Solvothermal Preparation and Characterization of Maleic Anhydride Grafting High Density Polyethylene Copolymer

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ABSTRACT: In this article, the grafting copolymerization of maleic anhydride (MAH) onto high density polyethylene (HDPE) was carried out through solvothermal process. Infrared spectra (IR) revealed that MAH had been successfully grafted onto the HDPE backbone. The influences of the reaction parameters on the grafting copolymerization, e.g., the concentration of the initiator, MAH and HDPE content, reaction time, reaction temperature, comonomer, and different solvents were also studied. Further studies found that MAH could be grafted onto HDPE in both good solvents and poor solvents, which was much different from the traditional solution grafting method. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3443–3452, 2007

Key words: solvothermal process; maleic anhydride; high density polyethylene; grafting

INTRODUCTION

High density polyethylene (HDPE), one of the most important commercial polyolefins, has been found in wide applications ranging from glands, jugs, and containers to kitchenware. However, some inherent drawbacks, e.g., lacking the chemical functionality (polar groups) and crystalline morphology, limited its applications in higher value products just as blends or composites.[1] To overcome these shortcomings and broaden its usage in current areas, functionalization of PE has been widely pursued with various monomers for specific purposes.[1–7]

As one of the most common ''star monomers'' to modify hydrocarbon substrates for its poor homopolymerization character toward free radicals,[8] the introduction of maleic anhydride (MAH) on the backbones of hydrocarbons can effectively improve their polarity and compatibility with other polar polymers,[9–12] and various kinds of PE grafting MAH copolymers have been obtained, e.g., LDPE-*g*-MAH, LLDPE-*g*-MAH, HDPE-*g*-MAH, etc.[13–15] through the traditional approaches including solution grafting method,[13,15–18] melt-state grafting method,[19–21] and radiation grafting method.[22–25] However, the grafting degree (GD) obtained by these traditional methods is usually low, especially for HDPE, because of the high crystalline nature and exiguous branched chain of the backbone. Therefore, how to prepare grafting copolymers with

high GD or low gel content (GC), as well as simplify the posttreatment and reclaim the waste solvent, is becoming the constant interest for many researchers.

In the past decades, as the development of hydrothermal method, solvothermal method has become one of the most effective methods to prepare novel inorganic materials and nanocomposites[26–28] because of its characteristic properties, such as autogenous pressures, near-supercritical fluids, high reactive, and so on. Recently, our group has successfully prepared the grafting copolymers of ABS-*g*-MAH and SBS-*g*-MAH through this method, and high GD (>10%) was obtained.[29] The results implied that solvothermal method could be a potential way for the graft-copolymerization because the solvents were sealed in the vessel, and the evaporation of the solvents and the monomer was avoided, which would be favorable for the environment. To prove that this is a general method and can be extended to other systems, HDPE-*g*-MAH copolymers were prepared in this work, and the experimental parameters, such as initiator's content, MAH concentration, HDPE content, reaction time, reaction temperature, comonomer, and different solvents were also investigated. The results showed that the grafting copolymerization could be carried out both in good solvents and poor solvents different from the traditional solution method, and higher GD could be obtained in good solvents.

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Materials

HDPE was purchased from Sabic (Saudi Arabia) (Product ID = 80,064, density = 0.95 g/cm^3 at 20°C,

TABLE I
The Influences of the Reaction Parameters on GD and GC (Solvent = Toluene)

Series	DCP (g/100 mL)	MAH (g/100 mL)	HDPE (g/100 mL)	Time (h)	Temperature (°C)	GD (%)	GC (%)
DCP	0.0125					0.17	0.64
	0.0625					0.34	23.2
	0.25					0.61	30.9
	[a]0.625	1.25	12.5			1.28	37.1
	0.875					1.93	39.2
	1.25					1.56	71.7
	1.875					1.05	88.5
	2.5					0.8	90.6
	0.625	0.25				0.2	6.15
		0.625				0.41	40.81
		0.875		5		0.68	34.84
		[a]1.25				1.28	37.4
MAH		1.875	12.5		150	2.03	21.08
		2.5				2.28	13.24
		3.75				1.85	12.57
		6.25				1.6	12.16
			2.5			0.8	39.53
			5			0.88	14.3
HDPE	0.625	1.25	7.5			1.54	17.6
			[a]12.5			1.28	37.4
			17.5			0.61	81.45
				2		0.75	21.2
				4		1.3	24.93
Reaction Time	0.625	1.25	12.5	[a]5		1.28	37.4
				6		0.89	28.45
				11		0.8	36.13
					130	2.1	57.36
					140	2.67	35.1
Reaction temperature	0.625	1.25	12.5	5	[a]150	1.28	37.4
					160	0.91	48.17
					170	0.8	14.87

[a] Typical dosage and reaction conditions.

and MFI = 8.3g/10 min). MAH and toluene were from Shanghai Linfeng Chemical Reagent. Potassium hydroxide, hydrochloric acid, dicumyl peroxide (DCP) (half-life = 533 s at 150°C), and xylene were from Sinopharm Group Chemical Reagent. Acetone and ethanol were purchased from Shanghai Zhenxing Chemical Factory.

DCP was purified by dissolution in ethanol in room temperature and recrystallized in cool ethanol for several times. All the other materials were used without further purification.

Grafting procedure

The grafting reactions were performed in a vessel with different solvents under various reaction conditions. The dosages and the reaction conditions were given in Tables I–III. In a typical process, 5 g HDPE, 0.5 g MAH, 0.25 g DCP (as the initiator), 40 mL toluene (as the solvent), and styrene (St)) (if necessary) were put into the vessel simultaneously, and then the vessel was sealed and maintained in a constant temperature oven (i.e. 150°C) for a certain time (i.e. 5 h).

TABLE II
Effect of the Comonomer on GD and GC (Solvent = Toluene)

Styrene/MAH composition (wt %)	DCP (g/100 mL)	MAH (g/100 mL)	HDPE (g/100 mL)	Time (h)	Temperature (°C)	GD (%)	GC (%)
[a]0						1.23	9.75
10						1.62	8.75
30	0.625	1.25	1.25	5	150	1.48	12.2
50						1.46	11.25
70						1.49	13.45
100						1.19	14.75

[a] Typical dosage and reaction conditions.

TABLE III
HDPE-*g*-MAH Copolymers Prepared in Different Solvents

Solvents	DCP (g/100 mL)	MAH (g/100 mL)	HDPE (g/100 mL)	Time (h)	Temperature (°C)	GD (%)
Water						0.1
Butanone	0.625	1.25	12.5	5	150	0.19
[a]Toluene						1.28
Xylene					170	1.09

[a] Typical dosage and reaction conditions.

After that, the vessel was naturally cooled to room temperature. Then, the grafting products were recovered and precipitated with acetone or ethanol to remove the residual MAH. The purified solid was collected and dried under vacuum oven (80°C) over night.

Characterization

Infrared spectroscopy information of HDPE and HDPE-*g*-MAH was obtained on a PerkinElmer Paragon 1000 FTIR spectrophotometer (USA) ranging from 450 to 4000 cm^{-1} at a resolution of 2 cm^{-1} and one scan. Films in 0.010–0.015-mm thickness for FTIR were compression molded (150°C, 12 MPa) for 5 min firstly, and then followed by the cool compression molded. No significant changes were observed in the FTIR spectrum after the process of purification, which indicated that the purification was effective.

Determination of GD of HDPE-*g*-MAH

The GD of MAH was determined by a back titration procedure. The MAH content of the xylene-soluble fraction in HDPE-*g*-MAH copolymer was determined by refluxing about 0.25 g (exact weighted W) samples in 150-mL xylene for 0.5 h. Then, 30-mL ethanol solution of KOH (0.05 mol/L) was added with phenolphthalein as an indicator (three drops of 1% ethanol solution of phenolphthalein). To make sure that the polymers were completely dissolved, the reaction was carried out for 4 h, and then titrated in the hot state. After the pink color of the solution was back-titrated to a colorless (end point) by the addition of 0.05 mol/L isopropanolic HCl to the hot solution, the MAH content (GD) of the maleated HDPE samples can be calculated as follows:

$$GD(\%) = \frac{(V_0 - V_1) \times 10^{-3} \times CM}{2W} \times 100\%$$

where V_0 is the amount of HCl consumed by using pure HDPE as reference (mL), V_1 the amount of HCl consumed by grafted sample (mL), C the molar concentration of HCl (mol/L), M the molecular weight of MAH, and W the weight of sample (g).

Determination of the GC of HDPE-*g*-MAH

0.25 g grafting products were sealed in a filter paper bag, and then the bag was weighed ($M1$) and extracted in boiling xylene for 24 h using a Soxhlet apparatus. After the extracting process was completed, the bag was dried to a constant weight ($M2$) in a vacuum oven at 80°C. The GC can be calculated as follows:

$$\text{Gel content (wt\%)} = \left(1 - \frac{M1 - M2}{0.25}\right) \times 100\%$$

RESULTS AND DISCUSSION

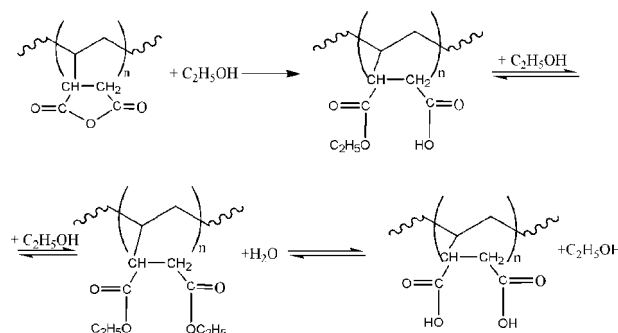### Characterization of grafting copolymers

The FTIR spectra of pure HDPE and the obtained products are shown in Figure 1. Comparing the FTIR spectra of curves 1 and 2, we can find that no grafting copolymerization occurs without the presence of DCP even under solvothermal condition. However, when the amount of DCP was added into the system and treated in the similar conditions, new peaks appeared in the obtained products besides the characteristic absorption peaks of HDPE, such as absorption peaks in 1864–1860 cm^{-1} for the asymmetric stretching of carbonyl V as (C=O), in 1786–1780 cm^{-1} for the symmetric stretching of carbonyl Vs (C=O), at 1224 cm^{-1} for the asymmetric ring stretching V(=C—O—C=), and at 1064 cm^{-1} for the symmetric ring stretching V(=C—O—C=). On the other hand, the appearance of the ring stretching vibration of saturated cyclic five-membered anhydride at 919 cm^{-1} instead of the two sharp bands of the C=C stretching of monomeric MAH at 867 and 892 cm^{-1} further implied that MAH had been successfully grafted onto the HDPE backbone. Careful observation on curves 3 and 4 revealed that the intensity of peaks in curve 4 at wave number of 1864, 1786, 1064, and 919 cm^{-1} decreased, but the intensity of peaks at 1710 cm^{-1} {V(C—O) of carboxylic
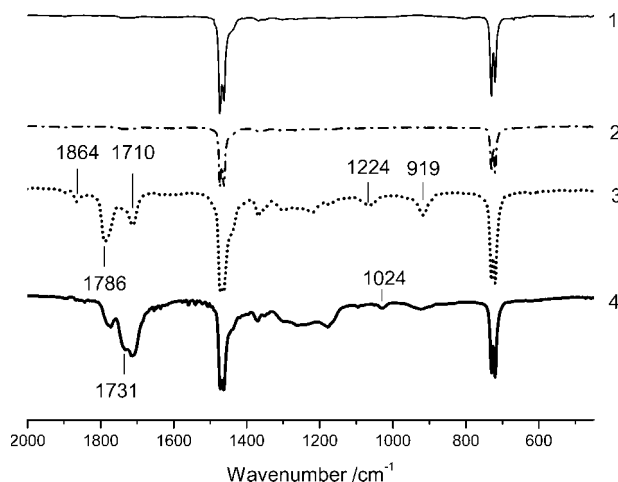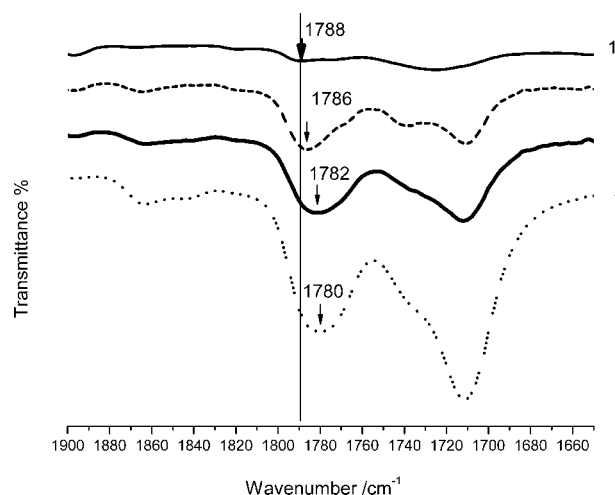
Figure 1 FTIR spectra of HDPE and HDPE-*g*-MAH. Curve 1: pure HDPE; Curve 2: HDPE underwent solvothermal process (HDPE = 5 g, MAH = 0.5 g, DCP = 0 g, and toluene = 40 mL); Curve 3: HDPE-*g*-MAH purified in acetone (HDPE = 5 g, MAH = 0.5 g, DCP = 0.25 g, and toluene = 40 mL); Curve 4: HDPE-*g*-MAH purified in ethanol (HDPE = 5 g, MAH = 0.5 g, DCP = 0.25 g, and toluene = 40 mL).


Figure 2 FTIR spectra of HDPE-*g*-MAH with different grafting degree: 1-GD = 0.17%; 2-GD = 0.61%; 3-GD = 1.93%; 4-GD = 2.67%.

acid dimmer} increased remarkably, and a new peak at 1731 cm^{-1} {V(C—O) of aryl ester of aliphatic acid} appeared. This phenomenon suggested that the grafting copolymer purified with different solvents could lead to the formation of new carbonyl compounds with carbonyl groups absorption at different peak bands. The reaction in the posttreatment might be followed in Scheme 1 if ethanol was used as a solvent. So, the following samples for investigating GD and GC were purified in acetone because acetone had no significant influence on the structure of the obtained copolymers.

Furthermore, the grafting samples with different GD were also characterized by FTIR. Figure 2 shows the absorption peak of Vs(C=O) shifted to lower wavenumber with the increase of GD of MAH, which is similar to the results of PE-*g*-MAH[15] and SBS-*g*-MAH[30] system. This result also meant that special hydrogen bonds in intermolecular or intramolecular

were formed when the hydrogen proton of a carboxyl group acted as the electron acceptor while the oxygen atom of the anhydride acted as the donor (Scheme 2), and the density of the hydrogen bond increased with the increase in the GD, which further lead the carboxyl bond at 1860 and 1780 cm^{-1} to shift to lower wavenumber.

Effect of initiator concentration

With the back titration procedure, the GD and GC of HDPE-*g*-MAH synthesized with different initiator concentration were analyzed and shown in Table I (DCP series) and Figure 3. From which we could find that the GD of HDPE-*g*-MAH copolymer initially increased with the increase of the initiator's concentration to a maximum point (from 0.0125 g/100 mL to 0.875 g/100 mL), and then decreased with the further increase of the concentration of initiator (from 0.875 g/100 mL to 2.5 g/100 mL).

It is well known that the grafting reaction and the crosslink reaction are the competitive reactions depended on the amount of free radicals.[31] When less amount of DCP (< 0.875 g/100 mL) was used, the amount of free radicals was also less, and further lower GD and GC were obtained because of the less grafting reaction and the crosslink reaction, in which the initiator radical mainly excited the PE chain through hydrogen attraction [Scheme 3(a)]. In a certain range of initiator concentration, the number of free radicals increased with increasing initiator's concentration, and so, GD and GC increased at the same time. When more DCP (> 0.875 g/100 mL) was used, the free radical would not only attack PE chain, but also make MAH undergo excitation to generate an

Scheme 1 Possible reaction in the ethanol posttreatment.

(a)

(b)
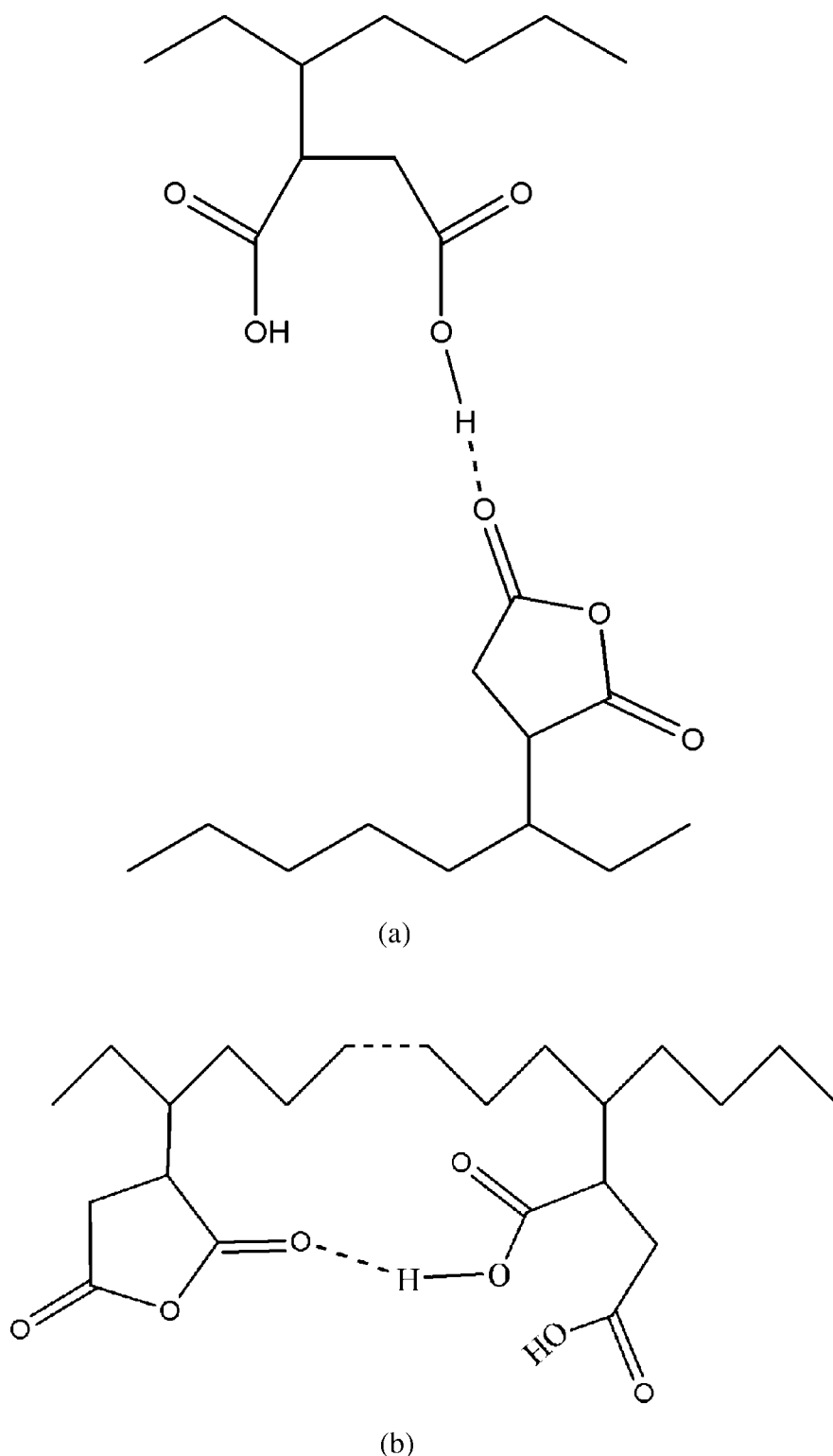
Scheme 2 Intermolecular (a) and intramolecular (b) hydrogen bond in the grafts.

excimer [Scheme 3(b)], which might lead GC increase because of the coupling of the PE macroradicals generated by a PE-excimer interaction in addition to or in lieu of those generated by the PE-peroxide interaction. Furthermore, since the PE macroradicals participated in the crosslinking reaction instead of grafting copolymerization, GD decreased while GC increased. As a result, a certain ratio of MAH and DCP will be beneficial for the grafting reaction as the amount of MAH is maintained in constant.
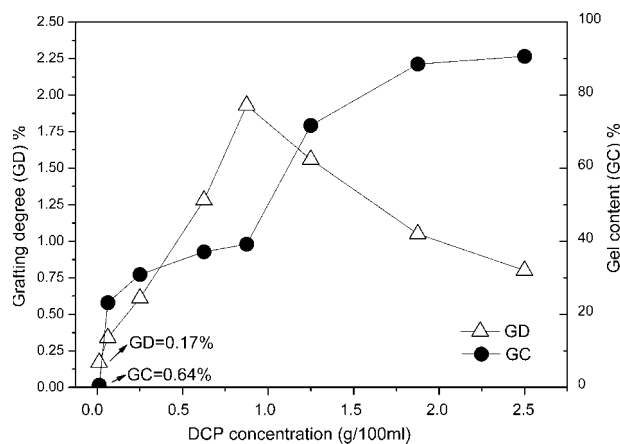
Figure 3 Effect of DCP concentration on GD and GC. Amount of HDPE = 5 g; MAH = 0.5 g; toluene = 40 mL; the reaction temperature = 150°C; the reaction time = 5 h.

Effect of MAH concentration

As can be seen in Table I (MAH series) and Figure 4, GD was about 0.2% when the amount of MAH was 0.25 g/100 mL and up to 2.3% when the amount of MAH was 2.5 g/100 mL, and then slightly decreased with further increasing MAH concentration. It is acceptable that the extent of grafting is dominated by the monomer numbers diffusing throughout the medium to attack the backbone of matrix when the concentration of monomer was not too high. So, the GD increased with the increase of MAH concentration when the amount of MAH was less than 2.5 g/100 mL. If the monomer concentration was high enough, the monomer numbers that could reach the backbone increased, but the grafting copolymerization was limited because the numbers of macroradicals were determined by the constant amount of the initiator. Moreover, a high concentration of MAH might cause homopolymerization itself. For the GC, it increased initially but then decreased to constant when too much MAH was added. Because the grafting copolymerization and the crosslinking interaction were two competitory reactions, the GC was low when GD was high, and vice versa. In addition, MAH homopolymerization could consume the radicals, which also resulted in the lower GC and GD.

Effect of HDPE concentration

The relationship between HDPE concentration and GD or GC of the copolymers was shown in Table I (HDPE series) and Figure 5. It is clear that the highest GD was obtained when the dosage of HDPE was 7.5 g/100 mL. In general, the extent of grafting reaction was depended on the availably active sites, and so, the more HDPE was added, the more opportunity the monomer could reach to the HDPE backbone when the dosage of DCP and MAH kept invariable. However, if too much HDPE was added, the viscosity of reaction medium increased remarkably that would make the diffusion of DCP and MAH monomer more difficult. Meanwhile, the opportunity caused crosslinking also increased because of coupling interaction between two PE macroradicals rather than grafting reaction with MAH, which might further lead to the decrease of GD, while the increase of GC.

Effect of reaction time

Figure 6 and Table I (Reaction Time Series) show the influence of the reaction time (ranging from 2 to 11 h) on GD and GC. From which we can find that the GD and GC are low in the initial stage and then level up to a maximum point in 4–5 h. After that, the GD slightly decreases and GC slightly increases. This is because certain period of reaction time is necessary for the decomposition of initiator, the diffusion of the monomer, the reaction system up to the reaction temperature, and even the disentanglement of the HDPE backbone. So, if the reaction time was not long enough, lower GD and GC were obtained because the grafting reaction was not sufficient. Given enough time, the reagents might reach a "favorable" status to have a good grafting copolymerization. However, if the reaction time was too long, the macroradicals would have more chance to take place the couple-termination reaction. As a result, highest GD and GC were obtained at the optimal reaction time, e.g., 4 h, and no significant effect on increasing GD and GC was observed with further prolonging reaction time because of the characteristic of the radical reaction.[32]
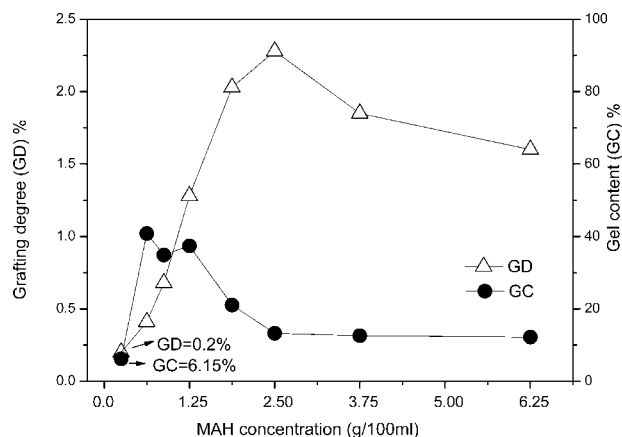
Effect of reaction temperature

The reaction temperature also had great effects on the grafting copolymerization. From Figure 7 and Table I (Reaction Temperature Series) we can find that grafting product with maximum GD and minimum GC could be obtained at 140°C. When the reaction temperature was lower or higher than 140°C, GD decreased slightly. Two facts might be responsible for the results. One is the half-life of DCP, e.g., the half-life of DCP is 4530 s at 130°C (constant difference of decomposition rate is 1.53×10^{-4} s^{-1}), which meant that 5 h were favorable for DCP to attack HDPE backbone substantially. While the half-time of DCP is about 533 s at 150°C (constant difference of decomposition rate is 1.37×10^{-3} s^{-1}), it leads to relatively quick decomposition of DCP at early stage and low GD was obtained. Furthermore, the higher reaction temperature, the more rapid decomposition of DCP, which might cause some unreacted radicals coupling, terminated instead of
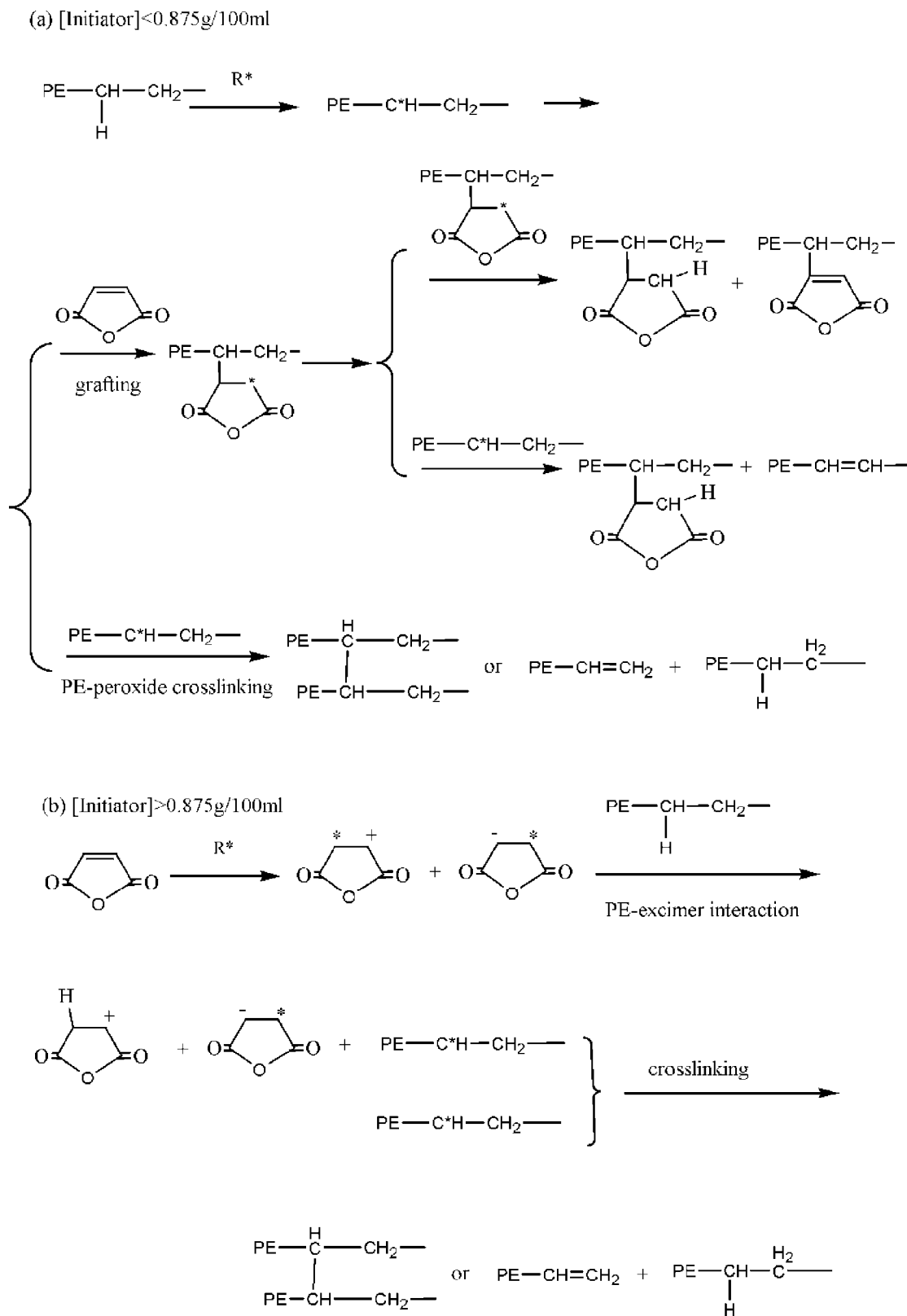
Scheme 3 Gaylord's mechanism about the crosslinking of PE: (a) PE-peroxide crosslinking and (b) PE-MAH excimer interaction.

taking grafting or crosslinking interaction, and the GD, as well as GC, decreased. The other factor might be the solution viscosity. With the decrease of solutio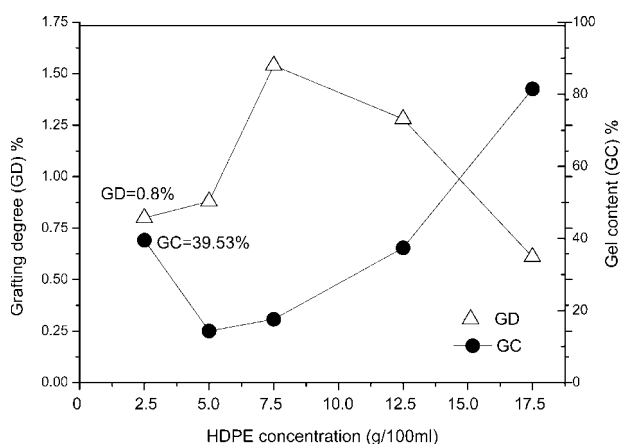n viscosity caused by higher reaction temperature, the radicals' mobility increased, which was favorable for the grafting copolymerization. The two effects made the grafting reaction should be carried out at a suitable reaction temperature.
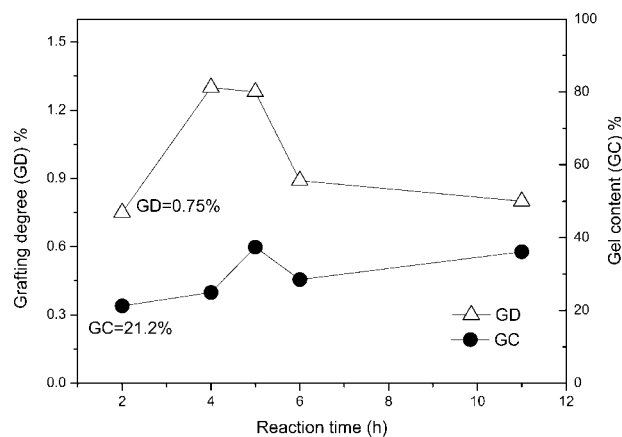
Figure 4 Effect of the monomer concentration on GD and GC. Amount of HDPE = 5 g; DCP = 0.25 g; toluene = 40 mL; the reaction temperature = 150°C; the reaction time = 5 h.
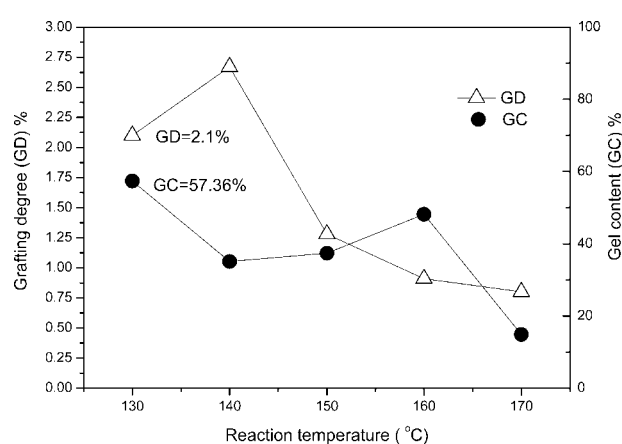

Figure 6 Effect of the reaction time on GD and GC. Amount of HDPE = 5 g; MAH = 0.5 g; DCP = 0.25 g; toluene = 40 mL; the reaction temperature = 150°C.

Effect of the comonomer

Gaylord et al.[31] pointed out that MAH could increase the crosslinking reaction of LDPE with the presence of DCP, and the presence of electron-donating compounds could inhibit the homopolymerization of MAH and crosslinking reaction of HDPE because electron-donating compound would prevent the coupling of PE macroradicals from the MAH$^+$ cations presented in the MAH excimers as well as in the excimers appended to the PE. In our previous work,[33] we also found that St, as the electron-donating compound because there exists floating electron cloud for its p–π conjugation, could effectively decrease the GC of the grafting copolymers. To investigate the effects of St on the HDPE-g-MAH copolymer, binary systems of St, and MAH with various compositions were used. From Figure 8 and Table II, we can see that GD initially increases with the increase of St content, and reaches a maximum (GD = 1.62 wt %) at a comonomer

composition of 10% (St/MAH wt %). Then, it decreases with further increasing St content. This result indicated that the synergistic effect brought by the appropriate addition of St had an obvious influence on the solvothermal grafting copolymerization.
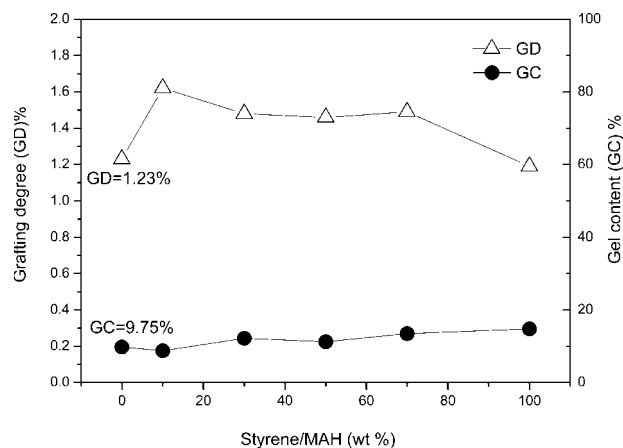
Effect of solvent

The polarity parameter (PP) of solvent is consistent with the polarity of solvent, and the higher PP means stronger polarity. It is well known that HDPE is well dissolved in nonpolar solvents other than in polar solvents. To study the influence of solvents on the grafting copolymerization, different kinds of solvents, such as toluene (PP = 0.001), xylene (PP = 0.001), butanone (PP = 0.510), and water (PP = 0.819) were selected as the reaction medium. As shown in Figure 9 and Table III, the grafting copolymerization can proceed in all these solvents, and grafting copolymers with higher GD (GD = 1.28 and 1.09%, respectively) were obtained

Figure 5 Effect of the HDPE concentration on GD and GC. Amount of MAH = 0.5 g; DCP = 0.25 g; toluene = 40 mL; the reaction temperature = 150°C; the reaction time = 5 h.
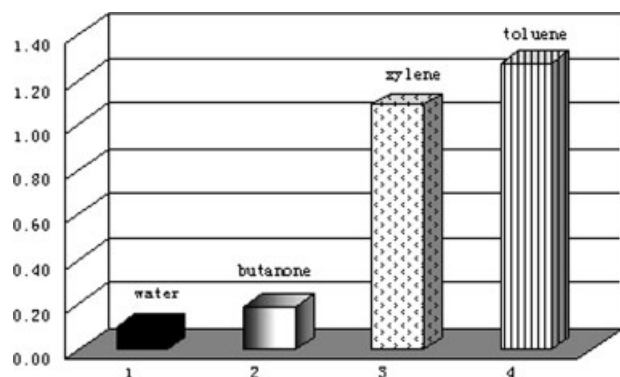

Figure 7 Effect of the reaction temperature on GD and gel content. Amount of HDPE = 5 g; MAH = 0.5 g; DCP = 0.25 g; toluene = 40 mL; the reaction time = 5 h.

Figure 8 Effect of the styrene/MAH comonomer composition on GD and gel content. Amount of HDPE = 5 g; MAH = 0.5 g; DCP = 0.25 g; toluene = 40 mL; the reaction time = 5 h; the reaction temperature = 140°C.

in good solvents for HDPE, e.g., toluene and xylene, while lower GD was obtained in poor solvents, e.g., 0.1% in water and 0.19% in butanone. Although the samples prepared in poor solvents had low GD, the grafting copolymerization did occur, which was much different from the solution grafting method. Similar with our previous work,[29] the grafting polymerization could be carried out in poor solvents because the elevated temperatures and autogenous pressures resulting from heating in sealed autoclave were favorable to increase the solubility and reactivity of polymers.

Figure 9 Effect of solvents on the grafting polymerization. Histogram 1: HDPE-*g*-MAH (GD = 0.10%) prepared in water (HDPE = 5 g; MAH = 0.5 g; DCP = 0.25 g; water = 40 mL; reaction temperature = 150°C; reaction time = 5 h). Histogram 2: HDPE-*g*-MAH (GD = 0.19%) prepared in butanone (HDPE = 5 g; MAH = 0.5 g; DCP = 0.25 g; butanone = 40 mL; reaction temperature = 150°C; reaction time = 5 h). Histogram3: HDPE-*g*-MAH (GD = 1.09%) prepared in xylene (HDPE = 5 g; MAH = 0.5 g; DCP = 0.25 g; xylene = 40 mL; reaction temperature = 170°C; reaction time = 5 h). Histogram4: HDPE-*g*-MAH (GD = 1.28%) prepared in toluene (HDPE = 5 g; MAH = 0.5 g; DCP = 0.25 g; toluene = 40 mL; reaction temperature = 150°C; reaction time = 5 h).

CONCLUSIONS

The HDPE-*g*-MAH samples were successfully obtained by solvothermal process. The effects of various reaction conditions on GD and GC were also studied. The important results were summarized as follows:

1. In the grafting copolymerization of MAH onto HDPE backbone, the GD increased with the increase of initiator concentration, MAH concentration, HDPE content, reaction time, reaction temperature, and St/MAH weight ratio, and reached a maximum, and then leveled off.
2. The GC representing the crosslinking extent of the grafting samples had a tendency to increase with the increase of initiator's concentration, HDPE concentration, and reaction time. And it initially increased with the increase of MAH concentration and reaction temperature, and reached to a maximum, and then decreased with a further increase of MAH concentration and reaction temperature.
3. The grafting copolymerization can proceed not only in good solvents but also in poor solvents, which is much different from the traditional solution grafting copolymerization because of the special characteristic of solvothermal method.

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