Investigation of Thiol-ene Addition Reaction on Poly(isoprene) Under UV Irradiation: Synthesis of Graft Copolymers with ''V''-Shaped Side Chains

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ABSTRACT: Poly(isoprene) (PI) with pendant functional groups was successfully synthesized by thiol-ene addition reaction under 365 nm UV irradiation, and the functionalized PI was further modified and used to prepare graft copolymers with "V"-shaped side chains. First, the pendant $-SCH_2CH(OH)CH_2OH$ groups were introduced to PI by thiol-ene addition reaction between 1-thioglycerol and double bonds, and the results showed that the addition reaction carried out only on double bonds of 1,2-addition isoprene units. After the esterification of hydroxyl groups by 2-bromoisobutyryl bromide, the forming macroinitiator was used to initiate the atom transfer radical polymerization (ATRP) of styrene (St) and *tert*-butyl acrylate (*t*BA), and the graft copolymers **PI-*g*-PS$_2$** and **PI-*g*-P*t*BA$_2$** or **PI-*g*-PAA$_2$** (by hydrolysis of **PI-*g*-P*t*BA$_2$**) were obtained, respectively. It was confirmed that the graft density of side chains on PI main chains could be easily controlled by variation of the contents of modified 1,2-addition isoprene units on PI. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3797–3806, 2010

KEYWORDS: atom transfer radical polymerization (ATRP); esterification; graft copolymers; poly(isoprene); thiol-ene addition reaction; UV-irradiation

INTRODUCTION Recently, the graft copolymers with different compositions were widely investigated in biomedical materials,[1] nanotechnology,[2] composite polymer materials,[3] and supramolecular science[4] with their unique properties. To date, the graft copolymers with linear or/and block,[5] hyperbranched,[6] "V"-shaped,[7] star-shaped[8], and dendritic[9] copolymers as side chains had been well researched. These graft copolymers were usually synthesized by "grafting from,"[10] "grafting onto"[11], or "grafting through"[12] strategies by combination of various controlled/"living" polymerization mechanisms[5,13–17] and some coupling techniques.[18]

The main chains of the graft copolymers were typically comprised of poly(ethylene oxide),[11b,19] polystyrene (PS),[20] poly(acrylic acid) (PAA),[21] poly(-hydroxyethyl methacrylate),[22] and so on. However, poly(isoprene) (PI) was difficultly and rarely constructed into the main chain of graft copolymers by the coupling reaction between "living" polymeric species and chlorosilane.[8a,23] The PI was a classical soft segment in the investigation of multiblock and multiconstitution copolymers, which might bring the copolymers with special properties.[24] On the other hand, for the graft copolymers, although the structure of main chain and side chain as molecular weight, numbers of graft sites and functionality of branching sites are the similar, but the linear and "V"-shaped side chains were used, they also showed the different effect on their mechanical properties and morphology in bulk.[25] Thus, finding a versatile protocol to prepare the graft copolymers with controlled molecular weight of PI main chain and controlled numbers of graft sites, functionality of branching sites and defined compositions of side chains (such as "V"-shaped PS, P*t*BA, and PAA) would be a very interesting work, in which the introduction of functional groups or graft sites onto PI main chain was the key point.

The thiol-ene addition reaction had been widely explored and used in polymer science because of its high efficiency and tolerance of oxygen and water, as well as its easy to operation under the photochemical initiation. A variety of vinyl and/or thiol groups contained monomers was designed and their photopolymerization were investigated,[26] and this technique had been used in nanotechnology,[27] composites,[28] biochemistry,[29] and adhesives.[30] By means of this technique, several dendrimers,[31] functionalized polymers (such as PS, poly(butadiene), poly[2-(3-butenyl)-2-oxazoline] and poly(propylene) (PP))[32], and telechelic polymers[33] had been prepared under feasible and mild conditions. The thiol-ene addition reaction was proved to be an efficient, robust, and orthogonal tool in the modification of copolymers contained vinyl groups.

Herein, based on the above thiol-ene addition reaction, the PI with pendant hydroxyl groups was successfully

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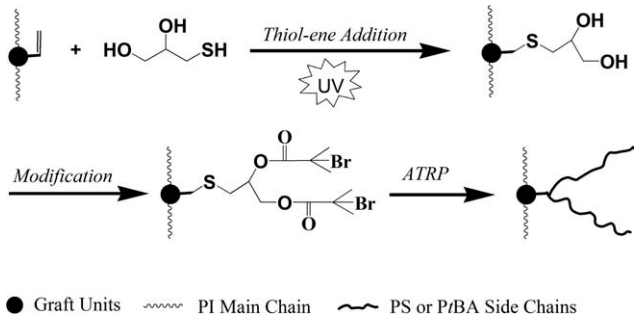


SCHEME 1 The illustration of synthesized macroinitiator and graft copolymers.

synthesized under 365 nm UV irradiation, and the hydroxyl groups were then transformed into the atom transfer radical polymerization (ATRP) initiators. Because of the limitations of "grafting onto" or/and "grafting through" strategies on the size of the main chain or/and the graft density,[7] the "grafting from" strategy were adopted, and the graft copolymer with PI main chain and "V" shaped side chains were prepared (Scheme 1).

EXPERIMENTAL

Materials

Tetrahydrofuran (THF, SCR, 99%) and pyridine (SCR, 99.5%) were refluxed over sodium wire, then distilled from sodium naphthalenide and sodium wire solution, respectively. Styrene (St, Aldrich, 98%) was washed with 10% NaOH aqueous solution followed by water three times successively, dried over CaH_2 and distilled under reduced pressure. *tert*-Butyl acrylate (*t*BA, Aldrich) were dried by CaH_2 and distilled under reduced pressure, stored at −20 °C before use. Cuprous bromide (CuBr, Acros, 98%) was purified by stirring overnight in acetic acid and filtered, then washed with ethanol and diethyl ether successively, and finally dried under vacuum. Benzil dimethyl ketal (BDK), 1-thioglycerol, 2-bromoisobutyryl bromide (98%), 2,2′-bipyridyl (bpy), and *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich and used as received. All other reagents were purchased from Sinopharm Chemical Reagent (SCR) and used as received, unless otherwise noted. Poly(isoprene)(**PI**(**1**)) ($M_{n(SEC)}$ = 35,100 g/mol, PDI = 1.03) was synthesized according to a previous work by "living" anionic polymerization.[34]

Measurements

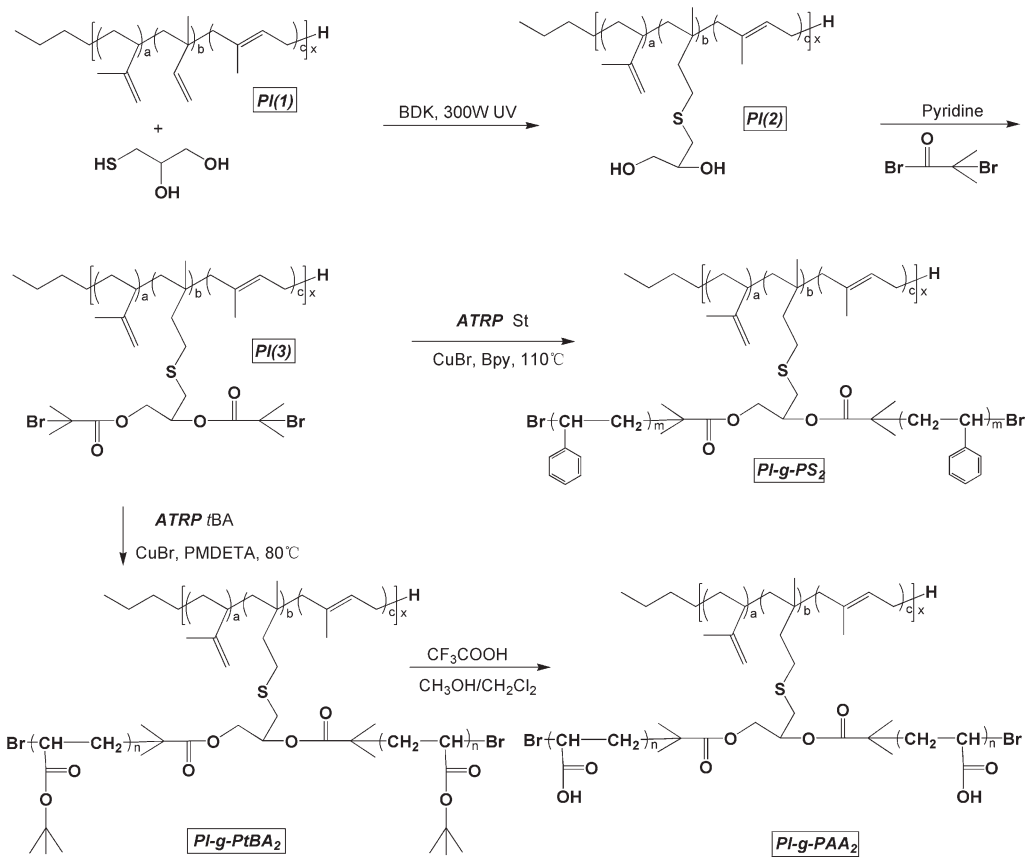
The number average molecular weight and polydispersity index (PDI) were estimated by Size Exclusion Chromatography (SEC). SEC traces were performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector, and PS standard samples were used for calibration. ^{1}H NMR spectra were obtained by a DMX 500 MHz spectrometer using tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent; except for the graft copolymer PI-*g*-PAA_2, which was measured in DMSO-d_6. Elemental analysis (EA) was performed on a vario EL III equipment. Fourier Transform Infrared (FTIR) spectra were recorded on NEXUS 470 FTIR instrument, the polymer samples were dissolved in dry dichloromethane (CH_2Cl_2) or methanol (CH_3OH) and then cast onto a NaCl disk. Differential scanning calorimetry (DSC) was carried on a DSC Q2000 thermal analysis system (Shimadzu, Japan). Samples were first heated from −80 to 150 °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 Poly(isoprene)(PI(2)) with Pendant Hydroxyl groups by Thiol-ene Addition Reaction (Scheme 2)

To a 250 mL round bottom flask, 10.0021 g poly(isoprene) (**PI**(**1**), $M_{n(SEC)}$=35,100 g/mol, PDI = 1.03), 3.1771 g (29.42 mmol) 1-thioglycerol, 1.5103 g (5.90 mmol) benzildimethylketal (BDK) photoinitiator, and 150 mL THF were added. After the dissolution of all chemicals, the solution was irradiated by a 300W high-pressure mercury lamp (Model GGZ-300, manufactured by Shanghai Ya Ming Lamp Factory) under magnetic stirring for 20 min at room temperature, and the cupric sulfate aqueous solution was used as the photofilter to obtain 365 nm monochromatic light. After that the system was concentrated and purified thrice by dissolving/precipitation with THF/methanol to remove the unreacted 1-thioglycerol and BDK. The obtained product with pendant hydroxyl groups (**PI**(**2**)) (Scheme 2) was dried in vacuo at 45 °C for 12 h till to a constant weight. ^{1}H NMR ($CDCl_3$, δ) of **PI**(**1**) (ppm): 0.80 (m, C***H***$_3$CH$_2$—), 1.26–2.25 (m, —C(C***H***$_3$)— and aliphatic main chain —C***H***$_2$C***H***— of PI), 1.86 (m, —C(C***H***$_3$)=CH—, —C(C***H***$_3$)=CH$_2$), 4.63–4.69 (m, —(CH$_3$)C=C***H***$_2$ of 3,4-addition), 4.95 (m, —CH=C***H***$_2$ of 1,2-addition), 5.08 (m, —C***H***=C(CH$_3$)— of 1,4-addition), 5.70 (m, —C***H***=CH$_2$ of 1,2-addition), $M_{n(SEC)}$=35,100 g/mol, PDI = 1.03. ^{1}H NMR ($CDCl_3$, δ) of **PI**(**2**) (ppm): 0.80 (m, C***H***$_3$CH$_2$—), 1.26–2.25 (m, —C(C***H***$_3$)— and aliphatic main chain —C***H***$_2$C***H***— of PI), 1.58 (m, —SCH$_2$C***H***$_2$—), 1.86 (m, —C(C***H***$_3$)= CH—, —C(C***H***$_3$)=CH$_2$), 2.37–2.77(m, —C***H***$_2$SC***H***$_2$—), 3.47–3.88(m, HO—C***H***$_2$C***H***(OH)—), 4.63–4.69 (m, —(CH$_3$)C=C***H***$_2$ of 3,4-addition), 5.08 (m, —C***H***=C(CH$_3$)— of 1,4-addition), $M_{n(NMR)}$ = 73,400 g/mol. Element Analysis of **PI**(**1**): found C, 87.16; H, 11.56. Element Analysis of **PI**(**2**): found C, 75.90; H, 10.69.

Synthesis of Macroinitiator PI(3) by Esterification of Hydroxyl groups on PI(2)

Typically, **PI**(**2**) (5.0154 g, 20.99 mmol hydroxyl groups) was dried by azeotropic distillation with toluene and dissolved in anhydrous pyridine (100 mL), to which 2-bromoisobutyryl bromide (5.00 mL, 40.43 mmol) was added dropwise at 0 °C over 60 min under stirring, and followed by stirring at room temperature for another 24 h. Afterwards the pyridine was distilled under reduced pressure, and then the residual was purified thrice by dissolving/precipitation with THF/methanol to ensure all the impurities were moved out. The obtained product **PI**(**3**) with light red color was dried *in vacuo* at 40 °C for 24 h. ^{1}H NMR ($CDCl_3$, δ) of **PI**(**3**) (ppm): 0.80 (m, C***H***$_3$CH$_2$—), 1.26–2.25 (m, —C(C***H***$_3$)— and aliphatic main chain



SCHEME 2 The synthesis procedure of macroinitiator and graft copolymers of **PI-*g*-PS$_2$**, **PI-*g*-P*t*BA$_2$**, and **PI-*g*-PAA$_2$**.

—C$\boldsymbol{H}_2$C$\boldsymbol{H}$— of PI), 1.58 (m, —SCH$_2$C$\boldsymbol{H}_2$—), 1.86 (m, —C(C$\boldsymbol{H}_3$)=CH—, —C(C$\boldsymbol{H}_3$)=CH$_2$), 1.94(m, —C(C$\boldsymbol{H}_3$)$_2$Br), 2.37–2.77(m, —C$\boldsymbol{H}_2$SC$\boldsymbol{H}_2$—), 4.37 and 4.55(m, —OCOC$\boldsymbol{H}_2$—), 4.63–4.69 (m, —(CH$_3$)C—C$\boldsymbol{H}_2$ of 3,4-addition), 5.08 (m, —C$\boldsymbol{H}$=C(CH$_3$)— of 1,4-addition), 5.18 (—OCOC$\boldsymbol{H}$(−)—). $M_{n(SEC)}$ = 40,700 g/mol, *PDI* = 1.07, $M_{n(NMR)}$ = 73,400 g/mol.

Synthesis of Graft Copolymers PI-*g*-PS$_2$ by ATRP Mechanism

The synthesis of graft copolymers with "V"-shaped PS side chains was proceeded as the following: into a 100 mL ampoule, 0.2415 g (0.63 mmol —C(CH$_3$)$_2$Br groups) **PI(3)**, 98.3 mg (0.63 mmol) Bpy, 90.1 mg (0.63 mmol) CuBr, 10.0 mL St and 5.0 mL toluene were charged. The system were vacuumed by three freeze-thaw cycles at the temperature of liquid nitrogen, then sealed and placed in an oil bath at 110 °C. After 5.0 h, the ampoule was taken out from the oil bath and the polymerized products was diluted by THF and passed through the activated neutral alumina column to remove the copper salts, then the colorless solution was concentrated and purified thrice by dissolving/precipitation with THF/methanol. The product was dried *in vacuo* at 40 °C for 24 h. ^{1}H NMR (CDCl$_3$, δ) (ppm): 0.80 (m, C$\boldsymbol{H}_3$CH$_2$—, —C(C$\boldsymbol{H}_3$)$_2$—), 1.26–2.25 (m, 3H, aliphatic main chain —C$\boldsymbol{H}_2$C$\boldsymbol{H}$— of PS; m, —C(C$\boldsymbol{H}_3$)— and aliphatic main chain —C$\boldsymbol{H}_2$C$\boldsymbol{H}$— of PI), 1.58 (m, —SCH$_2$C$\boldsymbol{H}_2$—), 1.86 (m, —C(C$\boldsymbol{H}_3$)=CH—, —C(C$\boldsymbol{H}_3$)=CH$_2$), 2.37–2.77(m, —C$\boldsymbol{H}_2$SC$\boldsymbol{H}_2$—), 4.34–4.47 and 4.55(m, —OCOC$\boldsymbol{H}_2$—, —C$\boldsymbol{H}$(C$_6$H$_5$)Br), 4.63–4.69 (m, —(CH$_3$)C=C$\boldsymbol{H}_2$ of 3,4-addition), 5.08 (m, —C$\boldsymbol{H}$=C(CH$_3$)— of 1,4-addition), 5.11 (—OCOC$\boldsymbol{H}$(−)—), 6.30–7.30 (m, 5H, aromatic —C$_6\boldsymbol{H}_5$ of PS). $M_{n(SEC)}$ = 7.61 × 10^4 g/mol, *PDI* = 1.26, $M_{n(NMR)}$= 7.57 × 10^5 g/mol.

Cleavage of the PS Side Chains from PI-*g*-PS$_2$

Typically, 0.5010 g **PI-*g*-PS$_2$** was dissolved in THF (50 mL), to which KOH solution (10 mL, 1.0 M in ethanol) was added and the mixture was refluxed for 48 h. After evaporation of the solution to dryness, the solid was washed with CH_2Cl_2 to remove the insoluble salts and the filtered polymer solution was concentrated and purified thrice by dissolution/precipitation with THF/methanol. The obtained PS homopolymer was dried at 40 °C for 24 h. ^{1}H NMR (CDCl$_3$, δ) (ppm): 0.80 (m, —C(C$\boldsymbol{H}_3$)$_2$—), 1.26–2.25 (m, 3H, aliphatic main chain —C$\boldsymbol{H}_2$C$\boldsymbol{H}$— of PS), 6.30–7.30 (m, 5H, aromatic —C$_6\boldsymbol{H}_5$ of PS). $M_{n(SEC)}$ = 3,500 g/mol, *PDI* =1.18, $M_{n(NMR)}$= 3,600 g/mol.

Synthesis of Graft Copolymers PI-*g*-P*t*BA$_2$ by ATRP Mechanism

The synthesis procedure of **PI-*g*-P*t*BA$_2$** was similar to the preparation of **PI-*g*-PS$_2$** except that the *t*BA and PMDETA were used to substitute St and Bpy, and the polymerization temperature was also changed to 80 °C. ^{1}H NMR (CDCl$_3$, δ) (ppm): 0.80 (m, C$\boldsymbol{H}_3$CH$_2$—), 1.06–2.06 (m, —C(C$\boldsymbol{H}_3$)$_3$ and —C$\boldsymbol{H}_2$CH— of P*t*BA; m, —C(C$\boldsymbol{H}_3$)— and aliphatic main chain

TABLE 1 The Data of Precursors **PI(1)** and **PI(2)** Characterized by Elemental Analysis

	Weight Percentage Elements (%)[a]						
Sample	C	H	O	S	$R_{f.}$[b]	$R_{a.}$[c]	**E.F.$_{a.}$** (%)[d]
PI(1)	87.16	12.84					
PI(2A)	75.90	10.69	6.71	6.70	5.00	5.43	92.08
PI(2B)	79.44	11.24	4.66	4.66	8.00	8.47	94.45
PI(2C)	75.85	10.56	6.80	6.79	2.00	5.35	37.38

[a] The weight percentage of "C" and "H" were obtained by the direct measurement, and that of "O" and "S" were calculated according to the Formula: $O\% = (100\% - C\% - H\%)/(15.99 \times 2 + 31.97) \times 15.99 \times 2 \times 100\%$ and Formula: $S\% = (100\% - C\% - H\%)/(15.99 \times 2 + 31.97) \times 31.97 \times 100\%$, respectively, where H% was the weight percentage of "H" elements, and the others were the same as we defined before.
[b] The $R_{f.}$ was the feed mole ratio of double bonds to sulfydryl groups and could be calculated according to the Formula: $R_{f.} = N_{i.}/N_{f.t.}$.
[c] The R_a was calculated according to the Formula 1.
[d] The efficiency of addition reaction (**E.F.$_{a.}$**) could be calculated according to the Formula: $E.F._{a.} = N_{a.i.}/N_{f.i.} \times 100\% = (N_{i.}/R_{a.})/(N_{i.}/R_{f.}) \times 100\% = R_{f.}/R_{a.} \times 100\%$.

—C***H***$_2$C***H***— of PI), 1.20(m, —C(C***H***$_3$)$_2$—), 1.58 (m, —SCH$_2$C***H***$_2$—), 1.86 (m, —C(C***H***$_3$)=CH—, —C(C***H***$_3$)=CH$_2$), 2.08–2.44 (m, —CH$_2$C***H***— of P*t*BA), 2.45–2.80(m, —C***H***$_2$SC***H***$_2$—), 4.01–4.20 (—C***H***(COO—)Br), 4.28–4.47 and 4.55 (m, —OCOC***H***$_2$—), 4.63–4.69 (m, —(CH$_3$)C=C***H***$_2$ of 3,4-addition), 5.08 (m, —C***H***=C(CH$_3$)— of 1,4-addition), 5.11 (—OCOC***H***(–)—). $M_{n(SEC)}$ =6.37 × 10^4 g/mol, *PDI* = 1.19, $M_{n(cal.)}$= 8.84 × 10^5 g/mol.

Hydrolysis of Graft Copolymers PI-*g*-P*t*BA$_2$ for PI-*g*-PAA$_2$

Typically, 0.5045 g **PI-*g*-P*t*BA$_2$** was dissolved in 20.0 mL CH_2Cl_2, and then a five-fold molar excess of trifluoroacetic acid (with respect to the amount of *t*-butyl groups in the side chains) was added. The reaction mixture was stirred at room temperature for 24 h. During the hydrolysis, the resulting graft copolymers **PI-*g*-PAA$_2$** with PAA side chains precipitated in CH_2Cl_2 gradually. The crude product was separated by filtration, washing with CH_2Cl_2, and then thoroughly dried in vacuo at 40 °C for 24 h. ^{1}H NMR ($CDCl_3$, δ) (ppm): 0.80 (m, C***H***$_3$CH$_2$—), 1.06–2.06 (m, —C***H***$_2$CH— of PAA; m, and aliphatic main chain —C***H***$_2$C***H***— of PI), 1.20(m, —C(C***H***$_3$)$_2$—), 1.58 (m, —SCH$_2$C***H***$_2$—), 1.86 (m, —C(C***H***$_3$)= CH—, —C(C***H***$_3$)=CH$_2$), 2.08–2.44 (m, —CH$_2$C***H***— of PAA), 2.45–2.80(m, —C***H***$_2$SC***H***$_2$—), 4.01–4.20(—C***H***(COO—)Br), 4.28–4.47 and 4.55 (m, —OCOC***H***$_2$—), 4.63–4.69 (m, —(CH$_3$)C=C***H***$_2$ of 3,4-addition), 5.08 (m, —C***H***=C(CH$_3$)— of 1,4-addition), 5.11 (—OCOC***H***(–)—). $M_{n(NMR)}$= 5.29 × 10^5 g/mol.

Cleavage of the PAA Side Chains from PI-*g*-PAA$_2$

The cleavage procedure of PAA side chains was similar to that for PS side chains. ^{1}H NMR ($CDCl_3$, δ) (ppm): 1.21 (m, (C***H***$_3$)$_2$C—), 1.25–1.86 (m, —CHC***H***$_2$— on PAA), 2.07–2.35(m, —C***H***CH$_2$—), $M_{n(NMR)}$ = 2400 g/mol.

RESULTS AND DISCUSSION

Modification of Poly(isoprene) by Thiol-ene Addition Reaction and Esterification

In the presence of benzyldimethylketal (BDK) as photoinitiators, the thiol-ene addition reaction between sulfydryl groups on 1-thioglycerol and pendant double bonds on poly(isoprene) (**PI(1)**) should be proceed successfully under the 365 nm UV irradiation (Scheme 2).

There was a double bond on each isoprene unit after polymerization of isoprene (1,4-addition, 1,2-addition or 3,4-addition) and only a sulfydryl group on each 1-thioglycerol molecule, thus, the feed mole ratio (**R$_{f.}$**) of double bonds to sulfydryl groups could be defined as the mole ratio of isoprene units (**N$_{i.}$**) to 1-thioglycerol molecules (**N$_{f.t.}$**) molecules. Using the elemental analysis, one could calculated the weight percentage of "O" and "S" element (labeled as O% and S%) on **PI(2)**, as well as the mole ratio (**R$_{a.}$**) of isoprene units (**N$_{i.}$**) to 1-thioglycerol (**N$_{a.t.}$**) molecules coupled on **PI(2)** after the addition reaction according to the Formula 1 (Table 1):

$$R_{a.} = \frac{N_{i.}}{N_{a.t.}} = \frac{31.97 \times \frac{C\%}{S\%} - 3 \times 12.00}{5 \times 12.00} \quad (1)$$

where 31.97 and 12.00 were the exact mass of "S" and "C" elements, C% and S% were the weight percentage of "S" and "C" elements, respectively.

According to ^{1}H NMR spectrum of **PI(1)** in Figure 1(A), the mole ratio of 1,2-addition (**N$_{1,2\text{-}a.}$**), 3,4-addition (**N$_{3,4\text{-}a.}$**) to 1,4-addition (**N$_{1,4\text{-}a.}$**) isoprene units on **PI(1)** could be determined by using Formula (2):

$$N_{1,2-a.} : N_{3,4-a.} : N_{1,4-a.} = A_j : \frac{A_h}{2} : (A_{n,k} - 2A_j) \quad (2)$$

where the A_j, A_h, and $A_{n,k}$ were the integral areas of the methyne protons (—C***H***=CH$_2$) on 1,2-addition units at 5.70 ppm, methylene protons (—(CH$_3$)C=C***H***$_2$) on 3,4-addition

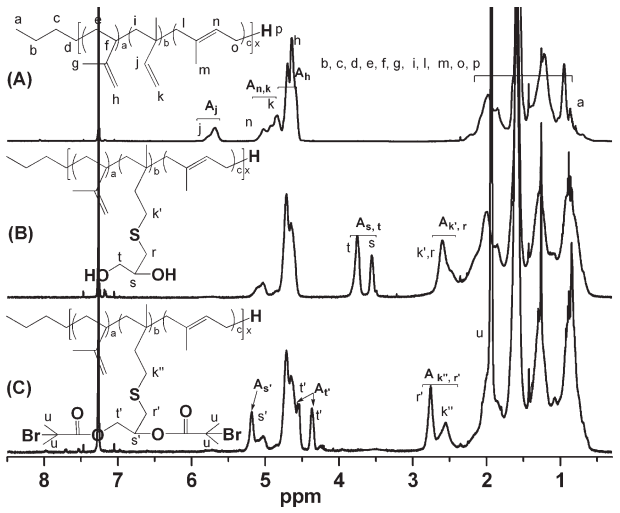


FIGURE 1 The ^{1}H NMR spectra of **PI(1)**(A), **PI(2A)**(B) and **PI(3A)**(C) (in $CDCl_3$).

TABLE 2 The Data of Precursors **PI(1)** and **PI(2)**, Macroinitiators **PI(3)** Characterized by SEC and ^{1}H NMR Measurement

	PI(1)		PI(2)		PI(3)		
Entry	$M_{n(SEC)}$[a] (g mol^{-1})	PDI[a]	$N_{g.s.}$[b]	$M_{n(NMR)}$[c] (g mol^{-1})	$M_{n(SEC)}$[a] (g mol^{-1})	PDI[a]	$M_{n(NMR)}$[d] (g mol^{-1})
A	35,100	1.03	95	45,400	40,700	1.07	73,400
B	35,100	1.03	61	41,700	36,800	1.05	59,600

[a] Determined by SEC with THF as solvent using PS standards.
[b] The $N_{g.s.}$ were the numbers of graft units on PI main chain and could be calculated according to the Formula: $N_{g.s.} = M_{n(SEC,\ PI(1))}/68/R_{c.}$, where 68 was the molecular weight of isoprene monomer.
[c] The molecular weight of **PI(2)** were calculated according to the ^{1}H NMR spectrum [Fig. 1(B)] and the Formula: $M_{n(NMR)} = M_{n(SEC,\ PI(1))} + N_{g.s.} \times 108$, where 108 was the molecular weight of 1-thioglycerol units.
[d] The molecular weight of **PI(3)** were calculated according to the ^{1}H NMR spectrum [Fig. 1(C)] and the Formula: $M_{n(NMR)} = M_{n(SEC,\ PI(1))} + N_{g.s.} \times 403$, where 403 was the sum mass of two 2-bromoisobutyryl groups and a 1-thioglycerol molecule.

units at 4.49–4.77ppm, methylene protons (—CH=C$\boldsymbol{H_2}$) on 3,4-addition units and methyne protons (—C**H**=C(CH$_3$)—) on 1,4-addition units at 4.77–5.16 ppm, respectively. Thus, the derived ratio of 1,2-addition, 3,4-addition to 1,4-addition isoprene units on PI was 18.18/70.10/11.72. According to the obtained mole ratio of different addition units, the mole ratio ($\mathbf{R_{1,2\text{-}a.}}$) of 1,2-addition units to the total isoprene units on **PI(1)** was obtained with the value of 5.50, which meant that there was about one 1,2-addition unit existed in 5.50 isoprene units.

From ^{1}H NMR spectrum of **PI(2A)** in Figure 1(B), it could be found that the resonance signals at 2.37–2.77 ppm attributed to the methylene protons (—C$\boldsymbol{H_2}$SC$\boldsymbol{H_2}$—) and signals at 3.47–3.88ppm attributed to the methylene protons and methyne protons (HOC$\boldsymbol{H_2}$C$\boldsymbol{H}$(OH)—) were observed, but the resonance signals at 5.70 ppm attributed to the methyne protons (—C$\boldsymbol{H}$=CH$_2$) and signals at 4.85 ppm attributed to the methylene protons (—CH=C$\boldsymbol{H_2}$) of 1,2-addition for **PI(1)** completely disappeared. Additionally, the intensity of signals attributed to the methylene protons of 3,4-addition (—C(CH$_3$)=C$\boldsymbol{H_2}$) at 4.49–4.77ppm and that attributed to the methyne protons (—C$\boldsymbol{H}$=C(CH$_3$)—) of 1,4-addition at 5.05 ppm did not show any change. Thus, it could be concluded that the thiol-ene addition reaction only occurred at double bonds corresponding to 1,2-addition of isoprene units.

To further affirm the above phenomenon, the $\mathbf{R_{f.}}$ values were controlled at 2.00 (Entry **PI(2C)**) and 5.00 (Entry **PI(2A)**) (Table 1), in which the mole ratio of fed 1-thioglycerol molecules to 1,2-addition isoprene units were 2.75 and 1.10 based on the $\mathbf{R_{f.}}$ and $\mathbf{R_{1,2\text{-}a.}}$ values, respectively. Clearly, the amount of 1-thioglycerol molecules was largely excessive in the former case. However, it was found that the final $\mathbf{R_{a.}}$ values in both cases were 5.35 and 5.43, which were very close to the $\mathbf{R_{1,2\text{-}a.}}$ of 5.50, and the distinct efficiency of addition reaction ($\mathbf{E.F._{a.}}$) with 37.38 and 92.08% were also obtained. Thus, it could be concluded that the excess added 1-thioglycerol molecules would not react with the double bond on 1,4-addition or 3,4-addition units once the 1,2-addition isoprene units were consumed in the case of Entry **PI(2C)**).

Based on this conclusion, it might be easy to control the density of reactive sites on **PI(2)** main chain by modulating the $\mathbf{R_{f.}}$ value, and finally controlled the contents of modified 1,2-addition isoprene units. For example in Entry **PI(2B)** with the $\mathbf{R_{f.}}$ at 8.00, in which the mole ratio of fed 1-thioglycerol molecules to 1,2-addition isoprene units was 0.69. The final calculated mole ratio of coupled 1-thioglycerol molecules to 1,2-addition isoprene units was 0.65 and $\mathbf{R_{a.}}$ value was 8.47, and the final $\mathbf{E.F._{a.}}$ of the thiol-ene addition reaction was as high as 94.45% (Table 1). According to the calculated $\mathbf{R_{a.}}$ values and molecular weight of **PI(1)** ($M_{n(SEC,\ PI(1))}$), the numbers of reactive sites on PI main chain ($\mathbf{N_{g.s.}}$) as well as the molecular weight of $\mathbf{M_{n(NMR,\ PI(2))}}$ were derived and listed in Table 2.

Using pyridine as medium, the macroinitiators **PI(3)** were prepared by esterification of the hydroxyl groups on **PI(2)** with 2-bromoisobutyryl bromide under 0 °C for 24.0 h. From the spectrum of **PI(3A)** [Fig. 1(C)], it was observed that the methylene protons (HOC$\boldsymbol{H_2}$CH(OH)—) at 3.47–3.88ppm were shifted to 4.37 and 4.55 ppm when the ester bond was formed (—OCOC$\boldsymbol{H_2}$—), whereas the methyne protons (HOCH$_2$C$\boldsymbol{H}$(OH)—) at 3.47–3.88 ppm were shifted to 5.18 ppm (—OCOC$\boldsymbol{H}$(−)—). The complete disappearance of signal at 3.47–3.88 ppm confirmed that the esterification was very successful (efficiency was almost 100%). Additionally, the characteristic signals of methyl protons (—C(C$\boldsymbol{H_3}$)$_2$Br) were also observed at 1.94ppm. According to ^{1}H NMR [Fig. 1(C)], the molecular weight of $\mathbf{M_{n(NMR,\ PI(3))}}$ could be calculated and listed in Table 2.

The precursors **PI(3)** were also characterized by SEC (Fig. 2), and it was found that **PI(3)** with higher content of reactive sites shifted to the shorter elution time when comparing with their precursor **PI(1)**. By comparing the SEC data in Table 2, it was found that the PDIs broadened slightly when 2-bromoisobutyryl groups were connected onto the main chain.

The precursors **PI(1)**, **PI(2)**, and **PI(3)** were also traced by FTIR spectra (Fig. 3). The characteristic carbon-carbon double bond stretch absorption at 1645 cm^{-1} was observed in all three spectra. The broad band at 3170–3607 cm^{-1} was attributed to the absorption of —OH groups introduced on **PI(2)** [Fig. 3(B)], and the absorption for ester carbonyl

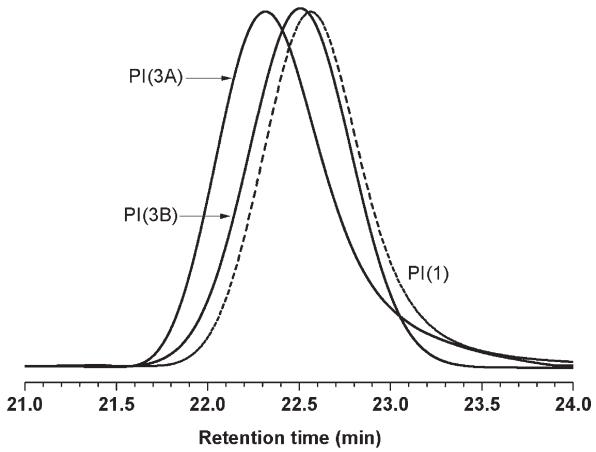


FIGURE 2 The SEC curves of precursors **PI(1)** ($M_{n(SEC)}$ = 35,100 kg mol^{-1}, PDI = 1.03) and PI(3) (**PI(3A)**, $M_{n(SEC)}$ = 40,700 kg mol^{-1}, PDI = 1.07; **PI(3B)**, $M_{n(SEC)}$ = 36,800 kg mol^{-1}, PDI = 1.05).

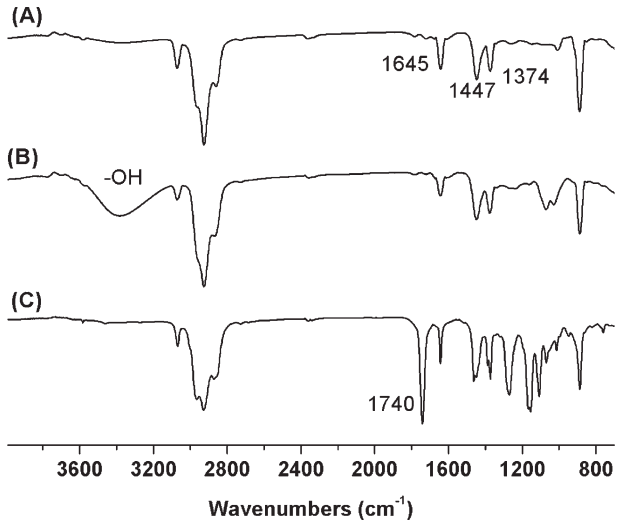


FIGURE 3 The FTIR spectra of precursors **PI(1)**(A), **PI(2)**(B), and **PI(3)**(C).

(—C=O) on **PI(3)** [Fig. 3(C)] at 1740 cm^{-1} was also discriminated clearly. The FT-IR results further confirmed that the synthesis of precursors and the macroinitiators, and the functional groups transformation on PI main chain by thiolene addition reaction and esterification were all successful.

Preparation of the Graft Copolymers PI-*g*-PS$_2$, PI-*g*-P*t*BA$_2$, and PI-*g*-PAA$_2$

In preparation of **PI-*g*-PS$_2$** and **PI-*g*-P*t*BA$_2$**, the polymerization of St and *t*BA was proceeded by ATRP using Bpy/CuBr and PMDETA/CuBr as catalyst systems at 110 °C and 80 °C, respectively. After the hydrolysis of **PI-*g*-P*t*BA$_2$** in trifluoroacetic acid (TFA)/CH_2Cl_2, the graft copolymers **PI-*g*-PAA$_2$** were also derived (Table 3, Table 4, and Scheme 2).

From Figure 4, it was observed that all of the SEC curves for graft copolymers **PI-*g*-PS$_2$, PI-*g*-P*t*BA$_2$**, and precursor **PI(1)** showed monomodal peaks with lower PDIs, and the curves shifted to the shorter elution time obviously for all grafted samples comparing with **PI(1)**. As it was well known, the SEC could not give the accurate molecular weight of graft copolymers because of the significantly different hydrodynamic volume of these branched copolymers with the linear PS standard.[35] From ^{1}H NMR spectra, one could observed the characteristic resonance signals of aromatic ring protons (—C_6H_5) on outer PS side chains at 6.30–7.30 ppm [Fig. 5(A)] and that of methane protons (—CH_2CH—) on outer P*t*BA side chains at 2.08–2.44 ppm clearly [Fig. 6(A)]. The resonance signals for protons on inner PI main chains, methyne protons (—C*H*(Br)—) at the end of side chain and methylene protons (—OCOCH_2—) close to the main chain were all observed at between 4.5–5.5 ppm. However, these signals could not be well assigned and used to calculate the molecular weight because of the immobilization of protons signals in ^{1}H NMR measurement.[36] Thus, ^{1}H NMR spectra of graft copolymers could also not provide the reliable molecular weight of graft copolymers.

To obtain the accurate molecular weight of graft copolymers **PI-*g*-PS$_2$**, the PS side chains were cleaved from the PI main chain by treatment in KOH/THF system. Figure 4(A) showed the SEC curve of PS side chain cleaved from **PI(3A)-*g*-PS$_2$**(C), and it was a monomodal peak with low PDI. From ^{1}H NMR spectrum [Fig. 5(B)], one could clearly

TABLE 3 The Data of Graft Copolymers **PI-*g*-PS$_2$**

	PS Side Chain			**PI-*g*-PS$_2$**		
Entry[a]	$M_{n(SEC)}$[b] (g mol^{-1})	PDI[b]	$M_{n(NMR)}$[c] (g mol^{-1})	$M_{n(SEC)}$[b] ($\times 10^4$ g mol^{-1})	PDI[b]	$M_{n(NMR)}$[d] ($\times 10^5$ g mol^{-1})
PI(3A)-*g*-PS$_2$(A)	1,700	1.14	1,800	4.55	1.25	4.15
PI(3A)-*g*-PS$_2$(B)	3,500	1.18	3,600	7.61	1.26	7.57
PI(3A)-*g*-PS$_2$(C)	6,700	1.19	7,100	16.3	1.22	14.2
PI(3B)-*g*-PS$_2$(D)	2,600	1.15	2,900	7.30	1.22	4.13
PI(3B)-*g*-PS$_2$(E)	5,700	1.13	6,000	10.5	1.28	7.92

[a] The **PI(3A)** or **PI(3B)** represent the different macroinitiators in Table 1, and the A, B, C, D, E in parenthesis represent the different series.
[b] Determined by SEC with THF as solvent using PS standards.
[c] The molecular weight of cleaved PS side chains was calculated according to ^{1}H NMR [Fig. 5(B)] and Formula 3.
[d] The molecular weight of **PI-*g*-PS$_2$** was calculated according to ^{1}H NMR and Formula **4**.

TABLE 4 The Data of Graft Copolymers **PI-*g*-P*t*BA$_2$** and **PI-*g*-PAA$_2$**

	PAA Side Chain	**PI-*g*-PAA$_2$**	**P*t*BA** Side Chain	**PI-*g*-P*t*BA$_2$**		
Entry	$M_{n(NMR)}$[a] (g mol^{-1})	$M_{n(NMR)}$[b] ($\times 10^5$ g mol^{-1})	$M_{n(cal.)}$[c] (g mol^{-1})	$M_{n(SEC)}$[d] ($\times 10^4$ g mol^{-1})	PDI[d]	$M_{n(cal.)}$[e] ($\times 10^5$ g mol^{-1})
PI(3A)-*g*-P*t*BA$_2$(A)	1,500	3.58	2,700	2.79	1.17	5.80
PI(3A)-*g*-P*t*BA$_2$(B)	2,400	5.29	4,300	6.37	1.19	8.84
PI(3A)-*g*-P*t*BA$_2$(C)	3,300	7.00	5,900	9.66	1.20	11.9
PI(3A)-*g*-P*t*BA$_2$(D)	5,600	11.34	10,000	12.8	1.24	19.7
PI(3B)-*g*-P*t*BA$_2$(E)	4,700	6.33	8,400	9.26	1.26	10.8
PI(3B)-*g*-P*t*BA$_2$(F)	7,600	9.87	13,500	11.6	1.27	17.1

[a] The molecular weight of cleaved PAA side chains was calculated according to the ^{1}H NMR [Fig. 6(B)] and Formula 5.
[b] The molecular weight of PI-*g*-PAA$_2$ was calculated according to Formula 6.
[c] The molecular weight of P*t*BA side chains was calculated according to Formula 7.
[d] Determined by SEC with THF as solvent using PS standards.
[e] The molecular weight of PI-*g*-P*t*BA$_2$ was calculated according to Formula 8.

discriminated the resonance signals of methyl protons (—C(C$\boldsymbol{H}_3$)$_2$—) at 0.80ppm at PS end and that of aromatic ring protons (—C$_6\boldsymbol{H}_5$) at 6.30–7.30ppm for cleaved PS main chains. Thus, the molecular weight of cleaved PS ($\mathbf{M_{n(NMR,\ Cleaved\ PS)}}$) could be obtained according to ^{1}H NMR spectrum by using the **Formula 3**, and the molecular weight of graft copolymer **PI-*g*-PS$_2$** ($\mathbf{M_{n(NMR,\ PI\text{-}g\text{-}PS2)}}$) could be derived by using the Formula 4 (Table 3):

$$M_{n(\text{NMR. Cleavaged PS})} = \frac{A_j/5}{A_e/6} \times 104 \tag{3}$$

$$M_{n(\text{NMR. PI-g-PS2})} = N_{g.s.} \times 2 \times M_{n(\text{NMR. Cleavaged PS side chain})} + M_{n(\text{NMR, PI(3)})} \tag{4}$$

where A$_j$ and A_e were the integral areas of resonance signals at 6.30–7.30 ppm and that at 0.80 ppm, 104 was the molecular weight of St monomers, $\mathbf{M_{n(NMR,\ PI(3))}}$ was the molecular weight of PI(3), and the others were the same as defined before.

Similarly, to avoid the integral error during the calculation of molecular weight by ^{1}H NMR and obtain the accurate molecular weight of graft copolymers **PI-*g*-P*t*BA$_2$** and **PI-*g*-PAA$_2$**, the *tert*-butyl groups on P*t*BA segment was selectively hydrolyzed under TFA/CH_2Cl_2 system for 24.0 h firstly[37] and the amphiphilic graft copolymers **PI-*g*-PAA$_2$** were achieved, then PAA side chains were cleaved from the PI main chain by treatment in KOH/THF system for 24.0 h. From the ^{1}H NMR spectrum [Fig. 6(B)] of cleaved PAA, one could observed the resonance signals of methyl protons (—C(C$\boldsymbol{H}_3$)$_2$—) at 1.21 ppm at PAA end and that of methyne protons (—CH$_2$C$\boldsymbol{H}$—) at 2.05–2.40 ppm for cleaved PAA main chains. The molecular weight of cleaved PAA ($\mathbf{M_{n(NMR,\ PAA)}}$) and that of P*t*BA ($\mathbf{M_{n(cal.,\ PtBA)}}$) were calculated by using the Formula 5 and Formula 7, respectively, and the molecular weight of graft copolymers PI-*g*-PAA$_2$ ($\mathbf{M_{n(NMR,\ PI\text{-}g\text{-}PAA2)}}$) and **PI-*g*-P*t*BA$_2$** ($\mathbf{M_{n(cal.,\ PI\text{-}g\text{-}PtBA2)}}$) could be obtained by using the Formula 6 and Formula 8 respectively, (Table 4).

$$M_{n(\text{NMR. Cleavahed PAA side chain})} = \frac{A_g}{A_e/6} \times 72 \tag{5}$$

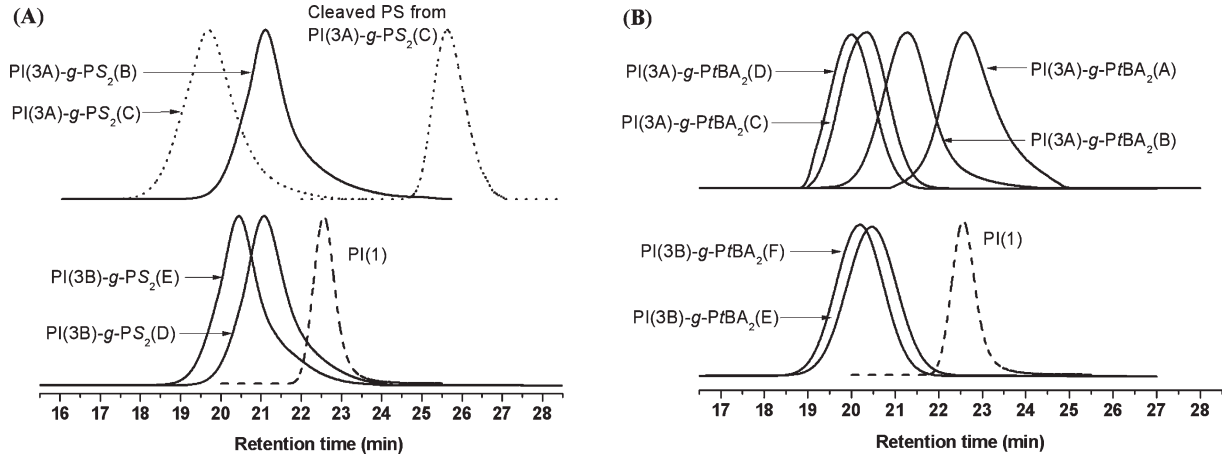


FIGURE 4 The SEC curves of (A): graft copolymers **PI-*g*-PS$_2$, PI(1)** and the PS side chain cleaved from **PI(3A)-*g*-PS$_2$(C)**, and (B): graft copolymers **PI-*g*-P*t*BA$_2$** and **PI(1)**.

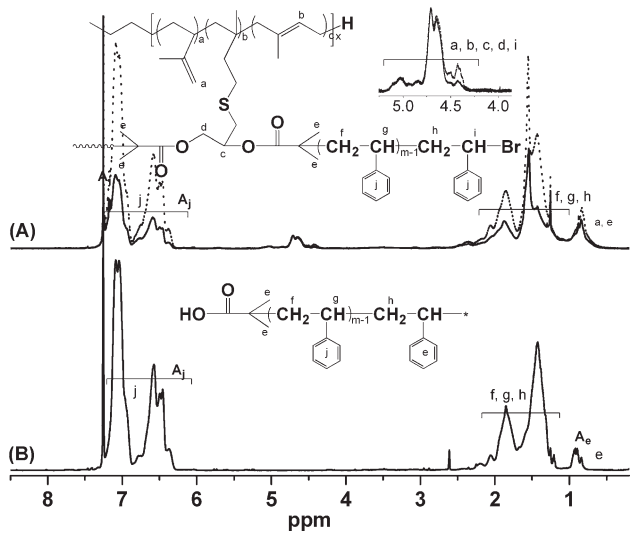


FIGURE 5 The ^{1}H NMR spectra of graft copolymers **PI(3A)-*g*-PS$_2$**(A) (Solid line), **PI(3A)-*g*-PS$_2$**(C) (Dash line) and the cleaved PS side chain (in $CDCl_3$).

$$M_{n(NMR,\,PI-g-PAA2)} N_{g.s.} \times 2 \times M_{n(NMR.\,Cleavaged\,PAA\,side\,chain)} \quad (6)$$

$$M_{n(cal.,\,PtB\,A\,side\,chain)} = \frac{A_g}{A_e/6} \times 128 \quad (7)$$

$$M_{n(cal.,\,PI-g-\,PtBA2)} = N_{g.s.} \times 2 \times M_{n(cal.,\,PtBA\,side\,chin)} \quad (8)$$

where A_g and A_e were the integral areas of resonance signal at 2.05–2.40 ppm and that at 1.21 ppm, 72 and 128 were the molecular weight of *t*BA and acrylic acid units respectively, and the others were the same as defined before.

The graft copolymers **PI-*g*-P*t*BA$_2$** and **PI-*g*-PAA$_2$** could also be verified by FTIR spectra (Fig. 7). In the spectrum of **PI-*g*-P*t*BA$_2$**, the absorption of ester carbonyl (—C=O) at 1710 cm^{-1} was observed. In that of **PI-*g*-PAA$_2$**, except the absorption for acid carbonyl (—C=O) at 1741 cm^{-1} was discriminated, the broad band at 2390–3700 cm^{-1} was attributed to the absorption of —COOH. The FTIR results were consistent well with the (co)polymer structure characterized before.

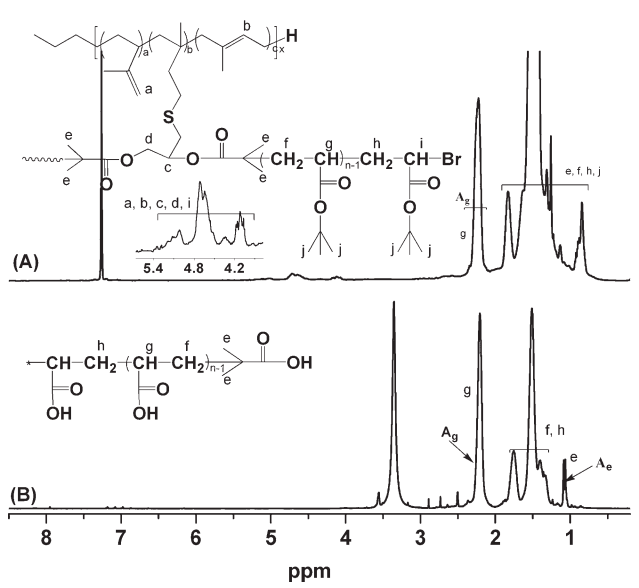


FIGURE 6 The ^{1}H NMR spectra of graft copolymers **PI-*g*-P*t*BA$_2$** (in $CDCl_3$) and the cleaved **PAA** side chains (in DMSO-d_6).

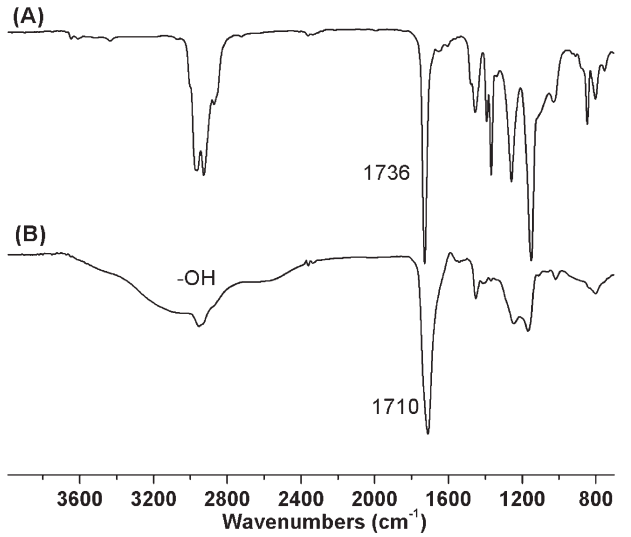


FIGURE 7 The FTIR spectra of graft copolymers **PI-*g*-P*t*BA$_2$**(A) and **PI-*g*-PAA$_2$**(B).

Finally, the glass transition temperatures (T_g) of the graft copolymers **PI-*g*-PS$_2$** and **PI-*g*-P*t*BA$_2$** were determined by DSC and obtained from the second heating run (Fig. 8). For **PI(3A)-*g*-PS$_2$(A)**, the T_g for PS segment was observed at 79.42 °C, and the T_g for PS segment on **PI(3A)-*g*-PS$_2$(C)** with the larger molecular weight was observed at 90.23 °C (T_g for linear PS homopolymer was near 90 °C[38]). Similarly, for the graft copolymer **PI(3A)-*g*-P*t*BA$_2$(B)**, the T_g for P*t*BA segment at 27.52 °C were observed, as the molecular weight increased, the T_g for P*t*BA segment on graft copolymer **PI(3A)-*g*-P*t*BA$_2$(D)** increased to 41.90 °C (T_g for P*t*BA homopolymer was near 45 °C[39]). On the other hand, in all

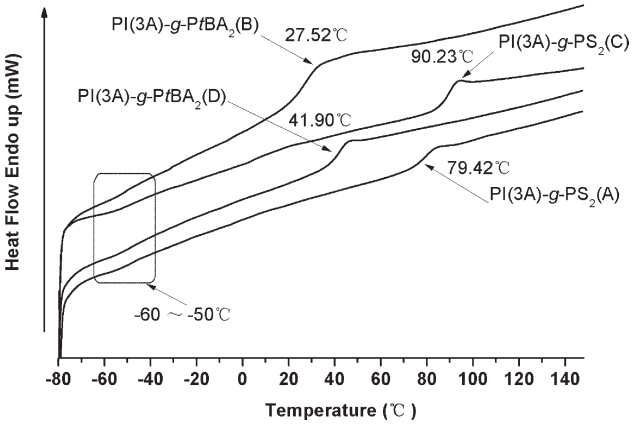


FIGURE 8 DSC curves of **PI(3A)-*g*-PS$_2$**(A), **PI(3A)-*g*-PS$_2$**(C), **PI(3A)-*g*-P*t*BA$_2$**(B), and **PI(3A)-*g*-P*t*BA$_2$**(D) in the second heating run.

chromatography at the low temperature, there was a small and almost negligible T_g observed near the −55 °C, which might be attributed to the T_g of enwrapped PI main chain. By analyzing two T_gs in **PI-*g*-PS$_2$**, one can speculated that the phase separation with hard-soft-hard segments had occurred and the graft copolymer could be regard as a thermoplastic elastomer. Thus, the DSC investigation provided another evidence for the successful synthesis of the graft copolymers.

CONCLUSIONS

PI with pendant functional groups was successfully synthesized by thiol-ene addition reaction under UV irradiation, and the results showed that the addition reaction carried out only on double bonds of 1,2-addition isoprene units. PI main chain could be further modified and used to prepare graft copolymers **PI-*g*-PS$_2$** and **PI-*g*-P*t*BA$_2$** with "V" shaped PS and P*t*BA as side chains, and the amphiphilic graft copolymers **PI-*g*-PAA$_2$** was achieved by the hydrolysis of **PI-*g*-P*t*BA$_2$**. It was confirmed that the graft density could be easily controlled by variation of the contents of modified 1,2-addition isoprene units on PI. Our work provided a versatile strategy to the graft copolymers with poly(diene) as main chain, and the graft copolymers **PI-*g*-PS$_2$** might also be used as a kind of novel toughened plastic materials because of the introduction of regular PS-grafted chains on PI main chain.

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