

# Graft Copolymerization of Maleic Anhydride onto Low-Molecular-Weight Polyisobutylene Through Solvothermal Method

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**ABSTRACT:** The free-radical graft copolymerization of maleic anhydride (MAH) onto highly reactive low molecular weight polyisobutylene was conducted by the use of benzoyl peroxide as an initiator through the solvothermal method. Fourier transform infrared spectra and  $^1\text{H-NMR}$  spectra confirmed that maleic anhydride was successfully grafted onto highly reactive low molecular weight polyisobutylene backbone, and the grafting mechanism also was proposed. The

effect of benzoyl peroxide content, MAH concentration, total reactant amount in the reaction vessels, reaction temperature and time, and different kinds and volumes of solvents on MAH's degree of grafting was investigated in detail. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1520–1528, 2009

**Key words:** low-molecular-weight polyisobutylene; solvothermal; MAH; graft copolymerization

## INTRODUCTION

Polyisobutylenes (PIBs) are mainly classified into low ( $500 < M_n < 5000$  g/mol), medium ( $4000 < M_n < 120,000$  g/mol) and high molecular weight ( $M_n > 300,000$  g/mol) according to the molecular weight.<sup>1</sup> Low molecular weight PIBs are in liquid state of oil-like to honey-like viscosity. Medium molecular weight PIBs are highly viscous polymers, and PIBs of high molecular weight are hard and elastic rubbers. Moreover, because of the exo-typed double-bond end groups, low molecular weight PIB can be divided into highly reactive (content of exo-typed double-bond end groups  $> 60\%$ ) and lowly reactive ones. High reactive low molecular weight PIB (HLPIB), which contains 85% exo-typed double bond end groups, was first explored by BASF in 1995.

As a result of their high chain flexibility, PIBs are very important toughening agents. However, there is poor compatibility between PIBs and other polar polymers, such as polyester, polylactic acid, polyvinyl acetate, which results in a great challenge for modification through polymer blending. That is why many researches resort to the copolymerization of PIBs with other polymers directly by cationic techniques,<sup>2–4</sup> the anionic method,<sup>5</sup> or atom transfer radical polymerization.<sup>6</sup> Although all these copolymerization methods

can produce a toughening effect successfully, they all have some fatal disadvantages, such as side reactions from cationic copolymerization, rigorous control of free water and oxygen for anionic polymerization, and potential concerns over the use of transition metal complexes for ATRP polymerization. These disadvantages limit their large-scale industrialized application. To simplify the preparation of modified PIBs as toughening agents, polar unsaturated monomers can be used to functionalize PIB to increase its polarity for better compatibility with polar polymers. There are very limited reports of PIB-grafting copolymers, especially for low molecular weight liquid PIB. Therefore, it is worthy to study the modified low molecular weight PIB.

Maleic anhydride (MAH) is a universal unsaturated polar monomer. Polyolefin functionalized by MAH can promote compatibilization between polar and nonpolar polymers. The graft polymerization of MAH onto polyolefin has been extensively studied.<sup>7–9</sup> Most of the grafting process is performed in the melt state in an extruder, that is, via reactive extrusion,<sup>10–13</sup> some in solution method,<sup>14,15</sup> and some in the solid phase method.<sup>16,17</sup> Considering that low molecular weight PIBs are in liquid state, reactive extrusion and solid graft are not appropriate. In addition, the solution method is an optional approach. However, the solution graft involves the copious use of solvent, which leads to the problems of high cost, difficult separation, purification, and environmental pollution.<sup>18</sup> Therefore, a new copolymerization method, solvothermal synthesis, is used to prepare MAH grafting low molecular weight PIB copolymer.

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The solvothermal method has been widely used to prepare inorganic materials, many kinds of inorganic nanomaterials, and polymer-inorganic nanocomposites.<sup>19–21</sup> In our group, the graft copolymers, such as POE-*g*-MAH,<sup>22</sup> HDPE-*g*-MAH,<sup>23</sup> and SBS-*g*-MAH,<sup>24</sup> also have been successfully developed with the use of this technique. Solvothermal synthesis allows materials to be prepared with more types and less amount of solvent compared with the aforementioned solution method, e.g. both good and poor solvent for polymer substrate can work.<sup>22</sup> High reactive low molecular PIB (HLPiB) is a liquid substrate, and MAH is volatile. If they are sealed in the reaction vessel, the evaporation of solvents and monomers will be avoided, which favors the environment and high grafting yield. When the temperature is increased, HLPiB's viscosity becomes much lower, and the pressure in the vessel caused by gaseous MAH and solvent becomes greater, which benefits sufficient interaction among reactants and high degree of grafting.

In this article, the solvothermal method was used to prepare HLPiB-*g*-MAH. The graft copolymerization was conducted first without any solvent. Moreover, the effect of BPO content, MAH concentration, total reactant amount in the reaction vessels, reaction temperature, reaction time, and different solvents onto MAH's degree of grafting (DG) also was investigated.

## EXPERIMENTAL

### Materials

High reactive low molecular PIB (HLPiB) (Glissopal 2300,  $M_n = 2300$ ) was purchased from BASF (Beijing, China). MAH from Shanghai Chemical Solvent Factory (Shanghai, China) was dried in vacuum drying oven for 2 h at room temperature before use. Benzoyl peroxide (BPO, offered by Sinoreagent Comp., Ltd., Shanghai, China) as an initiator was recrystallized by chloroform and ethanol. Acetone, chloroform, ethanol, and toluene were supplied by the Shanghai Chemical Solvent Factory.

### Grafting procedure

HLPiB, MAH, BPO, and solvent was placed into a high-pressure reaction vessel (HL-0.5-20, purchased from Jinan Henghua Chemistry Company, Jinan, China) under various reaction conditions (shown in Table I). Then, the sealed vessel was put into the constant temperature oven. After a certain time, the products were taken away from the vessel, purified with acetone for at least three times to remove the residual MAH monomer, and then were dried to a constant weight under vacuum at 60°C for 8 h.

### Characterization

#### Fourier transform infrared characterization

The liquid samples were dabbed into a KBr pellet for Fourier transform infrared (FTIR) characterization. Then FTIR spectroscopy was obtained on a PerkinElmer Paragon 1000 Fourier transform infrared spectrophotometer (PerkinElmer, Waltham, MA).

#### Degree of grafting

The degree of grafting was determined both by FTIR peak intensity ratio index and back-titration methods. The relative degree of grafting (RDG) can be calculated from the IR peak (shown in Fig. 1) intensity ratio by the following eq. (1):

$$\text{RDG} = \frac{I_{1690-1890 \text{ cm}^{-1}}}{I_{1390 \text{ cm}^{-1}} + I_{1366 \text{ cm}^{-1}}} \quad (1)$$

In eq. (1),  $I_{1690-1890 \text{ cm}^{-1}}$  are the intensities of MAH's characteristic peaks; and  $I_{1390 \text{ cm}^{-1}} + I_{1366 \text{ cm}^{-1}}$  are the total intensities of HLPiB's internal standard peaks.

The absolute degree of grafting of MAH is determined through back-titration procedure. A total of 2.0 g of purified HLPiB-*g*-MAH samples and pure HLPiB were first dissolved in 30 mL of toluene, and then 30 mL of 0.05M KOH/ethanol-benzyl alcohol (1 : 1 by volume)<sup>25</sup> and 0.05  $\mu\text{L}$  of water (for transformations of the grafted maleic anhydride groups into their acidic forms) was added. Then, the solution was kept refluxing for 2 h to sufficiently react the acid and KOH. Back-titration then was performed by the use of a 0.05 mol/L iso-propylalcohol solution of HCl with bromothymol blue as an indicator. The color of the solution changed from blue to yellow at the terminal point. Pure PIB also consumed a little volume of KOH solution and therefore for each absolute DG, a value of  $\text{DG}_{\text{blank}}$  should be subtracted. Then, the degree of grafting is calculated by eqs. (2) and (3):

$$\text{DG} = \frac{98.06 \times (C_{\text{KOH}}V_{\text{KOH}} - C_{\text{HCl}}V_{\text{HCl}}) \times 10^{-3}}{2m_{\text{sample}}} \times 100\% - \text{DG}_{\text{blank}} \quad (2)$$

$$\begin{aligned} \text{DG}_{\text{blank}} &= \frac{98.06 \times (C_{\text{KOH}}V_{\text{KOH}} - C_{\text{HCl}}V_{\text{HCl}}) \times 100^{-3}}{2m_{\text{blank}}} \times 100\% \\ &= \frac{98.06 \times (C_{\text{KOH}}V_{\text{KOH}} - C_{\text{HCl}}V_{\text{HCl}}) \times 100^{-3}}{2m_{\text{blank}}} \times 100\% \end{aligned} \quad (3)$$

In these equations,  $C_{\text{KOH}}$  (mol/L) is the concentration of standard KOH solution, and it is calibrated by 0.05 mol/L potassium acid phthalate solution ahead of time;  $C_{\text{HCl}}$  (mol/L) is calibrated by the known KOH solution;  $V_{\text{KOH}}$  (mL) is the volume of KOH standard solution (30 mL);  $V_{\text{HCl}}$  (mL) is the

TABLE I  
Effects of Different Parameters on the Degree of MAH Grafting Under Various Reaction Conditions

Parameters	BPO (g)	MAH (g)	Reaction temperature (°C)	Total HLPIB dosage (g)	Different kinds of solvent	Different volumes of solvent (mL)	Reaction time (h)	GD (wt %)
BPO	0.03	1.50	120	30			5	0.023 ± 0.003
	0.06							0.067 ± 0.004
	0.15							0.077 ± 0.004
	0.24							0.136 ± 0.003
	0.30							0.065 ± 0.003
MAH	0.242	0.3	120	30			5	0.052 ± 0.004
	0.252	1.50						0.136 ± 0.005
	0.264	3.0						0.139 ± 0.005
	0.276	4.5						0.258 ± 0.0055
	0.288	6.0						0.235 ± 0.0048
	0.3	7.5						0.173 ± 0.0051
	0.312	9.0						0.167 ± 0.0057
Reaction temperature	0.252	1.50	80	30			5	0.015 ± 0.005
			90					0.019 ± 0.009
			100					0.255 ± 0.020
			110					0.351 ± 0.010
			120					0.136 ± 0.010
			130					0.098 ± 0.008
			140					0.086 ± 0.006
			150					0.131 ± 0.007
			160					0.038 ± 0.009
Total HLPIB dosage	0.045	0.65	140	5			5	0.121 ± 0.008
	0.090	1.30		10				0.093 ± 0.007
	0.136	1.95		15				0.280 ± 0.008
	0.281	2.60		20				0.167 ± 0.009
	0.226	3.25		25				0.214 ± 0.005
	0.271	3.90		30				0.131 ± 0.008
Different kinds of solvent	0.136	1.95	140	15	None	0	5	0.172 ± 0.015
					Toluene	10		0.178 ± 0.011
					Acetone			0.165 ± 0.015
					Chloroform			0.543 ± 0.017
					De-ionized water			0.263 ± 0.02
Different volumes of solvent	0.136	1.95	110	15	Chloroform	5	5	0.768 ± 0.020
						10		0.852 ± 0.021
						15		0.985 ± 0.018
						20		0.885 ± 0.020
						25		0.752 ± 0.022
						30		0.451 ± 0.019
Reaction time	0.136	1.95	110	15	Chloroform	15		0.683 ± 0.017
						2.17		0.836 ± 0.021
						3.00		1.263 ± 0.020
						4.25		1.039 ± 0.018
						5.00		0.970 ± 0.015
						6.00		1.020 ± 0.016

used volume during back-titration; and  $m$  (g) is the mass of each sample.

The calibration curve is shown in Figure 2, from the linear relationship, it is concluded as eq. (4):

$$DG = 1.67 \text{ RDG} \quad (4)$$

## NMR

$^1\text{H-NMR}$  spectra were recorded on a Varian Mercury Plus-400 MHz spectrometer at 400 MHz, the

temperature was 25°C. 1,1,2,2-Tetrachloroethane- $d_2$  was used as solvent and tetramethylsilane as internal standard.

## RESULTS AND DISCUSSION

### Characterization of graft product

The structure of graft product was analyzed through both FTIR and NMR results. The samples of FTIR spectra are given in Figure 1. In Figure 1, compared with pure HLPIB, all the new peaks in MAH

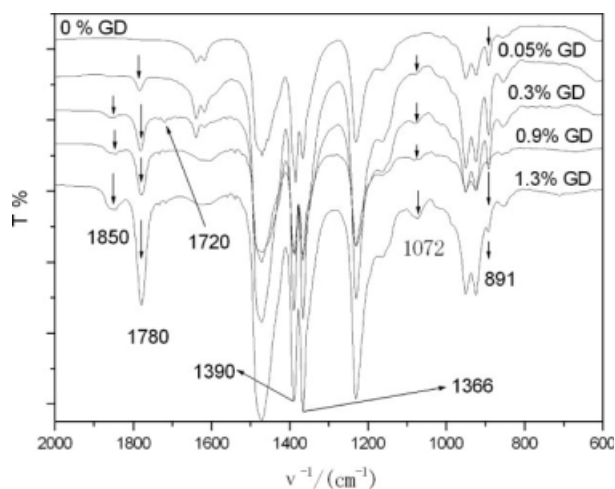


Figure 1 FTIR of HLPIB and HLPIB-g-MAH.

copolymers at 1850, 1780, 1720, and 1072  $\text{cm}^{-1}$  can be contributed to MAH. The broad and intense characteristic band at 1780  $\text{cm}^{-1}$  and the weak absorption band at 1850  $\text{cm}^{-1}$  are caused by symmetric (strong) and asymmetric (weak) C=O stretching vibrations of succinic anhydride rings, respectively,<sup>25</sup> and the two peaks' intensity summation refer to  $I_{1690-1890\text{cm}^{-1}}$  in eq. (1), which increases with the increased grafting degree as shown in Figure 1. The weak peak at 1720  $\text{cm}^{-1}$  existing in some samples is the result of the carboxylic acid caused by the hydrolysis of anhydride group,<sup>26</sup> and the peak at 1072  $\text{cm}^{-1}$  is assigned to the symmetric ring stretching of =C–O–C= group in MAH.<sup>23</sup>

At the same time, the characteristic peak of HLPIB at 1390 and 1366  $\text{cm}^{-1}$  for the C–H stretching vibrations of the methyl groups  $(-\text{CH}_2-\text{C}(\text{CH}_3)_2)_n-$  in the main chain remains nearly constant, which can be used as internal standard,<sup>27</sup> which refers to  $(I_{1390\text{cm}^{-1}} + I_{1366\text{cm}^{-1}})$  listed in eq. (1).

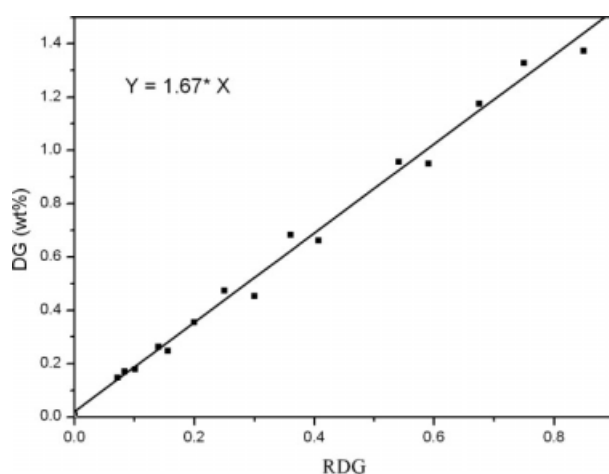


Figure 2 The calibration curve between IR intensity rate (RDG) and the absolute DG.

Furthermore, the absence of unreacted MAH can be verified by the disappearance of the characteristic band at 698  $\text{cm}^{-1}$  (C=C bond of MAH),<sup>25</sup> which means that the residual MAH monomers have been washed away completely. The absorption peak at 891  $\text{cm}^{-1}$  is attributed to the out-of-plane deformation of vinyl end groups in HLPIB chain.<sup>23</sup> From Figure 1, it is shown that the relative intensity rate of peak at 891  $\text{cm}^{-1}$  to the internal standard peak of HLPIB  $(I_{891\text{cm}^{-1}}/I_{1390\text{cm}^{-1}} + I_{1366\text{cm}^{-1}})$  is decreasing with the increasing DG of MAH. When DG is 0, 0.05%, 0.3%, 0.9%, and 1.3%, the ratio is 0.08, 0.07, 0.06, 0.011, and 0.010, respectively. In addition, it can be calculated that 87.5% of vinyl end group has been consumed when the sample's DG is 1.3%.

All the results testify that MAH is successfully grafted onto HLPIB. In addition, from the change of the ratio  $(I_{891\text{cm}^{-1}}/I_{1390\text{cm}^{-1}} + I_{1366\text{cm}^{-1}})$ , it is known that the vinyl end group is the preferential site of addition in the grafting reaction. The same conclusion can be gained from  $^1\text{H-NMR}$  analysis.

The  $^1\text{H-NMR}$  spectra of pure HLPIB and HLPIB-g-MAH is given in Figure 3 and the molecular structures of HLPIB are shown in Scheme 1. HLPIB is classified as three kinds as the result of its different ending groups, and its corresponding NMR chemical shift is listed in Figure 3 from a to g. The peaks at 0.99 ppm (a), 1.11 ppm (b), and 1.41 ppm (c) in Figure 3, which both existed in pure HLPIB and HLPIB-g-MAH, are attributed to the methyl proton (a), (b), and methylene proton (c) in the main chain<sup>28</sup> shown in Scheme 1. The peaks at 1.78 ppm (f), 1.99 ppm (g), 4.6 ppm (d), and 4.8 ppm (e) are caused by HLPIB with  $\alpha$ -olefin ending group protons. Because  $\beta$ -olefin ending groups are less than 20%, there are no visible corresponding peaks shown in NMR spectra. In FTIR

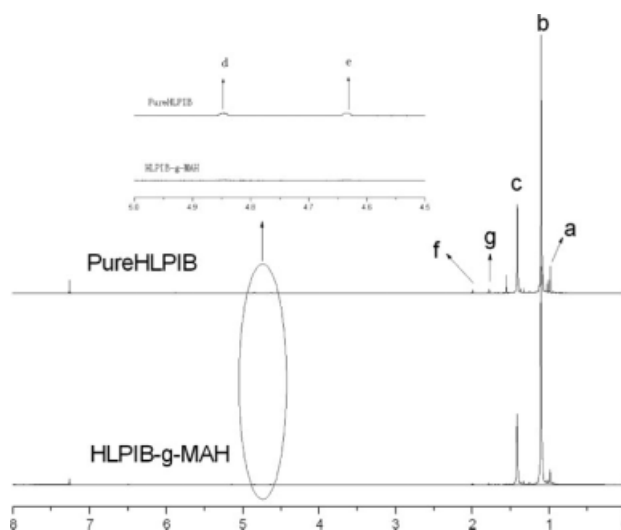
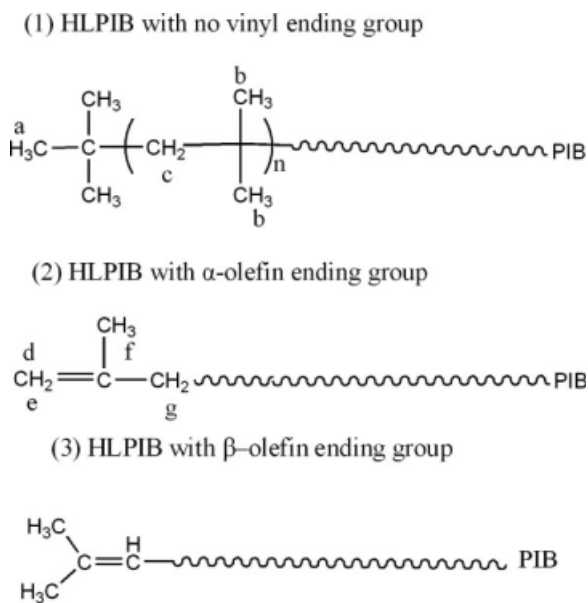


Figure 3  $^1\text{H-NMR}$  spectra of pure HLPIB and HLPIB-g-MAH with 1.3% DG.

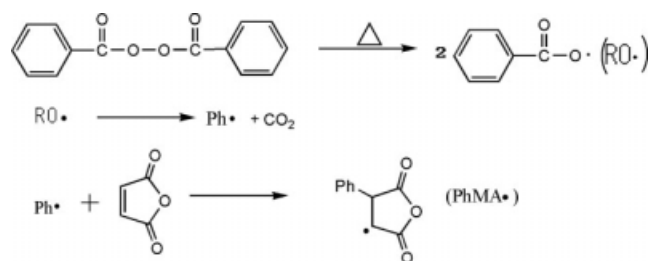


**Scheme 1** The molecular structures of HLPiB.

analysis, the C—H stretching vibrations of methyl in HLPiB main chain (b) has been chosen to be the internal standard, and in the same way the methyl protons (b) is chosen to be the internal standard in NMR analysis. The peak intensity ratios of peak f to peak b and peak g to peak b had reduced to 0.0064 and 0.0056 from 0.0071 and 0.011, respectively. Moreover, the intensity of the peaks at 4.6 ppm (e) and 4.8 ppm (d), which are due to the  $\alpha$ -olefin methylene protons,<sup>28</sup> decreased, and then nearly disappeared. All these results indicate that most  $\alpha$ -olefin ending groups were extinguished during the graft copolymerization. Although there is no visible characteristic peak of grafted MAH in NMR spectra because of its low degree of grafting, the reducing amount of vinyl in HLPiB combined with the appearance of MAH's peaks in FTIR spectra confirm the successfully grafting of MAH to HLPiB.

On the basis of the FTIR and NMR analysis, it can be concluded that most grafting reaction happened on the vinyl ending group, especially on  $\alpha$ -olefin ending group. Therefore, the proposed grafting procedure and some possible side reactions are shown in the following:

1. The decomposing of initiator and initiation of monomer as shown in Scheme 2.
2. The formation of macro radicals-addition of the radical to the double bond of the chain.<sup>29,30</sup> According to different end groups, there are several kinds of macromolecular radicals shown in the following as I-H (in Scheme 3).
3. Chain propagation: (take I· for example in Scheme 4).

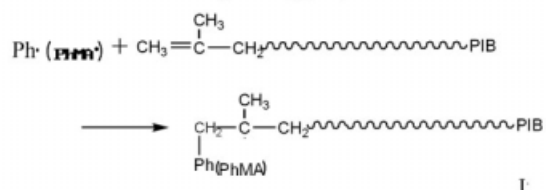


**Scheme 2** The decomposition of initiator and initiation of monomer.

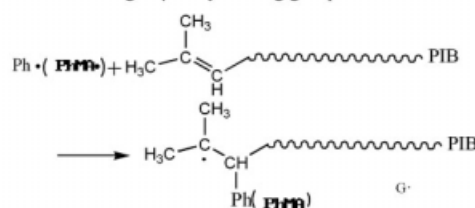
4. Chain termination: (take I· for example<sup>30</sup> in Scheme 5).
5. Side reactions<sup>30</sup> are shown in Scheme 6 include cross-link reaction, homopolymerization of MAH, intra molecular radical transferring, chain transferring to solvents and so on.

The graft copolymerization strongly depends on the reactive conditions. The solvothermal method was first used to prepare HLPiB grafting MAH copolymer, so it is necessary to investigate the effect of the various factors on the degree of grafting.

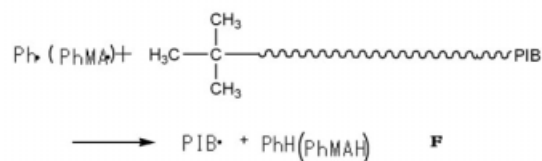
a. Radicals addition to  $\alpha$ -vinyl ending group HLPiB



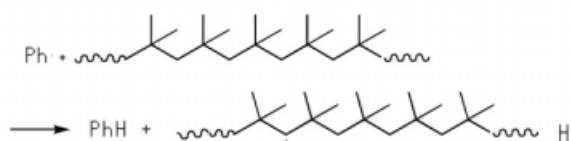
b. Radicals adding to  $\beta$ -vinyl ending group HLPiB



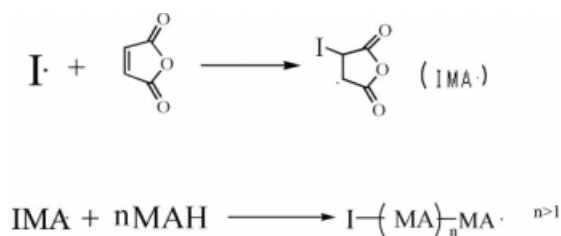
c. Radicals addition to no vinyl-ending group HLPiB



d. The formation of other macromolecular radical



**Scheme 3** The formation of macromolecular radicals.



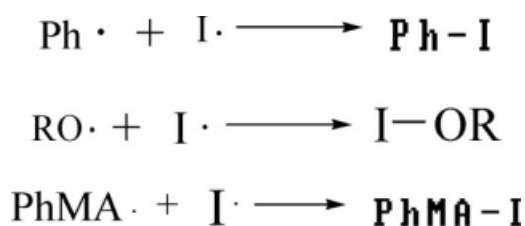
Scheme 4 Chain propagation.

### The effect of initiator concentration

The effect of initiator concentrations on the degree of grafting was investigated. The concentration of BPO varied from 0.1 to 1.0 phr, and a monomer concentration of 5 phr with 30 g of HLPPIB and a reaction temperature of 120°C for 5 h were fixed (as shown in Table I). It can be seen from Figure 4 that the degree of graft increases gradually from 0.02% to 0.14% when the concentration of BPO increases from 0.1 to 0.8 phr, and then it decreases. The reason is that the free radicals are formed by the decomposition of BPO, and so the increasing in the initiator concentration will lead to more free radicals, and then higher degree of grafting are obtained in the beginning. But extra initiator will cause more macro radicals, which will increase the side reactions such as the crosslinkage between HLPPIB molecules and the intra radical transferring in Scheme 6 so as to reducing degree of grafting and the initiation efficiency. In this work, BPO's optimal concentration of 0.8 phr was used in the following researching procedures.

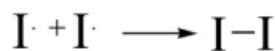
### The effect of monomer concentration

The effect of MAH content (from 0.99 to 28.6 phr, based on the whole reactant dosage) was investigated both at 120°C (shown in Table I) and 140°C. As shown in Figure 5, it can be observed that the two curves has very similar trend. That is, the degree of grafting initially increases with the increase of the monomer concentration, reaches a maximum at a monomer concentration of 13.0 phr, and then decreases with further increasing monomer concentration. In general, the graft reaction mainly depends on the diffusion of the MAH free radicals. More MAH content means more MAH free radicals and greater grafting degree. How-



Scheme 5 Chain termination.

Cross-link product (take I· for example)



Homopolymerization of MAH



Intra molecular radical transferring



Chain transferring to solvents



Scheme 6 Side reactions during grafting procedure.

ever, MAH also acts as the traps for free radicals, and more MAH also means relative less polymer radicals and more homopolymerization of MAH if MAH concentration was too high<sup>22</sup> in Scheme 6. Another explanation is that there exists limited reaction sites on the HLPPIB molecules for a given quantity of initiator used, and more monomer cannot induce greater DG infinitely.<sup>25</sup> The degree of grafting will decrease after certain concentration of MAH. Therefore, MAH's optimal content is 13 phr (based on the weight of whole reactant). In Figure 5, it is also shown that the degree of grafting at 120°C is greater than that of 140°C, which indicates that the reaction temperature also is an important factor. And in the following procedure, the effect of reaction temperature was researched in detail.

### The effect of reaction temperature

To find an optimum reaction temperature, the graft reactions were conducted from 80 to 160°C for 5 h.

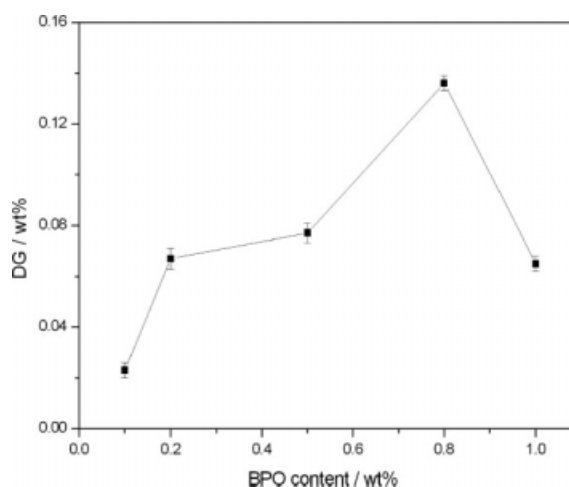
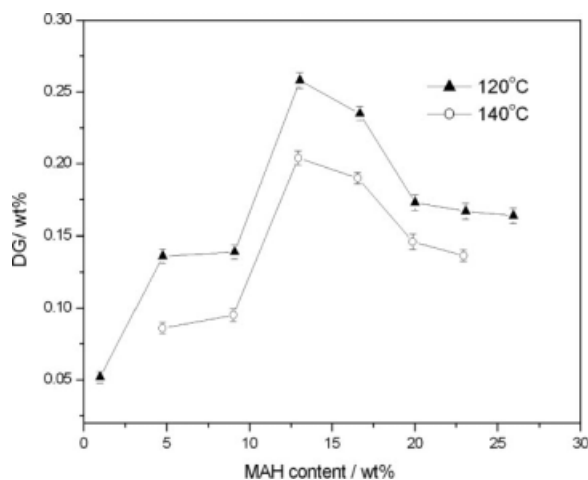
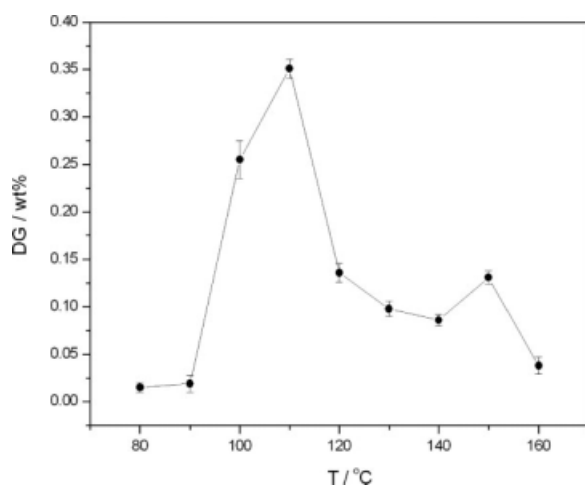


Figure 4 The effect of initiator's concentration on the degree of MAH grafting.



**Figure 5** The effect of monomer content on the degree of MAH grafting.

(The formulation was shown in Table I.) Obviously, in Figure 6, it is given an optimal temperature at  $\sim 110^\circ\text{C}$ . When the temperature is greater than  $110^\circ\text{C}$ , the degree of grafting decreased a lot. The reason is tightly connected with the half-life of BPO. BPO's half-lives ( $t_{1/2}$ ) at 74, 92, and  $130^\circ\text{C}$  are corresponding to 10 h, 1 h, and 1 min,<sup>31</sup> respectively. During graft copolymerization, it is desirable that the initiator be converted into radicals wholly within the reaction time. Thus, ideally, the half-life of the initiator should be short compared with reaction time, and if the reaction time corresponds to five half-lives, there will be 97% consumption of the initiator.<sup>32</sup> Therefore, BPO's half-life at very low ( $< 70^\circ\text{C}$ ) and very high temperature ( $> 130^\circ\text{C}$ ) doesn't match the reaction time, and the initiation efficiency is very low. And considering other factors such as reaction pressure, partition coefficient among the initiator, the HLPiB substrate and the monomer, and side reactions, the optimal tempera-



**Figure 6** The effect of reaction temperature on the degree of MAH grafting.

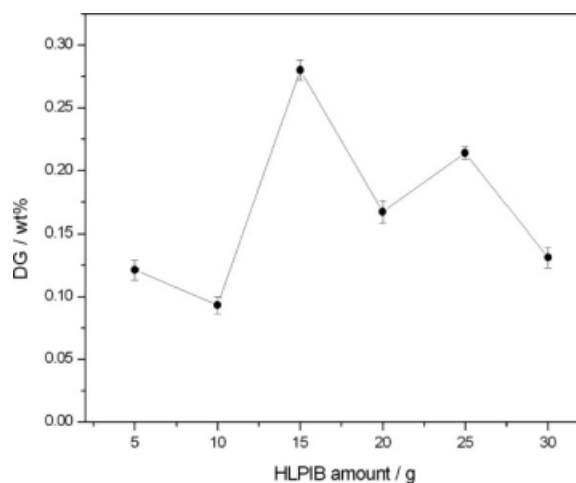
ture is  $110^\circ\text{C}$  in HLPiB-g-MAH reaction inside the high-pressure vessels.

#### The effect of HLPiB dosage in the reaction vessels

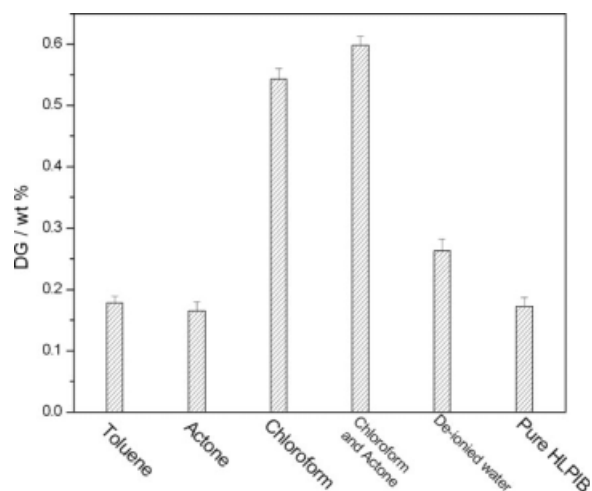
Because of HLPiB is in liquid state, in all the aforementioned experiments 30 g of HLPiB without any solvents was placed in the reaction vessels of 50 mL capacity. Although MAH can be grafted onto HLPiB in such conditions, the highest degree of grafting is lower than 0.4%. To increase the degree of grafting, solvents were needed. And before that, the effect of HLPiB dosage on the graft polymerization was investigated to know the maximal volume of solvent that could be added in the reaction vessel. The results are given in Figure 7, from which it was known that there exists an optimal point. The more mass of total reactant is in the sealed reactor, the greater the reaction pressure caused because of smaller volume of atmosphere in the vessel. As the pressure increases, the degree of grafting increases, that is, because monomers and initiators become easier to diffuse into the substrate with the increase of pressure. However, more reactants and greater pressure will increase the viscosity, which inhibits the polymerization instead.<sup>33</sup> When the dosage of HLPiB is lower than 15 g, greater pressure is the dominating reason, whereas that greater viscosity and the difficulty in diffusing of monomer radicals begin to preponderate over other factors when the dosage of HLPiB exceeds 15 g. Therefore, it had a maximum of 0.28%. And then 15 g of HLPiB was used in the following procedures.

#### The effect of different solvent

Acetone, toluene, chloroform, and de-ionized water were used to compare their different effects onto the graft copolymerization (in Table I). The results are



**Figure 7** The effect of HLPiB dosage on the degree of MAH grafting.



**Figure 8** The effect of different solvents on the degree of MAH grafting.

listed in Table I and Figure 8, from which it indicates that chloroform is the best for graft copolymerization (the DG increased from 0.172% to 0.598%), whereas other solvent only have a little effect. In fact, the influence of solvents to graft copolymerization is very complicated. Solvents may induce the decomposition of BPO, which benefits the grafting the chain transfer to solvent (in Scheme 6) and usually goes against the grafting. However, the solvating effect usually favors the copolymerization. In this work, the main reason may be the different solvating effects of different solvents, such as the boiling point, and the solubility to HLPiB. In Table II, it is shown that chloroform has a lower boiling point, which will bring greater pressure needed in grafting reaction in the vessel. Moreover, it is also a good solvent for HLPiB, which will lead to better mixture among reactants. In this reaction, 10 mL is not adequate for completely dissolving 15 g of HLPiB. When chloroform is in the sealed vessel at the beginning, it is first underneath the HLPiB substrate because of its heavier density than HLPiB (0.90 g/mL) and then is boiled away when heated up, which benefits sufficient mixture and contact between reactants and initiator compared with other solvents. Although toluene is also a good solvent of HLPiB, it increases the DG only a little because its lighter den-

**TABLE II**  
Different Physical Properties of the Solvents Used

	Boiling point (°C)	Density (g/cm <sup>3</sup> )	Solubility parameter
HLPiB	220 (Flash Point)	0.90	7.7–8.0
Toluene	111	0.87	8.9
Acetone	56	0.79	10.0
De-ionized water	100	1.0	23.2
Chloroform	61	1.48	9.3

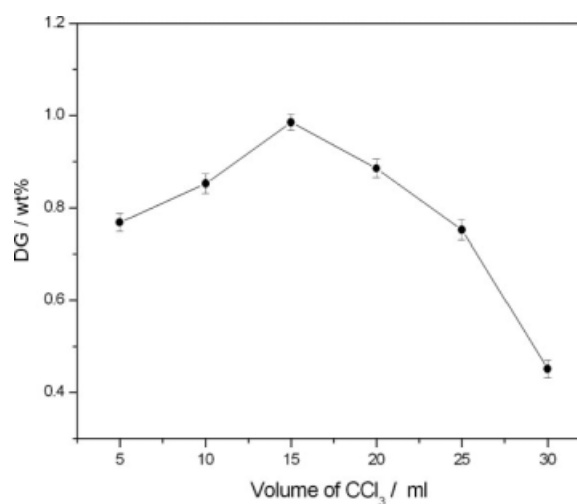
sity and high boiling point so that it cannot bring on adequate mixture among reactants and cannot induce the needed pressure for higher DG. The heavier density than HLPiB substrate for sufficient contact among reactants is also a main reason of de-ionized water's relative better effect on the DG than acetone even though both of them are bad solvents to HLPiB. However, the one with de-ionized water has a series of advantage of low-cost, easily-purification, innocuous and no contamination to the environment and humans. Therefore, when the DG is not needed to be too high, de-ionized water is the best choice.

### The effect of solvent's volume

A volume of chloroform from 5 to 30 mL and a temperature of 110°C for 5 h were used here (in Table I). The result is shown in Figure 9. When there was more solvents it will dilutes the initiator and the monomer's concentration, which will go against graft copolymerization. Besides, it may have the similar reason caused by reaction pressure discussed previously in the effect of total reactant mass. As a result, the best volume of solvent is 15 mL when the HLPiB is 15 g.

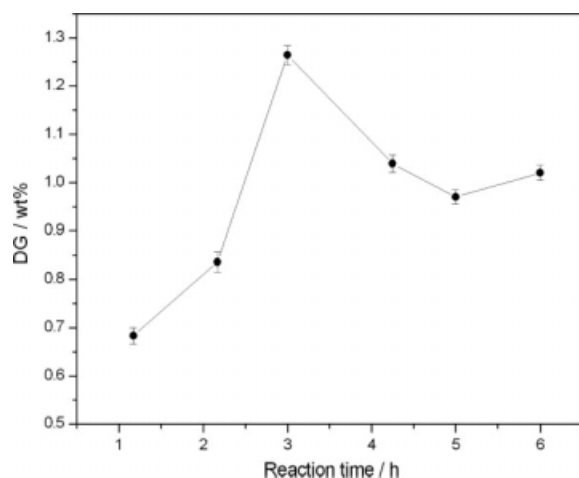
### The effect of reaction time

With 15 mL of chloroform added, the influence of reaction time varied from 1 h to 5 h at 110°C (The formulation was shown in Table I) was investigated. Figure 10 indicates that 3 h is just enough for the reaction. This could be explained by that the grafting reaction is carried out in a sealed vessel, and the reaction solution is cold in the early stage of the reaction, and a certain time is necessarily needed for



**Figure 9** The effect of chloroform's volume.





**Figure 10** The effect of reaction time onto the degree of MAH grafting.

the dissolution of reactants, the boil away for the solvent and the decompose of initiator, so lower DG was obtained in the beginning of the stage. When the reaction time is up to 3 h, the optimal reaction conditions for the grafting reaction were obtained, and as a result the DG was increased and the highest DG was obtained. Although the further prolong of the reaction time has not any useful for increasing the DG because all the initiator is used up.<sup>14</sup> Moreover, long time heating will cause thermal decomposition of HLPIB.<sup>34,35</sup>

## CONCLUSIONS

The HLPIB-g-MAH copolymer was successfully synthesized by solvothermal method. The influence of the reaction parameters on the DG was also investigated. The important results are summarized as follows: (1) The copolymerization can proceed without any solvent. When chloroform was used as solvent DG enhances a lot (nearly 200%). Deionized water is a best choice of solvent when the DG is not required too high because of its totally innocuous and no contamination and very low cost. (2) The optimal volume of solvent is 15 mL when the HLPIB is 15 g in 50 mL of high-pressure vessel. (3) When BPO was used as the initiator, the optimal initiator's concentration is 0.8 phr; the optimal reaction temperature is 110°C, and optimal MAH's content is 13 phr (based on the total reactant mass). (4) The DG was initially increased with the increasing of reaction time, and reached to a maximum (reaction time is 3 h), and then decreased.

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