Supplementary Information (SI) for Polymer Chemistry.
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Electronic Supplementary Information for:

Synthesis of Butadiene-Derived Polyolefin Graft Copolymers and Their Crystallization Behaviors

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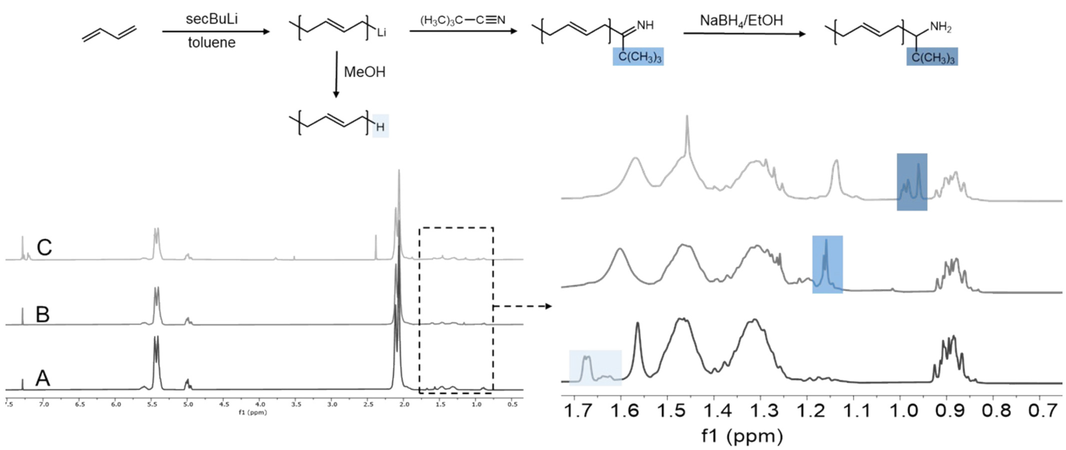

Figure S1. ^{1}H-NMR spectra in $CDCl_3$ of (A) unfunctionalized PB, (B) imine-terminated PB and (C) amine-terminated PB.

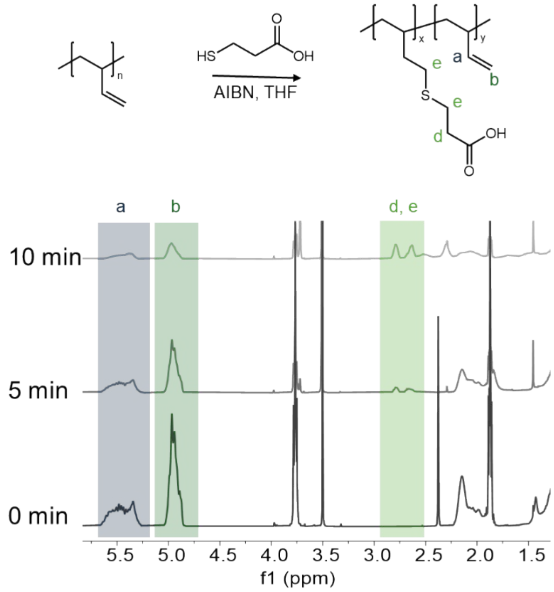

Figure S2. ^{1}H-NMR spectra in $CDCl_3$ of 1,2-PB and carboxyl functionalized 1,2-PB at 5 min and 10 min.

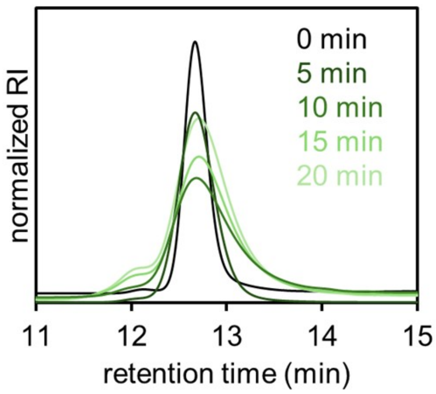

Figure S3. GPC traces of 1,2-PB and carboxyl functionalized 1,2-PB at 5 min, 10 min, 15 min and 20 min.

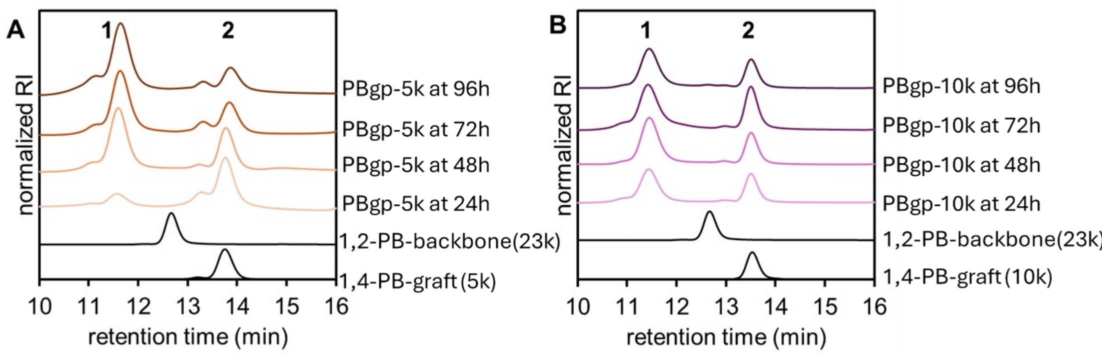

Figure S4. Stacks of GPC traces for the progress of reactions for (A) PBgp-5k and (B) PBgp-10k.

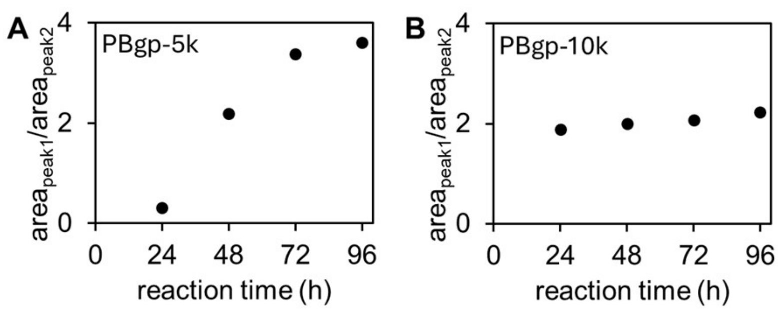

Figure S5. The ratio of peak area for PBgp (peak 1) and graft (peak 2) from the GPC of the crude mixtures of (A) PBgp-5k and (B) PBgp-10k.

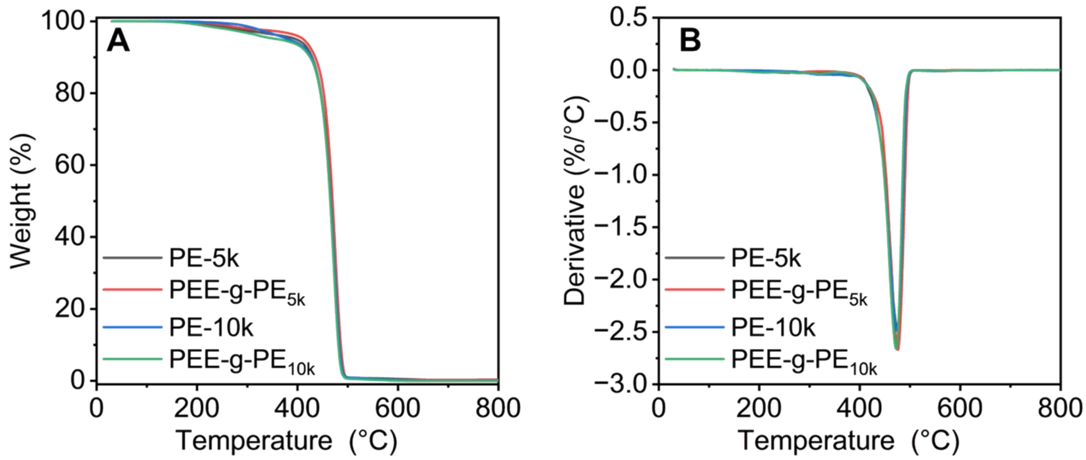

Figure S6. (A) TGA curves in nitrogen and (B) derivative thermogravimetric curve of PE-5k (T_{d5}=397 °C), PEE-g-PE_{5k} (T_{d5}=380 °C), PE-10k (T_{d5}=396 °C), and PEE-g-PE_{10k} (T_{d5}=378 °C).

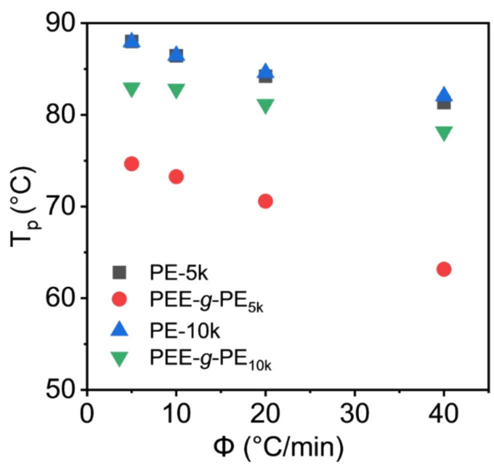

Figure S7. T_p of PE-5k, PE-10k, PEE-g-PE_{5k} and PEE-g-PE_{10k} during non-isothermal crystallization as function of cooling rates.

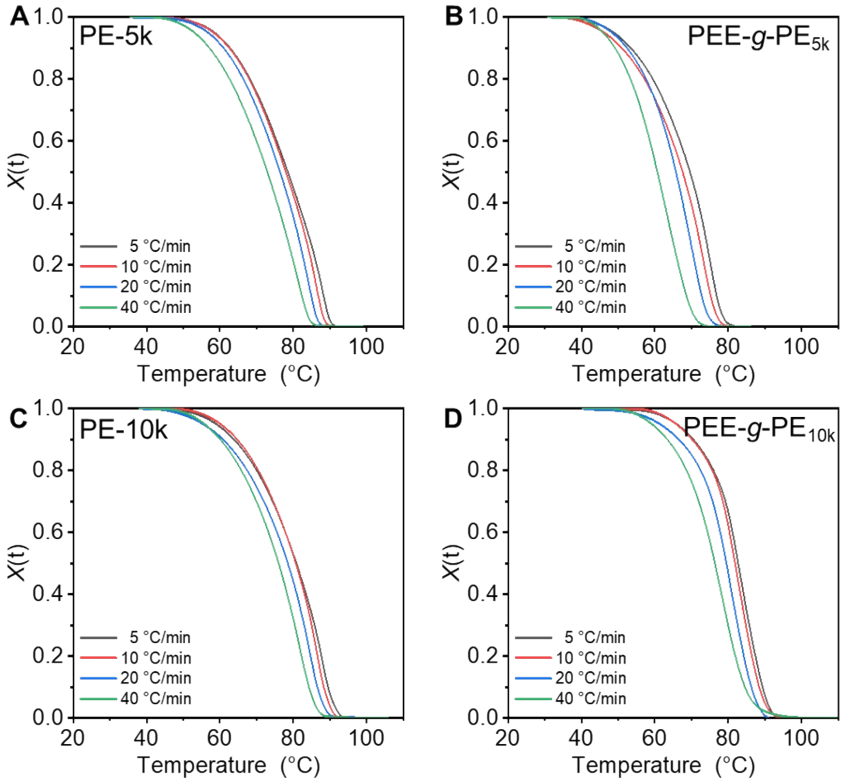

Figure S8. Development of relative crystallinity with temperature for non-isothermal crystallization of for (A) PE-5k, (B) PEE-g-PE$_{5k}$, (C) PE-10k, and (D) PEE-g-PE$_{10k}$.

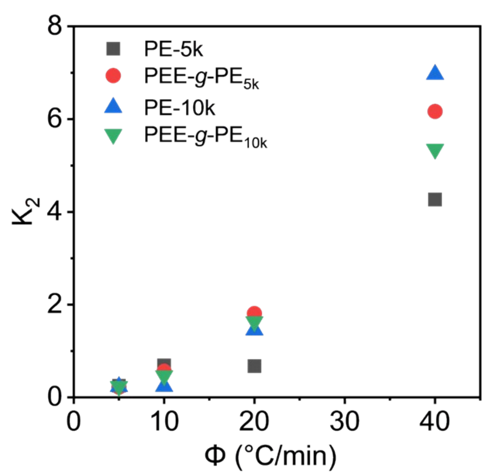

Figure S9. Avrami constant (before Jeziorny modification) for non-isothermal crystallization of PE-5k, PEE-g-PE$_{5k}$, PE-10k, and PEE-g-PE$_{10k}$.

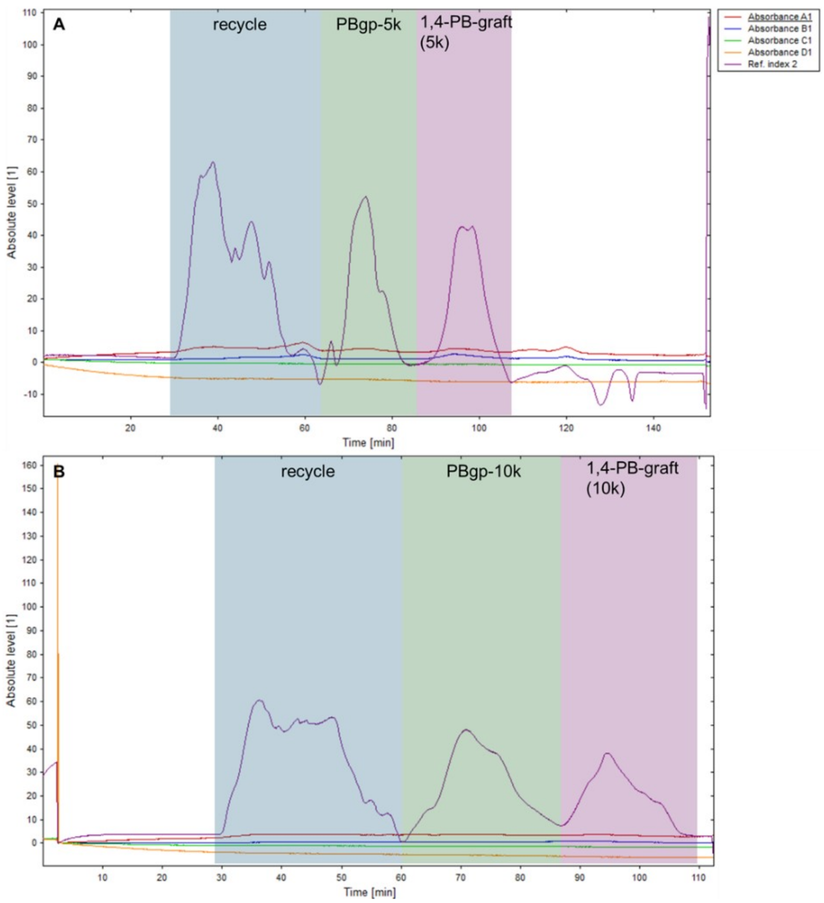

Figure S10. Preparative GPC traces of (A) PBgp-5k and (B) PBgp-10k.

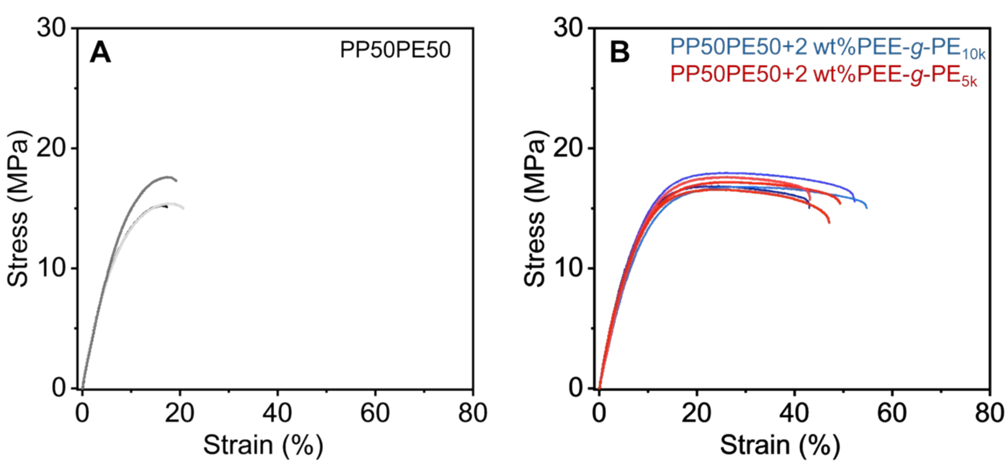

Figure S11. Stress−strain curves performed at 22 mm/min.

Table S1. Characterization data of PBgp-5k, PBgp-10k, 1,2-PB-COOH, 1,2-PB, 1,2-PB-5k and 1,2-PB-10k.

Polymers	M_n [a] (kg/mol)	$Đ$ [a]	1,2R [b]
PBgp-5k	153	1.11	0.24
PBgp-10k	167	1.43	0.21
1,2-PB-COOH	43	1.22	0.82
1,2-PB	46	1.03	0.89
1,4-PB-5k	11	1.08	0.12
1,4-PB-10k	22	1.08	0.12

[a] Measured by GPC in THF at 40 °C with PS standards. [b] The ratio of 1,2-butadiene units was calculated using eq1.

Table S2. Values of T_{onset}, T_p, and $t_{1/2}$ at various cooling rates (ϕ) for PEE-g-PE_{5k}, PEE-g-PE_{10k}, PE-5k and PE-10k.

Polymers	ϕ (°C /min)	T_{onset} (°C)	T_p (°C)	$t_{1/2}$ (min)
PEE-g-PE_{5k}	5	80.1	74.7	2.1
	10	78.6	73.3	1.1
	20	76.3	70.6	0.5
	40	73.0	63.2	0.3
PEE-g-PE_{10k}	5	93.5	82.9	2.1
	10	92.5	82.8	1.1
	20	90.8	81.1	0.6
	40	88.9	78.2	0.3
PE-5k	5	91.1	88.0	2.5
	10	89.6	86.4	1.2
	20	87.9	84.2	0.6
	40	89.6	81.3	0.4
PE-10k	5	92.5	87.9	2.4
	10	92.7	86.5	1.2
	20	90.9	84.6	0.6
	40	88.6	82.0	0.3

Table S3. Elastic modulus, strain at break and toughness of the neat blend (PP50PE50) and the blends of 2 wt% PEE-g-PE graft copolymers.

	Elastic modulus (MPa)[a]	Strain at break (%)	toughness (MJ/m^3)[b]
PP50PE50	147.8 ± 11.7	19.0 ± 1.6	2.2 ± 0.3
PP50PE50+2 wt% PEE-g-PE_{5k}	150.4 ± 3.3	46.5 ± 3.1	6.8 ± 0.4
PP50PE50+2 wt% PEE-g-PE_{10k}	139.6 ± 5.9	50.0 ± 6.2	7.5 ± 1.1

[a] Calculated as the slope of the linear region of the curve prior to yield. [b] Determined by integrating the stress−strain curves for each sample.

The ratio of 1,2-butadiene units ($1{,}2R$) is calculated as

$$1{,}2R = \frac{2I_b}{2I_{a,c} + I_b} \qquad \text{eq.1}$$

where I_b and $I_{a,c}$ are the integration of peak b and peak a,c in Figure 2, respectively.

The graft density (G) of -COOH on 1,2-PB-COOH was calculated as:

$$G = \frac{N_{COOH}}{N_{COOH} + N_{butadiene}} = \frac{\frac{I_d + I_e}{6}}{\frac{I_d + I_e}{6} + \frac{2I_a + I_b}{4}} \qquad \text{eq.2}$$

where N_{COOH} and $N_{butadiene}$ are the number of -COOH and butadiene units; I_a, I_b, I_c and I_d are the integration of peak a, b, c and d in Figure S2, respectively.

The number of graft in the copolymer PBgp is calculated as:

$$1{,}2R_{gp} = \frac{1{,}2R_{PB-COOH} \times RU_{PB-COOH} + 1{,}2R_{graft} \times RU_{graft} \times N}{RU_{PB-COOH} + RU_{graft} \times N} \qquad \text{eq.3}$$

where $1{,}2R_{gp}$, $1{,}2R_{PB-COOH}$, and $1{,}2R_{graft}$ are the 1, 2 ratios of the graft polymer PBgp, 1,2-PB-COOH backbone (after thiol-ene reaction), and 1,4-PB-NH_2 graft, respectively; $RU_{PB-COOH}$ and RU_{grafts} are the number of butadiene units of 1,2-PB-COOH backbone and 1,4-PB-NH_2 grafts , respectively; N is the number of grafts per 1,2-PB backbone.

Therefore,

$$1{,}2R_{gp} = \frac{1{,}2R_{PB-COOH} \times \frac{Mn_{1,2-PB}}{MW_{BD}} \times (1-G) + 1{,}2R_{graft} \times \frac{Mn_{graft}}{MW_{BD}} \times N}{\frac{Mn_{1,2-PB}}{MW_{BD}} \times (1-G) + \frac{Mn_{graft}}{MW_{BD}} \times N}$$

$$= \frac{1{,}2R_{PB-COOH} \times Mn_{1,2-PB} \times (1-G) + 1{,}2R_{graft} \times Mn_{graft} \times N}{Mn_{1,2-PB} \times (1-G) + Mn_{graft} \times N}$$

where G is the graft density of -COOH on 1,2-PB-COOH obtained from eq.2, $M_{n,1,2-PB}$ and $M_{n,graft}$ are the molecular weight of 1,2-PB and 1,4-PB, respectively, and MW_{BD} is the molecular weight of butadiene.

The number of grafts per 1,2-PB backbone (N) can be obtained as:

$$N = \frac{Mn_{1,2-PB} \times (1-G) \times (1{,}2R_{PB-COOH} - 1{,}2R_{gp})}{Mn_{graft} \times (1{,}2R_{gp} - 1{,}2R_{graft})} \qquad \text{eq.4}$$

In this work, $M_{n,\,1,2-PB} = 23{,}000\ g/mol$, $G = 0.1$, and $M_{n,graft} = 10{,}000\ g/mol\ and\ 5{,}000\ g/mol$ for 1,4-PB-NH_2-10k and 1,2-PB- NH_2-5k, respectively. $1{,}2R_{gp}$, $1{,}2R_{PB-COOH}$, and $1{,}2R_{graft}$ were obtained from the ^{1}H-NMR spectra of PBgp after prepGPC, 1,2-PB-COOH, and 1,2-PB-NH_2 using eq.1.

The weight fraction of the graft in the copolymer PEE-g-PE (W_{graft}) is calculated as:

$$W_{graft} = \frac{N \times M_{n,PE}}{N \times M_{n,PE} + M_{n,PEE}} \qquad \text{eq.5}$$

where N is the number of grafts per backbone as calculated by eq.4, $M_{n,PE}$ and $M_{n,PEE}$ are the molecular weight of graft and backbone of PEE-g-PE, respectively, which are calculated as:

$$M_{n,PE} = \frac{M_{n,graft}}{54\ g/mol} \times 56\ g/mol \qquad \text{eq.6}$$

where $M_{n,graft} = 10{,}000\ and\ 5{,}000$ for 1,4-PB-NH_2-10k and 1,2-PB- NH_2-5k, respectively. 54 g/mol and 56 g/mol are the molecular weight of the repeating unit of PB before and after hydrogenation (the molecular weight of -NH- is neglected).

$$M_{n,PEE} = \frac{M_{n,1,2-PB}}{54\ g/mol} \times 56\ g/mol + \frac{M_{n,1,2-PB}}{54\ g/mol} \times G \times 88\ g/mol \qquad \text{eq.7}$$

where $M_{n,\,1,2-PB} = 23{,}000\ g/mol$, G is the graft density of -COOH on 1,2-PB-COOH obtained from eq.2, and 88 g/mol is the molecular weight of -SCH_2CH_2CO-.