Synthesis of Graft Polymers with Poly(isoprene) as Main Chain by Living Anionic Polymerization Mechanism

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ABSTRACT: The graft polymers [poly(isoprene)-*graft*-poly(styrene)] (PI-*g*-PS), [poly(isoprene)-*graft*-poly(isoprene)] (PI-*g*-PI), [poly(isoprene)-*graft*-(poly(isoprene)-*block*-poly(styrene))] PI-*g*-(PI-*b*-PS), and [poly(isoprene)-*graft*-(poly(styrene)-*block*-poly(isoprene))] PI-*g*-(PS-*b*-PI) with PI as main chain were synthesized through living anionic polymerization (LAP) mechanism and the efficient coupling reaction. First, the PI was synthesized by LAP mechanism and epoxidized in H_2O_2/HCOOH system for epoxidized PI (EPI). Then, the graft polymers with controlled molecular weight of main chain and side chains, and grafting ratios were obtained by coupling reaction between PI^-Li^+, PS^-Li^+, PS-*b*-PI^-Li^+, or PI-*b*-PS^-Li^+ macroanions and the epoxide on EPI. The target polymers and all intermediates were well characterized by SEC, ^{1}H NMR, as well as their thermal properties were also evaluated by DSC. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 5144–5150, 2012

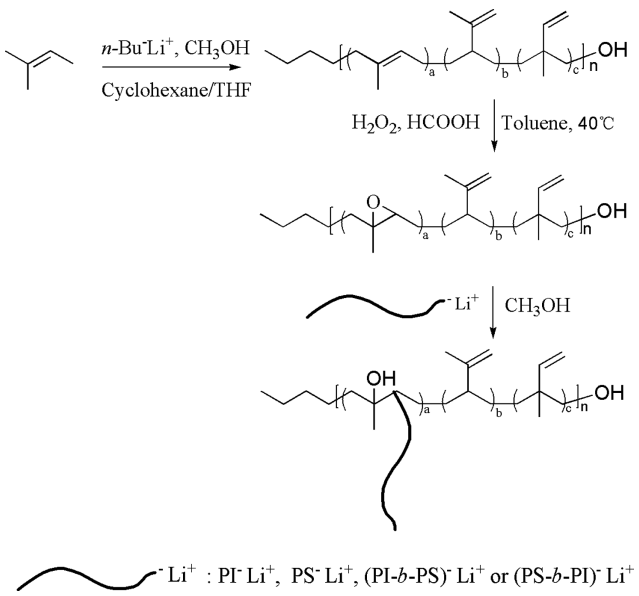
KEYWORDS: graft polymer; living anionic polymerization (LAP); poly(isoprene) (PI); polystyrene (PS)

INTRODUCTION Graft polymers represent a category of important and easily accessible class of materials;[1] they can impart the materials with properties of both individual polymers as well as new properties of the combination.[2] Those graft polymers can be applied to surface patterning in microelectronics, biomaterials, generation of masks and templates, and optical components.[3] Meanwhile, those graft polymers can also be applied to lubrication, pH, temperature, solvent or concentration responsive-modification.[4,5]

During the past decades, graft polymers with different compositions and topologies have been synthesized through "grafting from,"[6] "grafting onto,"[7] or "grafting through"[8] strategies by combination of multiple controlled/"living" polymerization mechanisms[9–14] and/or some efficient coupling techniques.[7a,15] For example, the amphiphilic [poly(methyl methacrylate)-*graft*-poly(ethylene oxide)],[16] [poly(*N*,*N*-dimethylamino-2-ethylmethacrylate)-*graft*-poly(epsilon-caprolactone)],[17] [poly(ethylene oxide)-*graft*-poly(styrene)][18] have been synthesized successively. The topologies of graft polymers usually included the comb, comb-on-comb and star-comb, H-shaped and super H-shaped,[19] V-shaped,[20] and Y-shaped.[21] However, the main chains of the graft copolymers were typically comprised of PEO,[7b,18] PS,[22] poly(acrylic acid),[7g] poly(-hydroxyethyl methacrylate)[23] and so on, and poly(isoprene) (PI) was difficultly and rarely constructed into the main chain of graft polymers because the PI segment with controlled molecular weight and low PDIs was always synthesized by LAP mechanism and there were no accessible functional groups on PI for further modification.[24]

On the other hand, the PI was a classical soft segment in the investigation of multiblock and multiconstitution copolymers, which might bring the copolymers with special properties and favored by polymer chemists and polymer physicists.[25] One successful route to graft polymer with PI as main chain was the coupling reaction between "living" polymeric species and chlorosilane by Mays and coworkers[24,26] and Hadjichristidis and coworkers[19a,27] Another route was previously explored by our group; the graft polymer [poly(isoprene)-*graft*-poly(styrene)] (PI-*g*-PS) and PI-*g*-P*t*BA were realized by using the thiol-ene coupling reaction to modify the PI main chain, which had also been proved as an efficient method to graft polymers with controlled compositions.[20] However, the synthetic routes to graft polymers with PI as main chain (especially with the high molecular weight, $M_n > 5 \times 10^4$ g/mol) and regular PS or PI segments as side chains were still a challenge.

Recently, Yuan and Gauthier had introduced the epoxide onto PI segment by *in situ* peroxidation reaction and synthesized hyperbranched arborescent isoprene homopolymers,[28] which opened another novel way to functional PI. Herein, we used this peroxidation reaction from H_2O_2/HCOOH system to introduce epoxide onto PI main chain and use the formed



SCHEME 1 The synthetic procedure of graft polymers.

epoxide as branch points, and a series of graft polymers with PS, PI, and PI-*b*-PS as side chains were synthesized. Meanwhile, the thermal properties of graft polymers were also investigated.

RESULTS AND DISCUSSION

The synthetical procedure of graft polymers were as follows (Scheme 1): (1) the main chain of PI was synthesized by LAP mechanism and epoxidized in H_2O_2/HCOOH system for epoxidized PI (EPI), (2) the macroanions of PI^-Li^+ or PS^-Li^+ was obtained by LAP of isoprene or styrene monomers and reacted with epoxide on EPI for graft polymers [poly(isoprene)-*graft*-poly(isoprene)] (PI-*g*-PI) or PI-*g*-PS, and (3) the macroanions of PS-*b*-PI^-Li^+ or PI-*b*-PS^-Li^+ was obtained by sequential LAP of isoprene or styrene monomers and reacted with epoxide on EPI for graft polymers [poly(isoprene)-*graft*-(poly(styrene)-*block*-poly(isoprene))] PI-*g*-(PS-*b*-PI) or [poly(isoprene)-*graft*-(poly(isoprene)-*block*-poly(styrene))] PI-*g*-(PI-*b*-PS).

Synthesis and Characterization of PI and EPI

The homopolymer PI was obtained by LAP mechanism of isoprene monomers using *n*-Bu^-Li^+ as initiator and end-capped with methanol. Then, the PI was epoxidized with performic acid generated *in situ* from H_2O_2/HCOOH system,[29] which was an excellent reagent due to its low cost and relatively good reproducibility of the substitution level.[28] Figure 1 showed the size exclusion chromatography (SEC) traces of PI and EPI, their monomodal peaks and low PDIs confirmed that the LAP and subsequent epoxidation were successful. The increasing of apparent molecular weight for EPI was also an evidence for the structure transformation from PI to EPI.

From the ^{1}H NMR spectrum for PI [Fig. 2(A)], the characteristic resonance signals ascribed to the mixed microstructure of 1,4-addition, 1,2-addition, and 3,4-addition isoprene units

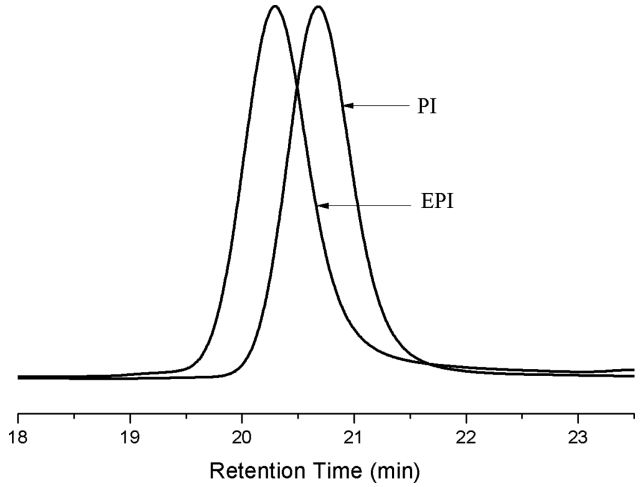


FIGURE 1 SEC traces of EPI ($M_n = 1.04 \times 10^5$ g/mol, $D = 1.05$) and PI ($M_n = 8.59 \times 10^4$ g/mol, $D = 1.03$).

could be discriminated, and their ratio was evaluated according to ^{1}H NMR spectrum for PI [Fig. 2(A)] and Formula (1):

$$R_{1,2}:R_{1,4}:R_{3,4} = A_a:A_c:(A_{b+d} - 2A_a)/2 \quad (1)$$

where A_a represented the integral area of methyne protons (—C***H***=CH_2, a) on 1,2-addition units at 5.57–5.90 ppm, A_{b+d} represented the integral area of methylene protons (—CH=C***H*****$_2$**, d) on 1,2-addition units and methylene protons (C***H*****$_2$**=C(CH_3) —, b) on 3,4-addition units at 4.41–4.78 ppm, and A_c represented the integral area of methyne protons (—C***H***=C(CH_3) —, c) on 1,4-addition at 4.78–5.17 ppm, respectively. The obtained percentage of 1,4-addition, 1,2-addition, and 3,4-addition isoprene units were 26.2%, 13.8%, and 60.0%, respectively.

From the ^{1}H NMR spectrum for EPI [Fig. 2(B)], the occurrence of resonance signal at 2.40–2.80 ppm ascribed to epoxide proton (—C(CH_3)OC***H***—, e) could be observed, which confirmed that the double bond on PI main chain were

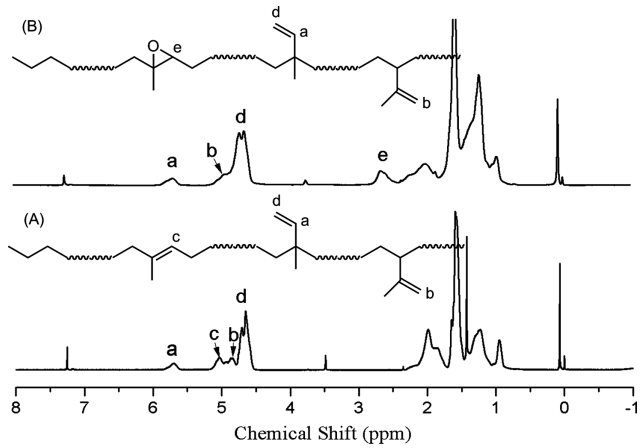


FIGURE 2 ^{1}H NMR spectra for PI (A) and EPI (B).

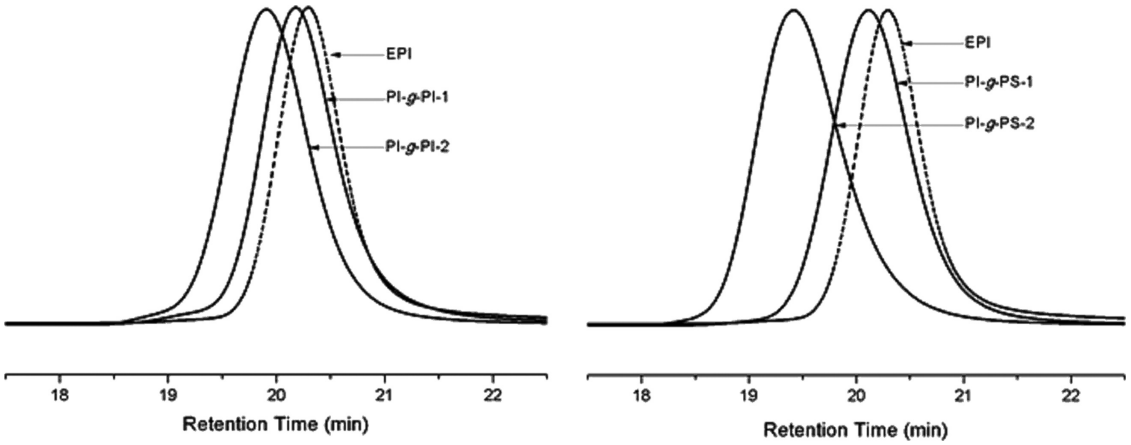


FIGURE 3 SEC traces of EPI and graft polymers PI-*g*-PI-1 ($M_n = 1.32 \times 10^5$ g/mol, $D = 1.10$), PI-*g*-PI-2 ($M_n = 1.66 \times 10^5$ g/mol, $D = 1.10$), PI-*g*-PS-1 ($M_n = 1.36 \times 10^5$ g/mol, $D = 1.08$), and PI-*g*-PS-2 ($M_n = 2.17 \times 10^5$ g/mol, $D = 1.12$).

actually transformed into epoxide. Through the comparison of spectra for PI [Fig. 2(A)] and EPI [Fig. 2(B)], we could discriminated that the resonance signals at 4.78–5.17 ppm for methylene proton (—C***H***=C(CH_3) —, c) on 1,4-addition disappeared, and that for methyne protons (—C***H***=C(CH_3) —, b) on 3,4-addition decreased. However, the other resonance signals for protons on 1,2-additon (—C***H***=C***H***$_2$, d) almost had no change. Thus, we gave the conclusion that the epoxidation mainly happened to double bond on 1,4-addition and 3,4-addition microstructure. Taking the resonance signals for protons (—C***H***=CH_2, a) on 1,2-addition as reference, the percentage of epoxidation (PE) was evaluated according to ^{1}H NMR spectrum for PI [Fig. 2(B)] and Formula (2):

$$\mathrm{PE} = \frac{A_e}{A_a/13.8\%} \quad (2)$$

which the A_e represented the integral area of resonance signal for methyne proton (—C(CH_3)OC***H***—, e) on epoxide, and the obtained PE value was 33.0%. That was, there was about 416 epoxide groups on each EPI main chain. Usually, the PE value could also be adjusted by controlling the temperature, reaction time, and the ratio of H_2O_2/HCOOH or H_2O_2/C=C.[28,30]

Thus, the main chain of EPI embedded epoxide was successfully synthesized from its precursor of PI (which was obtained by LAP of isoprene monomers). Importantly, the molecular weight, PDIs, and the PE of the precursors could be well modulated.

Synthesis and Characterization of Graft Polymers

The coupling reaction between epoxide on EPI and the living macroanions of PI^-Li^+ or PS^-Li^+ were proceeded for graft polymers PI-*g*-PI and PI-*g*-PS. After removing the excess PI or PS homopolymers by fractional precipitation, the pure graft polymers of PI-*g*-PI-1, PI-*g*-PI-2, PI-*g*-PS-1, and PI-*g*-PS-2 with low PDIs were obtained (Fig. 3). These two pairs of polymers, PI-*g*-PI-1 and PI-*g*-PI-2, PI-*g*-PS-1 and PI-*g*-PS-2 have the same backbone but different side chains. Comparing the SEC curve of EPI with that of graft polymers, we could observe the obvious increasing of apparent molecular weight of graft polymers, which could be regarded as one of the evidence for the successful coupling reaction.

From the ^{1}H NMR spectrum for PI-*g*-PI-1 [Fig. 4(B)], the characteristic resonance signal for protons on PI segments could be discriminated, which had no obvious difference with its precursor of EPI because they almost have the same compositions. Compared the ^{1}H NMR spectrum for PI-*g*-PI-1 with that for EPI, only the ratio of 1,4-addition, 1,2-addition, and 3,4-addition was changed as the different microstructure of the branch and the main chain. That was, the ratio of integral areas A_a:A_c:A_e for EPI 1.00:12.22:2.57, and for PI-*g*-PI-1 was 1.00:11.47:0.8, which could also be regarded as one of the evidence for the successful coupling reaction between EPI and PI^-Li^+. From the ^{1}H NMR spectrum for PI-*g*-PS-1 [Fig. 4(C)], except for the resonance signals for protons on PI main chain, the characteristic resonance signals for aromatic protons (—C_6***H***$_5$) on PS segment at 6.2–7.4 ppm were also discriminated clearly, which proved the successful introduction of PS side chain onto PI main chain.

To get graft polymers with block side chains, we also synthesized the block macroaninons first by sequential LAP of isoprene or styrene monomers using *n*-Bu^-Li^+ as initiator, and the macroanions of PS-*b*-PI^-Li^+ or PI-*b*-PS^-Li^+ were reacted with epoxide on EPI for PI-*g*-(PI-*b*-PS) or PI-*g*-(PS-*b*-PI). Figure 5 showed the SEC traces of PI-*g*-(PI-*b*-PS) and PI-*g*-(PS-*b*-PI), and the monomodal peaks and low PDIs confirmed the successful synthesis of graft polymers. From the ^{1}H NMR spectra of PI-*g*-(PI-*b*-PS) and PI-*g*-(PS-*b*-PI) (Fig. 4), the characteristic resonance signals for aromatic proton (—C_6***H***$_5$) on PS segment at 6.3–7.5 ppm and that of protons on PI segment between 4.41 and 5.90 ppm could all be discriminated. These results efficiently confirmed that the graft polymers of PI-*g*-(PI-*b*-PS) and PI-*g*-(PS-*b*-PI) were successfully synthesized.

As the complicated structure and compositions, the accurate molecular weight of graft polymers could not be directly obtained by SEC and ^{1}H NMR measurements. Finally, the

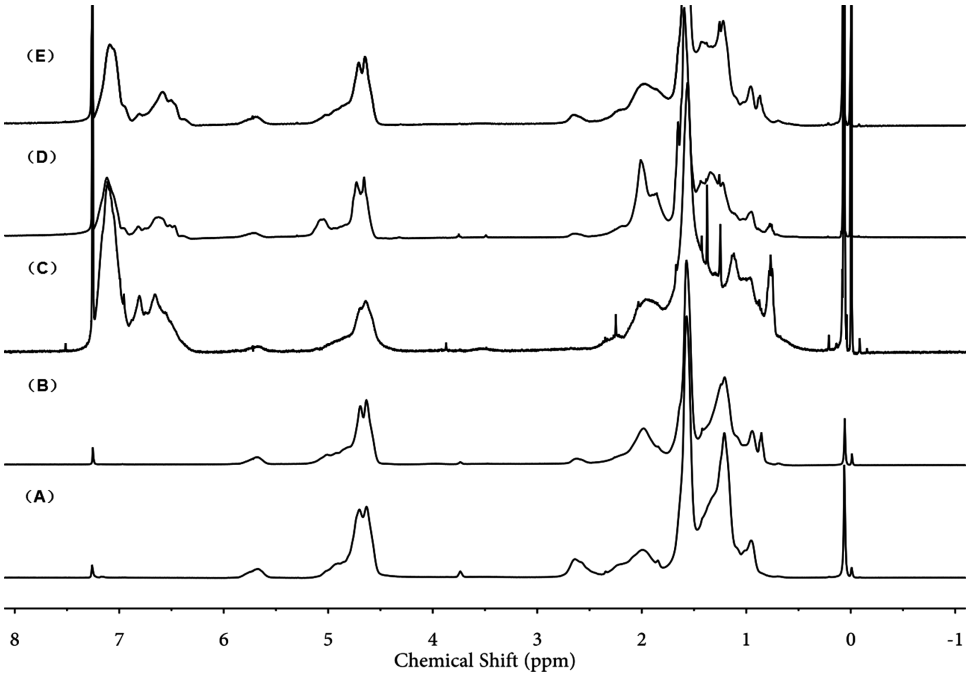


FIGURE 4 ^{1}H NMR spectra for EPI (A) and graft polymers: PI-*g*-PI-1(B), PI-*g*-PS-1 (C), PI-*g*-(PI-*b*-PS) (D), and PI-*g*-(PS-*b*-PI) (E).

static light scattering was adopted, and the total molecular weights of graft polymers were listed in Table 1. Based on the obtained actual molecular weight of side chains and the total molecular weight of graft polymers, the grafting ratio of PI-*g*-PI-1 (38.2%), PI-*g*-PI-2 (12.3%), PI-*g*-PS-1 (37.3%), PI-*g*-PS-2 (49.0%), PI-*g*-(PI-*b*-PS) (10.6%), and PI-*g*-(PS-*b*-PI) (5.0%) were evaluated (Table 1).

The Thermal Properties of Graft Copolymers

To study the influence of side chains on thermal properties of graft polymers, the glass transition temperature (T_g) of EPI and the graft polymers were also evaluated by differential scanning calorimetry (DSC) measurement and obtained from the second heating run (Fig. 6).

For the precursor of EPI, the T_g was 22.1 °C, which was larger than the usually T_g of PI homopolymer (−70 to −50 °C[20,31]). After the PS side chains were grafted onto PI main chain, the T_g for PI-*g*-PS-1(shorter side chains) and PI-*g*-PS-2 (longer side chains) were increased to 64.9 °C and 84.7 °C, respectively. However, these T_gs were lower than the T_g for linear PS homopolymer (near 90 °C[32]). When the side chains were designed as block copolymers, specifically, the PI-*g*-(PI-*b*-PS) and PI-*g*-(PS-*b*-PI) had the similar molecular weights of side chains and the molar ratio of isoprene unit to styrene unit (1:1), but with different sequence of PI and PS on the side chains. The PI-*g*-(PI-*b*-PS) clearly display a T_g at about 21.9 °C;however, the PI-*g*-(PS-*b*-PI) has a T_g at 41.6 °C. Thus, by modulating the length, compositions, and sequence of side chains, the thermal properties of graft polymers could be controlled and might be used for some special applications.

EXPERIMENTAL

Materials

Styrene [St, 99%, Sinopharm Chemical Reagent Co. (SCR)] was washed with 10% NaOH aqueous solution followed by water three times, dried over anhydrous $MgSO_4$, further dried over CaH_2, and distilled under reduced pressure. The isoprene monomer and cyclohexane (AR, 99.5%, Shanghai DaHe Chemical Reagent Co.) were dried by CaH_2 and then distilled. Tetrahydrofuran (THF, >99%, SCR) were refluxed and distilled from sodium naphthalenide solution. The hydrogen peroxide (H_2O_2, >99%, Jiangsu TongSheng Chemical Reagent Co.), HCOOH (AR, ≥ 88%, Shanghai Ling Feng

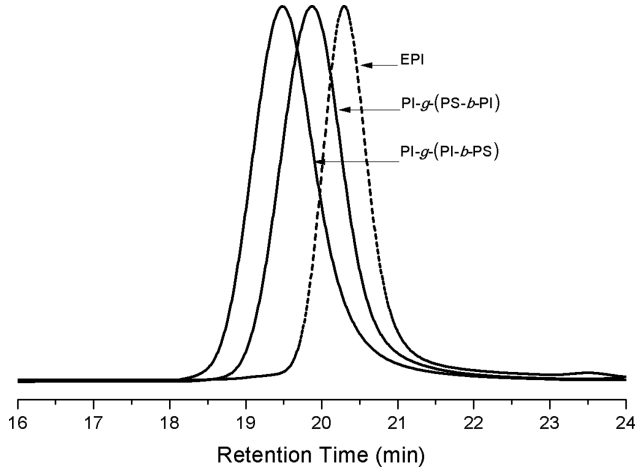


FIGURE 5 SEC traces of EPI and graft polymers PI-*g*-(PI-*b*-PS) (M_n = 1.77 × 10^5 g/mol, PDI = 1.14) and PI-*g*-(PS-*b*-PI) (M_n = 1.68 × 10^5 g/mol, PDI = 1.13).

TABLE 1 The Molecular Characteristics for Graft Polymers

	Graft Polymers				Side Chains	
Sample	$M_{n,SEC}$[a] (10^5g/mol)	PDI[a]	$M_{w,MALLS}$[b] (10^5g/mol)	$M_{n,SEC}$[a] (10^3g/mol)	Numbers of Side Chains	Grafting Ratio[c] (%)
PI-*g*-PI-1	1.32	1.10	1.70	0.53	159	38.2
PI-*g*-PI-2	1.66	1.10	2.50	3.16	51	12.3
PI-*g*-PS-1	1.36	1.12	2.27	0.91	155	37.3
PI-*g*-PS-2	2.17	1.08	5.70	2.38	203	49.0
PI-*g*-(PI-*b*-PS)	1.77	1.14	2.80	4.34	44	10.6
PI-*g*-(PS-*b*-PI)	1.68	1.13	2.00	5.30	21	5.0

[a] Determined by SEC with THF as solvent using PS standards.
[b] Determined by static light scattering in THF at 25 °C, the d*n*/d*c* were calculated from $dn/dc = w(dn/dc)_{PS} + (1 - w)(dn/dc)_{PI}$[30], where *w* was the wt % of PS.
[c] Calculated from the formula: Grafting ratio = $n_{branch\ numbers}/n_{epoxide\ numbers}$

Chemical Reagent Co.). *n*-butyllithium (*n*-Bu$^-$Li$^+$) (1.6 M in hexane, Amethyst Chemicals.) and CH_3OH (AR, 99.5%, Shanghai Ling Feng Chemical Reagent Co.) were used as received.

Measurements

The apparent molecular weight were performed by SEC analysis in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector. One 5 μm LP gel column (500 Å, molecular range 500–2 × 104 g/mol) and two 5 μm LP gel mixed bed column (molecular range 200–3 × 106 g/mol) were calibrated by PS standard samples. The injection volume was 20.0 μL, and the concentration was 5.0 mg/mL. The absolute molecular weight were performed by SEC analysis through three Waters Styragel columns (pore size 10^2, 10^3 and 10^4Å), calibrated by narrow polystyrene standards, and equipped with three detectors: a DAWN H ELEOS (14−154°)(Wyatt multiangle laser light scattering detector, He −Ne 632.8 nm), nm), ViscoStar (Wyatt), and Optilab rEX (Wyatt). THF was used as the eluent at a flow rate of 1.0 mL/min at 35 °C. 1H NMR spectra were recorded on a DMX 500 MHz spectrometer in CDCl3 with tetramethylsilane (TMS) as the internal reference for chemical shifts. DSC was carried on a DSC Q2000 thermal analysis system (Shimadzu, Japan). Samples were first heated from −80 to150 °C at a heating rate of 10 °C/min under nitrogen atmosphere, followed by cooling to −80 °C at 10 °C/min after stopping at 150 °C for 3 min, and finally heating to 150 °C at 10 °C/min after stopping at −80 °C for 3 min.

Synthesis of PI Precursor

The PI precursor was obtained by LAP mechanism of isoprene monomers using *n*-Bu$^-$Li$^+$ as initiator and end-capped with methanol. Typically, into a 500-mL dried ampoule, purified isoprene (60.0 mL, 600 mmol), cyclohexane (340 mL), and THF (4.0 mL) were charged under nitrogen atmosphere, then *n*-Bu$^-$Li$^+$ solution (0.28 mL, 0.45 mmol) was injected by a syringe under magnetic stirring. After the reaction was kept at room temperature for 8.0 h, the system was terminated by methanol. The product was purified by dissolution/precipitation twice with THF/methanol, and the obtained product of PI was dried under vacuum at 40 °C for 12 h till to a constant weight. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 4.41–4.78 (s, —C(CH_3) =C***H***$_2$), 4.78–4.90 (d, —CH=C***H***$_2$), 4.90–5.17 (t, —C***H***=C(CH_3) —), 5.57–5.90 (t, —C***H***=CH_2). $M_{n(SEC)} = 8.59 \times 10^4$ g/mol, PDI = 1.03.

Synthesis of EPI Precursor

The EPI precursor was obtained by epoxidation of PI with performic acid generated *in situ* from H_2O_2/HCOOH system. The reaction was carried out in a 500-mL round bottomed flask with a magnetic stirring bar under 40 °C. First, the PI (13.8 g, 240 mmol) was dissolved in toluene (300 mL), and the HCOOH (4.2 mL, 97 mmol) was added. Then, the H_2O_2 was added dropwise with stirring over 20 min. Finally, the mixture was washed with saturated NaCl solution till the aqueous layer reached pH 7.0. The organic phase was evaporated and precipitated in methanol/deionized water, and the obtained EPI was dried under vacuum at 40 °C for 12 h till to a constant weight. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 2.40–2.80 (—C(CH_3)OC***H***—), 4.78–4.90 (d, —CH=C***H***$_2$), 5.57–5.90 (t, —C***H***=CH_2), 4.41–4.78 (s, —C(CH_3)=C***H***$_2$). $M_{n(SEC)} = 1.04 \times 10^5$ g/mol, PDI = 1.05.

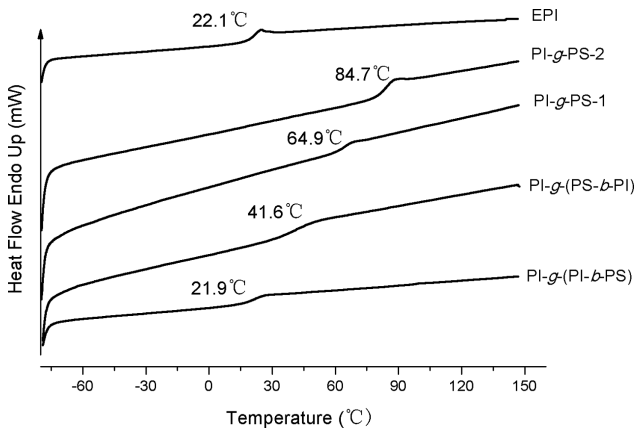


FIGURE 6 DSC traces of EPI, PI-*g*-PS-1, PI-*g*-PS-2, PI-*g*-(PI-*b*-PS), and PI-*g*-(PS-*b*-PI).

Synthesis of PI-*g*-PI and PI-*g*-PS Graft Polymers

The graft polymers of PI-*g*-PI or PI-*g*-PS were obtained by coupling reaction between the epoxide on EPI and the living macroanions of $PI^-\ Li^+$ or PS^-L^+, respectively. Taking the preparation of PI-*g*-PI-1 as an example, into a 500-mL dried ampoule, purified isoprene (5.7 mL, 57.1 mmol), cyclohexane (100 mL), and THF (2.0 mL) were charged under nitrogen atmosphere. Then, *n*-Bu^-Li^+ solution (4.2 mL, 6.72 mmol) was injected by a syringe under magnetic stirring, and the macroanion PI^-Li^+ produced. After 2.0 h, the backbone of EPI (1.1 g, 0.012 mmol) purified with three azeotropic drying cycles by toluene was introduced into the ampoule, and the viscosity of solution increased rapidly. Finally, the reaction was terminated by methanol, and the unreacted homopolymer of PI was removed by fractional precipitation using THF/methanol as solvent/precipitant. The final products were dried under vacuum at 40 °C for 12 h till to a constant weight. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 2.48–2.75 (t, —C(CH_3)OC***H***—), 4.95 (d, —CH=C***H***$_2$), 4.41–4.78 (s, —C(CH_3)=C***H***$_2$), 4.78–5.17 (t, —C***H***=C(CH_3) —), 5.54–5.84 (t, —C***H***=CH_2). PI-*g*-PI-1: $M_{n(SEC)} = 1.32 \times 10^5$ g/mol, PDI = 1.10. PI-*g*-PI-2: $M_{n(SEC)} = 1.67 \times 10^5$ g/mol, PDI = 1.10.

Similarly, the graft polymers of PI-*g*-PS were also obtained by changing isoprene monomers as styrene monomers. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 4.95 (d, —CH=C***H***$_2$), 4.41–4.78 (s, —C(CH_3)=C***H***$_2$), 5.54–5.84 (t, —C***H***=CH_2), 6.3–7.5 (m, (—C_6***H***$_5$)). PI-*g*-PS-1*:* $M_{n(SEC)} = 1.36 \times 10^5$ g/mol, PDI = 1.08. PI-*g*-PS-2: $M_{n(SEC)} = 2.17 \times 10^5$ g/mol, PDI = 1.12.

Synthesis of PI-*g*-(PI-*b*-PS) and PI-*g*-(PS-*b*-PI) Graft Polymers

The graft polymers of PI-*g*-(PI-*b*-PS) or PI-*g*-(PS-*b*-PI) were obtained by coupling reaction between the epoxide on EPI and the living macroanions PS-*b*-PI^-Li^+ or PI-*b*-PS^-Li^+, respectively. Typically, into a 500-mL dried ampoule, purified isoprene (4.3 mL, 43.1 mmol), cyclohexane (200 mL), and THF (2.0 mL) were charged under nitrogen atmosphere. Then, *n*-Bu^-Li^+ solution (2.5 mL, 4.00 mmol) was injected by a syringe under magnetic stirring, and the macroanion PI^-Li^+ produced. After 2.0 h, the purified styrene (3.25 mL, 28.2 mmol) were introduced into the ampoule, and the solution turned red immediately. After another 2.0 h, the backbone of EPI (1.1 g, 0.012 mmol) purified with three azeotropic drying cycles by toluene was introduced into the ampoule, and the viscosity of solution increased rapidly. The purification procedure was similar to that for PI-*g*-PI and PI-*g*-PS. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 2.50–2.75 (t, —C(CH_3)OC***H***—), 4.95 (d, —CH=C***H***$_2$), 4.41–4.78 (s, —C(CH_3)=C***H***$_2$), 4.89–5.20 (t, —C***H***=C(CH_3) —), 6.30–7.50 (m, (—C_6***H***$_5$)). PI-*g*-(PI-*b*-PS): $M_{n(SEC)} = 1.77 \times 10^5$ g/mol, PDI = 1.14. PI-*g*-(PS-*b*-PI): $M_{n(SEC)} = 1.68 \times 10^5$ g/mol, PDI = 1.13.

CONCLUSIONS

The graft polymers PI-*g*-PI, PI-*g*-PS, PI-*g*-(PI-*b*-PS), and PI-*g*-(PS-*b*-PI) were synthesized by LAP mechanism and coupling reaction between epoxide and macroanions of PI^-Li^+ PS^-Li^+ PS-*b*-PI^-Li^+ or PI-*b*-PS^-Li^+, respectively. The structure of target graft polymers and all intermediates were well characterized by ^{1}H NMR and SEC in detail, and the thermal properties of graft polymers were also investigated by DSC. This work provided a versatile and efficient route to the graft polymers with PI as main chain. Especially, the molecular weight of main chain and side chains, the sequence of side chains, and the grafting ratio could all be well modulated elaborately.

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