Supporting Information

Gas-phase Copolymerization of Ethylene, Propene and Hydrogen under Controlled Atmosphere Composition in Reactor

Zheng Zheng[*]

Zhejiang Industrial Vocational College, 151 Qutun Road, Yuecheng District, Shaoxing,

Zhejiang, China 312000

E-mail: *20240017@zjipc.edu.cn*

Contents

Atmosphere compositions in reactor and monomer consumption rates during gas-phase copolymerization 3

GPC curves, ^{13}C NMR spectra and DSC heating curves of the polymers 5

GPC, DSC, SSA and ^{13}C NMR analysis of Fractions A-C of the polymers 5

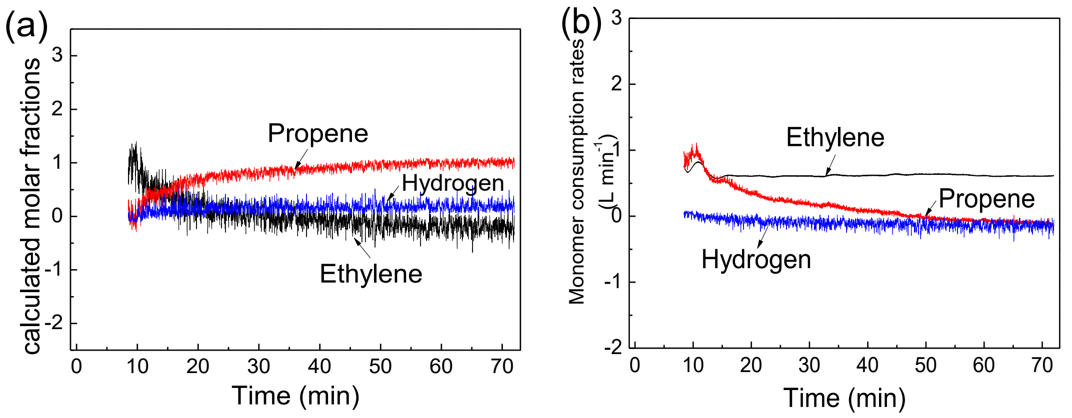

Figure S1. Atmosphere compositions in reactor (a) and monomer consumption rates (b) during gas-phase copolymerization in run 7

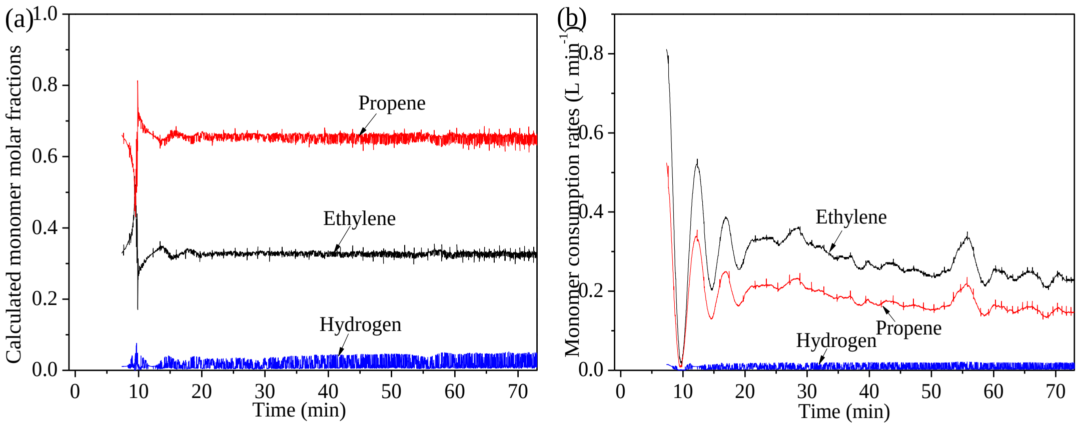

Figure S2. Atmosphere compositions in reactor (a) and monomer consumption rates (b) during gas-phase copolymerization in run 2

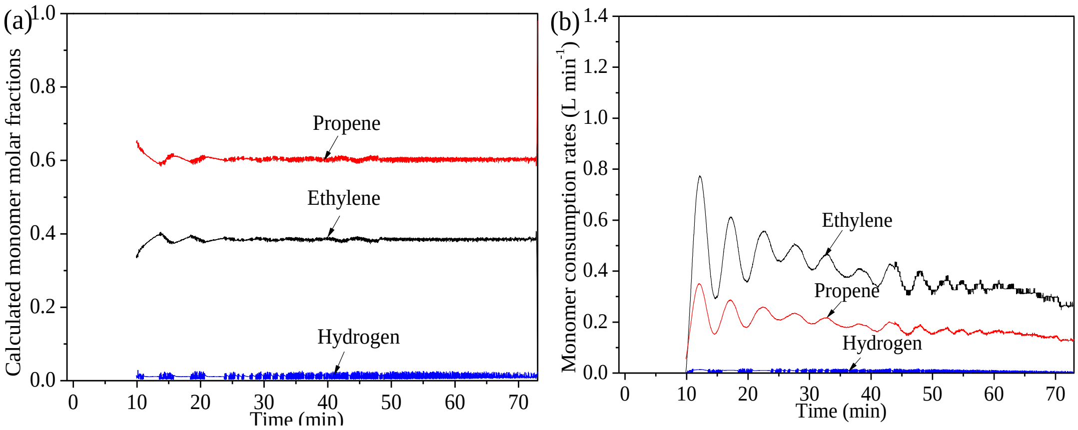

Figure S3. Atmosphere compositions in reactor (a) and monomer consumption rates (b) during gas-phase copolymerization in run 3

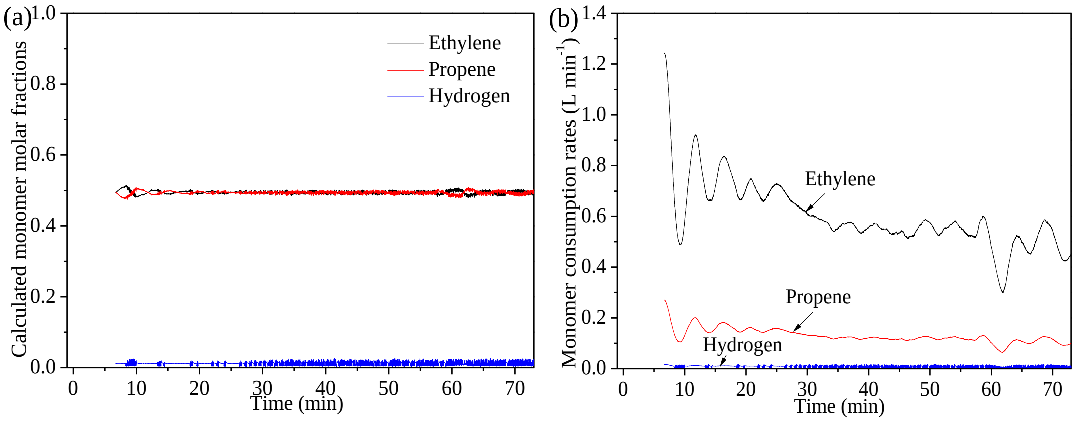

Figure S4. Atmosphere compositions in reactor (a) and monomer consumption rates (b) during gas-phase copolymerization in run 4

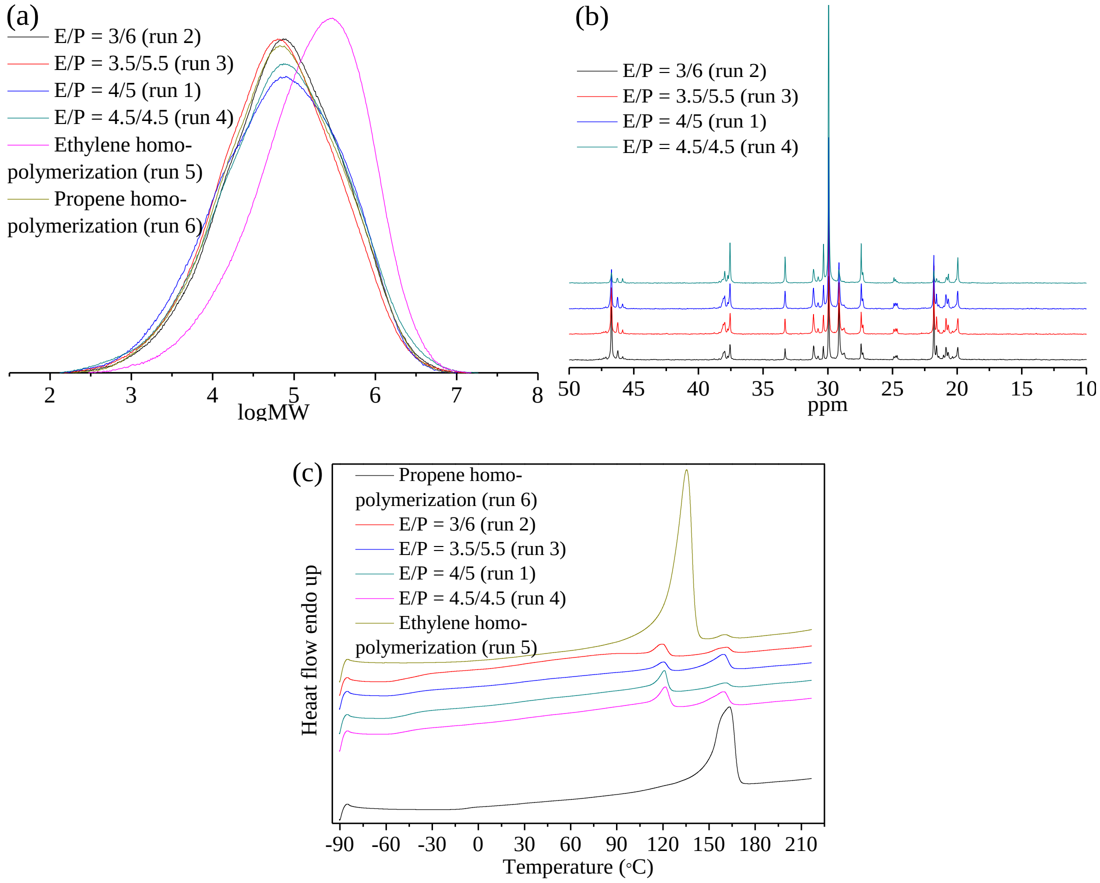

Figure S5. GPC curves (a), ^{13}C NMR spectra (b) and DSC heating curves (c) of the polymers

GPC, DSC, SSA and ^{13}C NMR analysis of Fractions A-C of the polymer samples in runs 1-4

Molecular weight and molecular weight distribution (MWD) of Fractions A-C of the polymers were shown in Table S1 and Figure S6. The weight average molecular weights (M_w) of Fractions A and B were about 100,000, and those of Fractions C were the highest, ranging from 250,000 to 420,000. The MWDs of Fractions A-C of all samples were single peak.

Table S1. Molecular weight and polydispersity index of Fractions A-C of the polymer samples determined by GPC

Run	Fraction A		Fraction B		Fraction C	
	M_w (10^4)	PDI	M_w (10^4)	PDI	M_w (10^4)	PDI
1	14.3	13.5	19.0	9.6	41.7	10.4
2	7.3	9.5	9.4	5.8	25.8	8.2
3	10.2	11.1	13.5	8.6	36.9	6.9
4	9.4	9.0	12.8	11.1	27.0	7.4

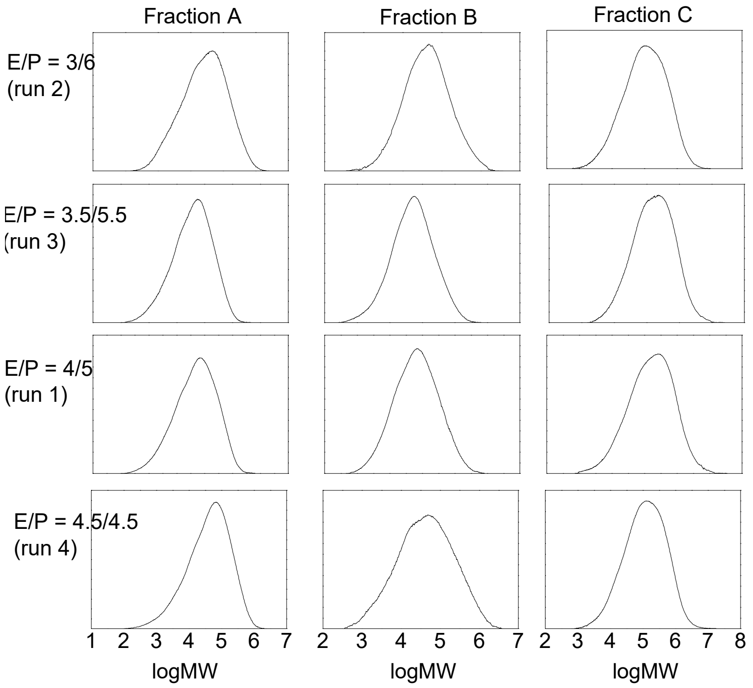

Figure S6. MWDs of Fractions A-C of the polymer samples in runs 1-4

Figure S7(a) shows the DSC crystallization and melting curves of Fraction A of the polymer sample in run 1. It can be seen that there is no obvious melting or crystallization peak, and there is obvious glass transition near -45 °C (Figure S7(b)), which show that Fraction A is amorphous. Figure S8(a-b) show the DSC melting and crystallization curves of Fraction B. There are two or three melting peaks at 60-135 °C, and one or two crystallization peaks at 50-90 °C. Therefore, there is no polyethylene or polypropylene in Fraction B (because the melting temperatures of polyethylene and polypropylene are about 135 °C and 165 °C, respectively). The melting and crystallization peaks of Fraction B are contributed by long ethylene or propylene chain segments (from segmented ethylene/propene copolymer).

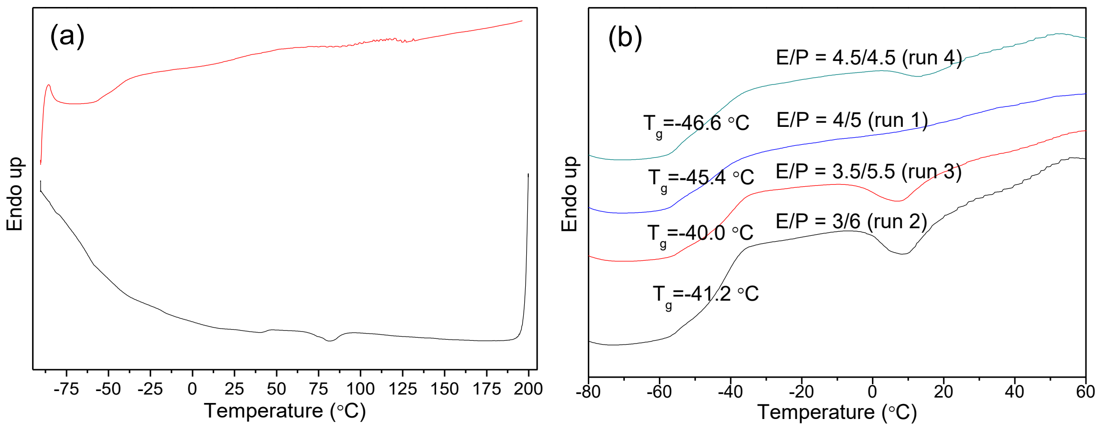

Figure S7. DSC curves of Fraction A in run 1 (a) and glass transition of Fraction A (b)

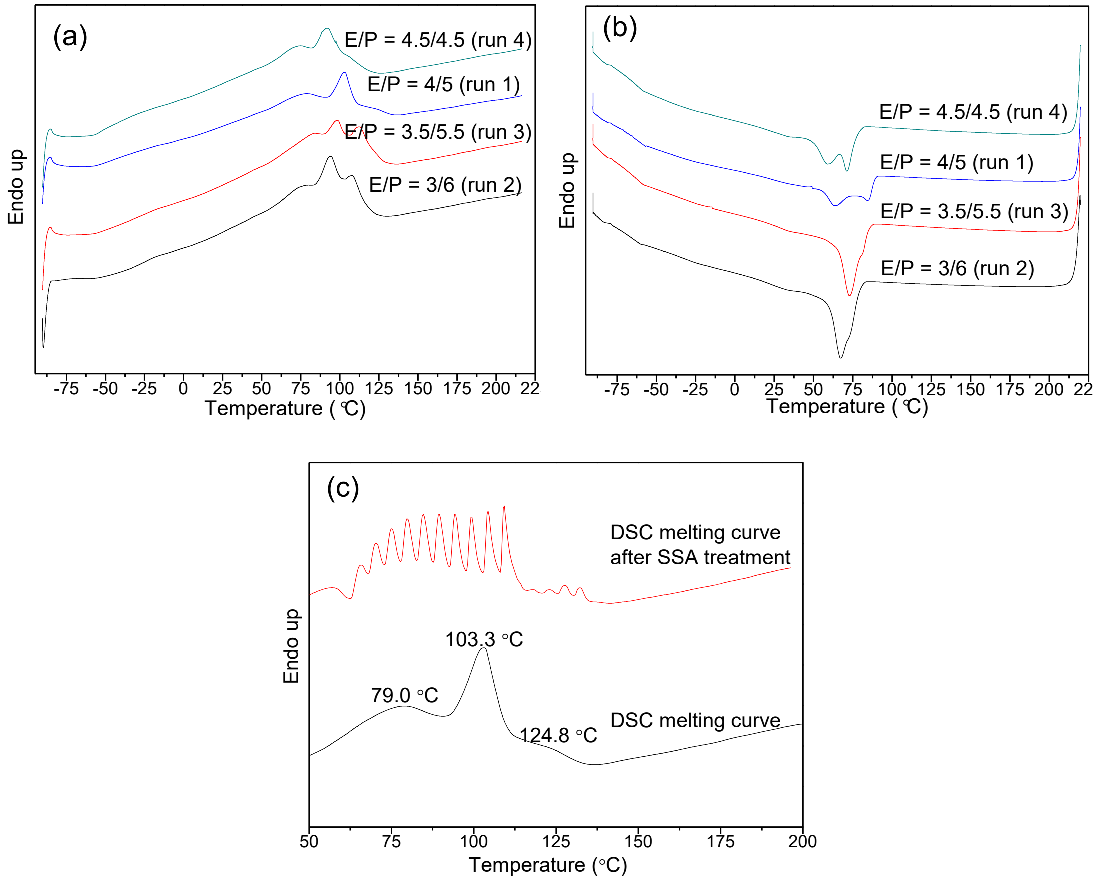

Figure S8. DSC melting and crystallization curves of Fraction B (a-b), and melting curves of Fraction B after SSA treatment (c) of the polymer in run 1

Successive Self-nucleation and Annealing (SSA) was used to analyze Fraction B of the sample in run 1. The analysis was carried out with TA Q200 thermal analyzer, and the analysis procedure was as follows: the polymer sample (about 5 mg) was heated to 200 °C at 30 °C/min and maintained at 200 °C for 5 minutes. The sample was then cooled to 25 °C at 10 °C/min and kept at 25 °C for 2 minutes. The samples were then heated to the first self-nucleating temperature (170 °C) at 10 °C/min and isothermal for 5 minutes, and then cooled to 25 °C at 10 °C/min and isothermal for 2 minutes, marking this as the first cycle. The samples were then heated to the second self-nucleation temperature (165 °C) at 10 °C/min and isothermal for 5 minutes, and then cooled to 25 °C at 10 °C/min and isothermal for 2 minutes, marking this as the second cycle. By analogy, the next self-nucleation temperature should be reduced by 5 °C (160 °C, 155 °C, etc.). The last self-nucleation temperature was selected at 60 °C. At this temperature, the sample was kept isothermal for 5 minutes. The sample was cooled to 25 °C at 10 °C/min and kept isothermal for 2 minutes at 25 °C. At last, the sample was heated to 200 °C at 10 °C/min, and the heating curve was recorded. The temperature control process in SSA analysis was shown in Figure S9.

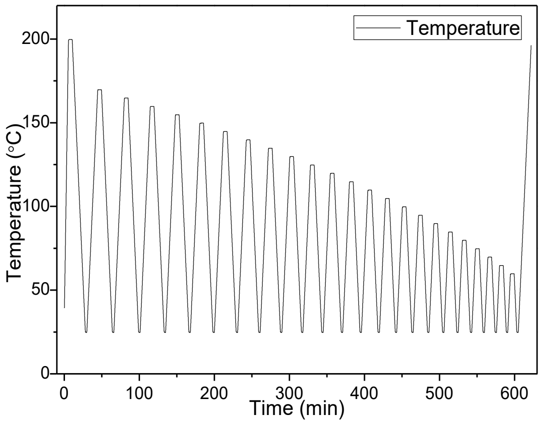

Figure S9. Temperature program applied in SSA analysis

As shown in Figure S8(c), the original melting peaks were further differentiated into several small peaks. Because each small peak corresponds to crystallizable segments (long ethylene or propylene sequence) of different lengths, the distribution of crystallizable segment (sequence) lengths in Fraction B is wide.

Figure S10 shows the DSC crystallization and melting curves of Fraction C of the polymer sample in run 1. The melting peak temperature is 161.7 ℃, and the crystallization peak temparature is 110.3 ℃, which indicates that Fraction C is highly isotactic polypropylene.

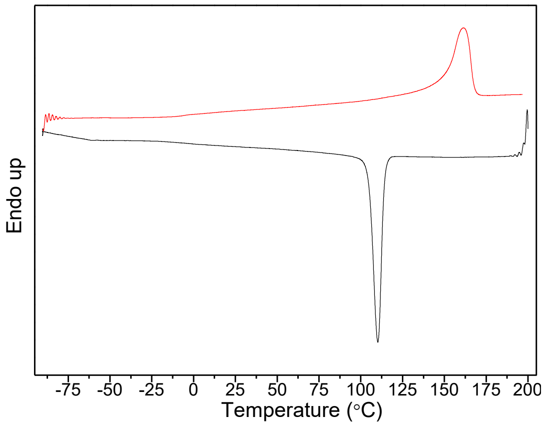

Figure S10. DSC crystallization and melting curves of Fraction C of the polymer in run 1

Further, in order to obtain the sequence distribution of Fractions A and B, ^{13}C NMR analysis was carried out. The ^{13}C NMR spectra are shown in Figure S11. The calculated sequence distribution is listed in Table S2.

As shown in Table S2, propylene contents in Fraction A ranged from 46% to 53%, propylene contents in Fraction B ranged from 32% to 46%, and ethylene contents were higher than propylene contents in Fraction B. The contents of EP sequence in Fraction A (about 40%) were higher than those in Fraction B (about 25%). The average sequence lengths of ethylene and propylene in Fraction A were about 2.5. The contents of (EEE+PPP) sequence in Fraction B (over 62%) were higher than those in Fraction A (about 40%). In Fraction B, the average sequence length of ethylene were between 4.6

and 6, and the average sequence length of propylene were between 2.6 and 4, which were larger than the corresponding values in Fraction A. Combined with the DSC analysis, the Fraction A is amorphous ethylene/propylene random copolymer and the Fraction B is ethylene/propylene segmented copolymer with long ethylene or propylene sequence.

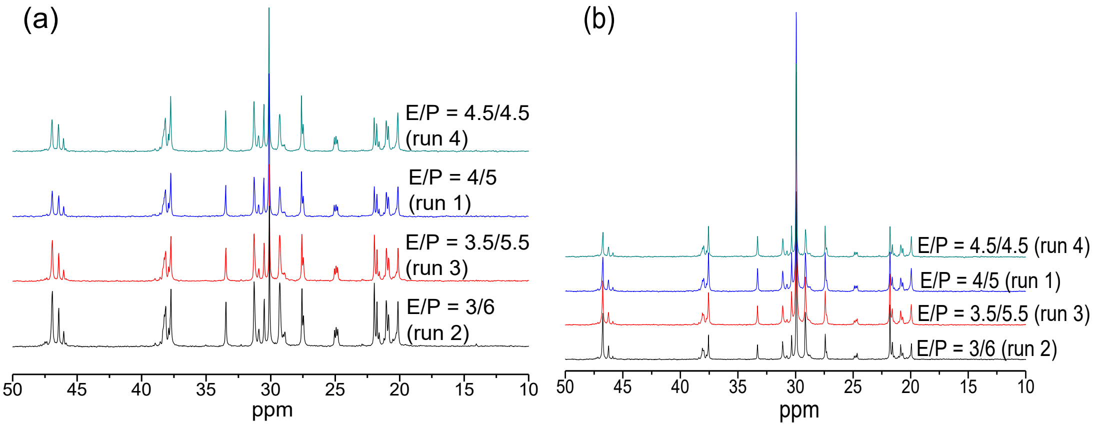

Figure S11. ^{13}C NMR spectra of Fractions A (a) and B (b) of the polymer samples in runs 1-4

Table S2. Composition and sequence distribution of Fractions A and B of the polymer samples in runs 1-4

Sample	Content of unit (mol%)											n_{E}a)	n_{P}b)
	E	P	EE	EP	PP	EEE	EEP	PEP	EPE	PPE	PPP		
run1-A	53.85	46.15	34.88	39.87	25.25	25.19	19.39	9.27	11.74	18.32	16.09	2.70	2.32
run1-B	67.64	32.36	55.20	24.01	20.79	47.49	15.42	4.73	8.39	6.37	17.61	5.63	2.70
run2-A	47.47	52.53	27.92	37.95	34.12	18.51	18.82	10.14	10.10	16.61	25.82	2.50	2.77
run2-B	53.96	46.04	42.57	23.16	34.27	35.87	13.39	4.70	6.64	10.27	29.14	4.66	3.98
run3-A	50.98	49.02	30.58	37.99	31.43	21.06	19.03	10.89	9.82	15.55	23.65	2.68	2.58
run3-B	64.94	35.06	53.05	21.69	25.26	46.03	14.03	4.87	6.51	6.58	21.96	5.99	3.23
run4-A	52.26	47.74	32.51	40.66	26.83	22.14	20.75	9.38	10.90	20.03	16.81	2.57	2.35
run4-B	64.77	35.23	51.22	26.63	22.14	43.27	15.90	5.59	9.86	6.45	18.92	4.86	2.65

[a] Average ethylene sequence length, $n_E = \frac{2[\mathrm{E}]}{[\mathrm{EP}]}$.

[b] Average propene sequence length, $n_P = \frac{2[\mathrm{P}]}{[\mathrm{EP}]}$.