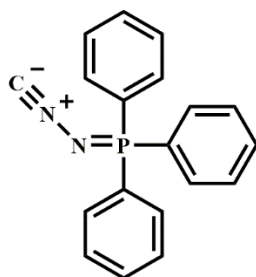


Supporting Information

Preparation and Characterization of Soft-Hard Block Copolymer of 3,4-IP-*b-s*-1,2-PBD Using a Robust Iron-Based Catalyst System

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(isocyanoimino) triphenylphosphorane (IITP)

Figure S1. The additive employed in iron-catalyzed IP polymerization.

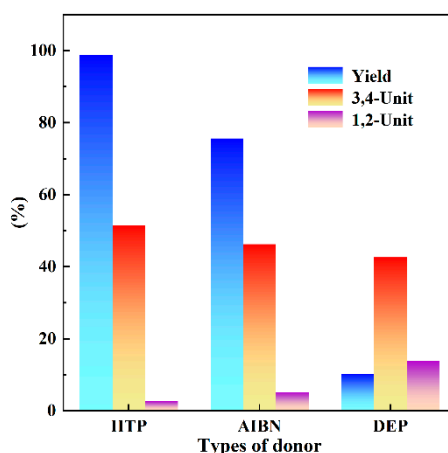


Figure S2. Comparison of polymerization behavior of three commercially available donors for IP polymerization. Polymerization conditions: in hexane at 50 °C for 4 h, [IP]=2.3 mol L⁻¹, [IP]/[Fe]=7000, [P]/[Fe]=3, and [Al]/[Fe]=20 (mol/mol).

Table S1. Variation of temperature and time on IP polymerization ^a

Run	Temp. (°C)	Time (h)	Yield (%)	Activity ^b	M_n^c ($\times 10^4$)	PDI ^c	Microstructure ^d			T_g^e (°C)
							(%)			
							3,4	1,2	1,4	
1	0	24	7.9	3.4	29.2	1.64	54.6	2.2	43.2	−15.8
2	10	2	4.0	20.4	22.6	1.90	54.1	2.5	43.5	−14.5
3	20	2	13.9	70.9	45.6	1.77	52.7	2.6	44.7	−16.3
4	30	2	81.5	415.7	63.7	1.77	52.7	2.5	44.9	−16.3
5	50	0.6	79.9	1358.3	76.6	1.95	49.7	3.7	46.7	−16.8
6	50	2	96.7	493.2	90.4	1.93	51.3	3.3	45.4	−16.8
7	70	0.15	79.5	5406.0	81.6	1.88	49.5	3.8	46.7	−17.5
8	70	0.25	92.7	3782.2	74.6	1.92	49.8	3.5	46.7	−17.2

^a Polymerization conditions: in hexane, [IP]=2.3 mol L⁻¹, [IP]/[Fe]=15000, [P]/[Fe]=3, and [Al]/[Fe]=20 (mol/mol); ^b Activity in units of g mol_(Fe)⁻¹ h⁻¹; ^c Determined by GPC (using polystyrene as calibration); ^d Determined by NMR; ^e Determined by DSC.

Table S2. Mechanical properties of 3,4-PI, *s*-1,2-PBD and 3,4-PI-*b*-*s*-1,2-PBD with various soft to hard segment lengths.

Samples	Tensile strength (MPa)	Elongation at break (%)
Run 19	0.58±0.09	586±39
Run 20	4.75±0.12	579±14
Run 21	5.83±0.26	492±31
Run 22	7.46±0.24	434±27
Run 23	8.66±0.12	400±19
Run 24	13.36±0.13	348±25

Table S3. Tan δ values of 3,4-PI, *s*-1,2-PBD and representative 3,4-PI-*b*-*s*-1,2-PBD (Run 22).

Samples	Tan δ at 0°C	Tan δ at 60°C
Run 19	2.278	0.032
Run 20	1.635	0.048
Run 24	0.211	0.088

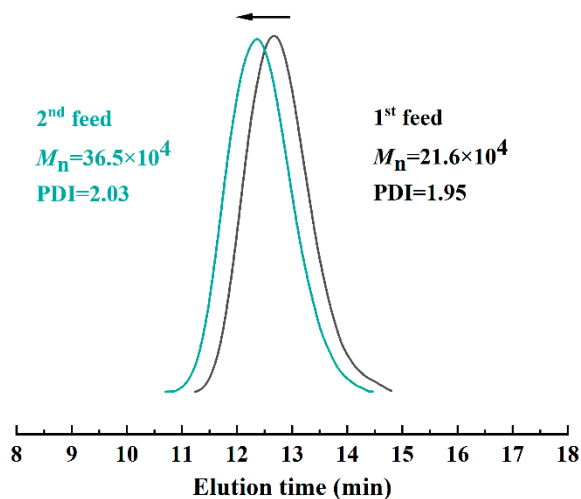


Figure S3. GPC profiles of polymers obtained from two-step polymerization of IP. Polymerization conditions: in hexane, $[IP]_0 = 0.5 \text{ mol L}^{-1}$, $[IP]_0/[Fe] = 600$, $[P]/[Fe] = 3$, $[Al]/[Fe] = 20$, and $[IP]_{\text{total}}/[Fe] = 1200 \text{ (mol/mol)}$.