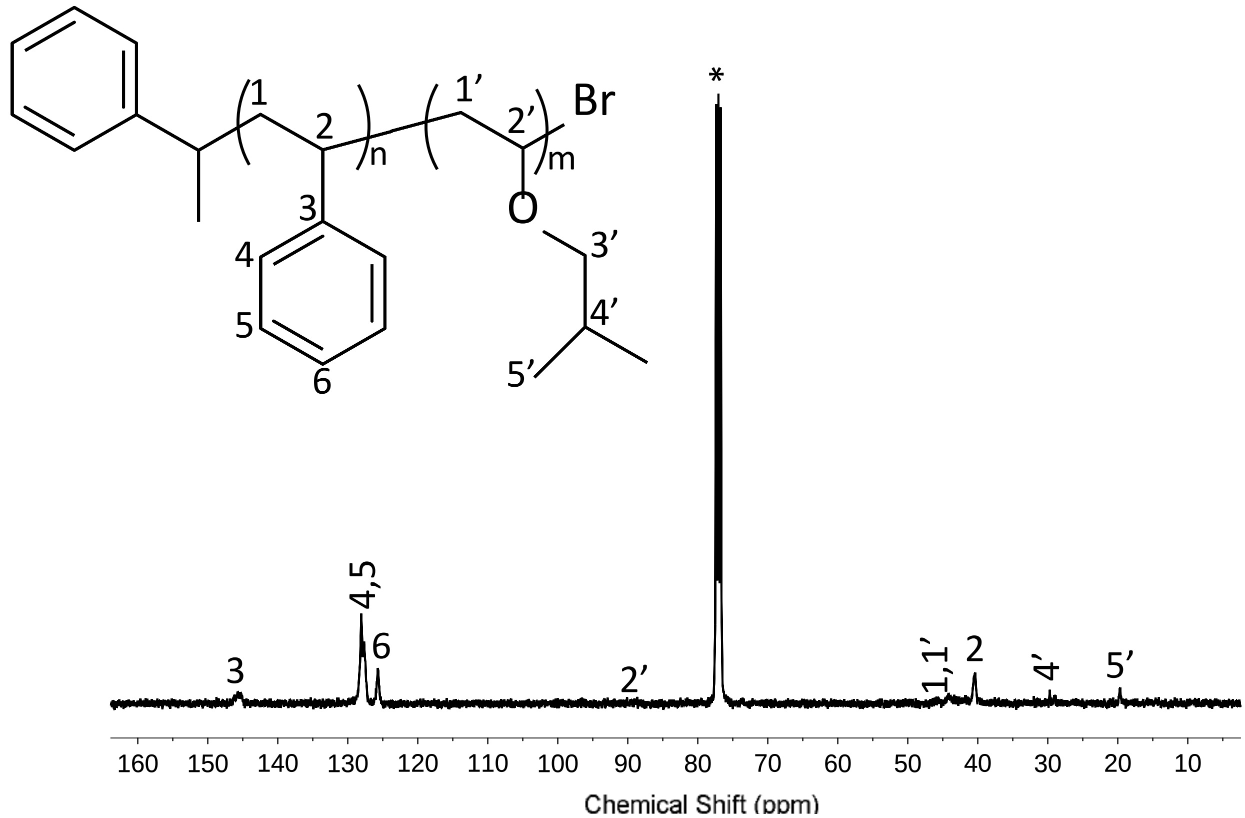


Fig. S10 ^{13}C NMR spectrum ($CDCl_3$, 20 °C) of PSt-*b*-PIBVE (P19, Table S5) prepared by IL-mediated cationic polymerization of St at 25 ^{o}C using BEB as the initiator. (*) Solvent ($CDCl_3$) peak.

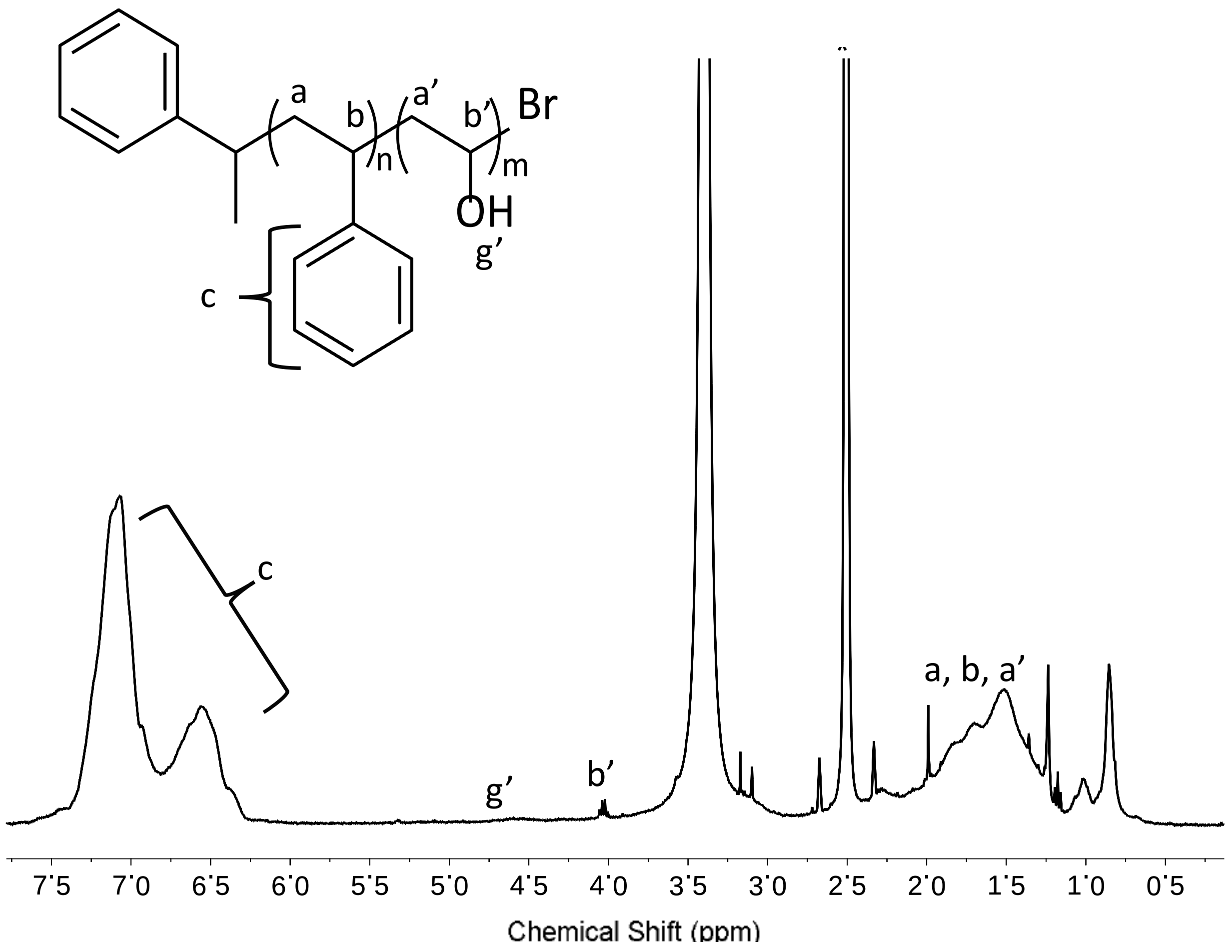


Fig. S11 ^{1}H NMR spectrum (DMSO-d_6, 20 °C) of PSt-*b*-PVA obtained via hydrolysis of PSt-*b*-PIBVE (P19, Table S5). (*) Solvent (DMSO-d_6) peak.

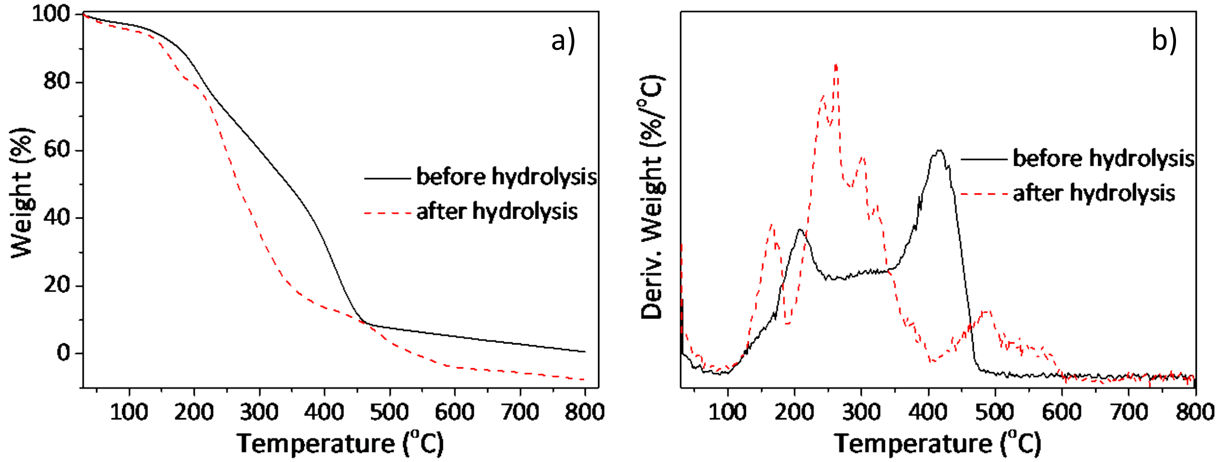


Fig. S12 TGA thermograms (a) and the corresponding first derivative plot of the weight percentage with respect to the temperature (b) of the PSt-*b*-PIBVE copolymer (P19, Table S5) before (solid line) and after (dashed line) hydrolysis of the isobutyl groups, heated at 10 °C min^{-1} under air.