Grafting Copolymerization of Maleic Anhydride onto Styrene-Butadiene-Styrene Block Copolymer through Solvothermal Process

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ABSTRACT: The grafting copolymerization of maleic anhydride (MAH) onto styrene-butadiene-styrene terpolymer (SBS) was carried out through a new synthesis method—solvothermal synthesis. Infrared (IR) spectra and solid state ^{13}C-NMR confirmed that maleic anhydride was successfully grafted onto the SBS backbone. The effects of different solvents, different initiators and their concentration, the amount of MAH, SBS concentration, and reaction time on the graft degree were evaluated, and the optimal conditions were obtained. Results indicated that the grafting reaction of MAH onto SBS through solvothermal method can be carried out in both good solvents and poor solvents, which are much different from the traditional solution grafting method, and high grafting degree can be obtained in good solvents. Finally, we also compared the grafting degree (GD) prepared by the solvothermal method with that by the melt grafting method and solution grafting method. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5274–5279, 2006

Key words: SBS; MAH; solvothermal synthesis; grafting copolymerization

INTRODUCTION

Styrene-butadiene-styrene (SBS) block copolymer, a microphase separated polymer with excellent mechanical properties and comprising glassy and rubbery microdomains, has been widely used as a thermoplastic elastomer.[1,2] It behaves as a vulcanized rubber at room temperature and can be processed as a thermoplastic at an elevated temperature. In the other hand, SBS could be used to toughen semicrystalline polymers,[3] such as nylon 6. However, the nylon cannot be toughed with rubbers because the rubber particles formed in melt blending are too larger and the adhesion is not adequate.[4] This fact stimulates the applications of more effective compatibilizer in blends to improve the adhesion between the phases. In general, the compatibilizer is the same elastomer grafted with reactive group. The grafting polymerization is a well-known method to modify the chemical and physical structure of polymers and to tailor properties for a specifically application.[5,6] Several studies have appeared dealing with grafting vinyl monomers onto polymers such as styrene-butadiene block copoly-mers,[7] styrene-isoprene copolymers,[8] styrene-(ethylene-*co*-butadiene)-styrene triblock copolymers,[9–11] poly-*cis*-butadiene rubber (PcBR),[12] and acrylonitrile-buta-diene-styrene (ABS) terpolymer.[13,14] The typical method of grafting polymerization is a radical polymerization of various monomers initiated by a chemical initiator (including grafting polymerization in solution and in melt),[14–18] plasma,[19] high energy irradiation (electromagnetism, gamma ray),[20,21] and ultraviolet light (UV) photografting.[22,23] However, the grafting degree (GD) obtained by the traditional methods is usually low, and how to get high grafting degree (GD) is pursued by many researchers.

In the past years, as one of the most effective methods, solvothermal method has been widely used to prepare inorganic materials, and many kinds of new materials have been prepared.[24] In this process, the solvents are sealed in vessel (bomb, autoclave, etc.), and can be brought to temperatures well above their boiling points by the increase in autogenous pressures resulting from heating. Some solvothermal process indeed involves supercritical solvents. However, most of the processes just take advantage of the increased solubility and reactivity of metal salts and complexes at elevated temperatures and pressures without bringing the solvent to its critical point. In any event, solvothermal synthesis allows many materials to be prepared at temperatures substantially below those required by traditional solid-state reactions.[25,26]

Because of the increased solubility and reactivity of compounds and complexes at elevated temperatures and pressures, the solvothermal method has been widely used to prepare inorganic nanomaterials[27] and polymer-inorganic nanocomposites.[28] In this study, the solvothermal method was first successfully used to prepare the SBS-*g*-MAH copolymers, the effects of different solvent, different initiators and their concentration, the amount of MAH, SBS concentration, and reaction time on the grafting degree and the reactive mechanism were also studied. Different from the traditional solution grafting method, the grafting copolymerization can be carried out in both good solvents and poor solvents, and high grafting degree can be obtained in good solvents. Furthermore, the solvents and monomers are sealed in autoclave, and it can also avoid the evaporation of solvents and monomers, which benefits the environment and high grafting yield. In this study, we also compared the grafting degree (GD) prepared by the solvothermal method with that by the melt grafting method and solution grafting method.

EXPERIMENTAL

Materials

SBS was purchased from Taiwan Li Changrong chemical technology (Taiwan, China) as 501 line type and contains about 69 wt % butadiene and 31 wt % styrene. Benzoyl peroxide (BPO) was purified by dissolution in chloroform at room temperature and precipitation in cool methanol. Azobisisobutyronitrile (AIBN) was purified by dissolution in ethanol at 50°C and recrystallized in ice salt bath. Dicumyl peroxide (DCP) was purified by dissolution in hot ethanol, then filtrated and recrystallized at room temperature. BPO, AIBN, and DCP were supplied by Shanghai Lingfeng Chemical Solvent Factory, Shanghai, China. MAH (Shanghai Chemical Solvent Factory) were used without further purification.

Synthesis of the grafted copolymers

The grafting reactions were performed in a sealed vessel with different solvents under various processing conditions (the detailed reacting conditions are shown in Figs. 3–8). In a typical process, an appropriate amount of SBS, MAH, initiator, and toluene (as a solvent) were introduced into a sealed vessel simultaneously. Then the sealed vessel was put into constant temperature oven after purged by nitrogen. After the grafting reaction was taken at a certain time, the obtained products were taken away from the sealed vessel and precipitated in ethanol, and then the solid residue was washed several times in ethanol to remove any uncreative MAH.

Melt grafting was carried out in the molten state using a HAAKE mixer at various processing conditions. SBS, maleic anhydride (MAH), and initiators were simultaneously introduced into the mixer after dry blending. The obtained product was dissolved in chloroform and then unreacted MAH was extracted using ethanol.

Solution grafting was carried out with toluene as solvent at 150°C in a flask equipped with stirrer, thermometer, condenser, and nitrogen inlet. In a typical experiment, amount of SBS, MAH, and DCP was dissolved in 100 mL toluene. The reaction was terminated after 8 h. Then, the volatile component was removed by reduced pressure distillation; the nonvolatile sample was recovered and air-dried at room temperature. The residual MAH was extracted by ethanol.

The all purified polymer was collected and dried to constant weight in a vacuum oven at 80°C.

Characterization

The samples were cast into films (0.010–0.015 mm thickness) with chloroform as a solvent. IR spectroscopy information on SBS and grafted SBS was obtained on a PerkinElmer Paragon 1000 Fourier transform infrared (FTIR) spectrophotometer (USA). No significant changes were observed in the FTIR spectrum of the grafted SBS after further purification, and this indicated that the procedure was effective.

All solid state ^{13}C-NMR experiments were performed with Varian UNITYINOVA 400 MHz spectrometer with 5 mm AutoMAS DR and 4 mm T3 DR probes. The sample spinning speeds were stabilized in ±5 Hz.

Determination of the GD of MAH

The GD of MAH was determined by a back titration procedure. 1.0 g purified sample was dissolved in 100 mL chloroform, and then 50 mL ethanol solution of KOH (0.1 mol/L) was added. The mixed solution was refluxed for 60 min with stirring, then back-titrated by 0.1 mol/L HCl, with bromothymol blue as an indicator.

GD was defined as the amount of grafted maleic anhydride as a percentage of SBS and calculated by:

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

where V_0 is the amount of HCl consumed by using pure SBS 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 maleic anhydride, and W is the weight of sample (g).

RESULTS AND DISCUSSION

Characterization of grafting

The reaction was carried out by solvothermal method at 40–50°C higher than the boiling point of the solvent, so that the autogenous pressure in autoclave far exceeds the ambient pressure. Furthermore, the high temperature and the autogenous pressures resulting from heating increased solubility and reactivity of MAH and SBS, and that is favorable to the grafting reaction at low temperature than that in the ambient pressure. On other hand, the reaction is confined in the sealed autoclave, and it can also avoid the evaporation of MAH and solvent, and more favorable to the reaction. Compared the FTIR spectra of SBS and SBS-*g*-MAH copolymer (Fig. 1), the asymmetric and symmetric carbonyl vibrations at 1860, 1780 cm^{-1} and the C—O—C vibrations at the 1200–1100 cm^{-1} region are observed in SBS-*g*-MAH copolymer besides the inherent vibrations of SBS, it indicated that MAH has been grafted onto SBS.[14]

To further confirm that MAH was grafted on the backbones of SBS, the solid state NMR were used because the obtained samples do not dissolve in any solvents due to the crosslink reaction. The solid state ^{13}C-NMR spectra of pure SBS and SBS-*g*-MAH are shown in Figure 2. Compared to the solid state ^{13}C-NMR spectra of pure SBS and SBS-*g*-MAH, a new peak at 173.8 ppm, which was assigned to carbonyl signal,[29] was observed in SBS-*g*-MAH besides the expected signals for the block copolymer. The results
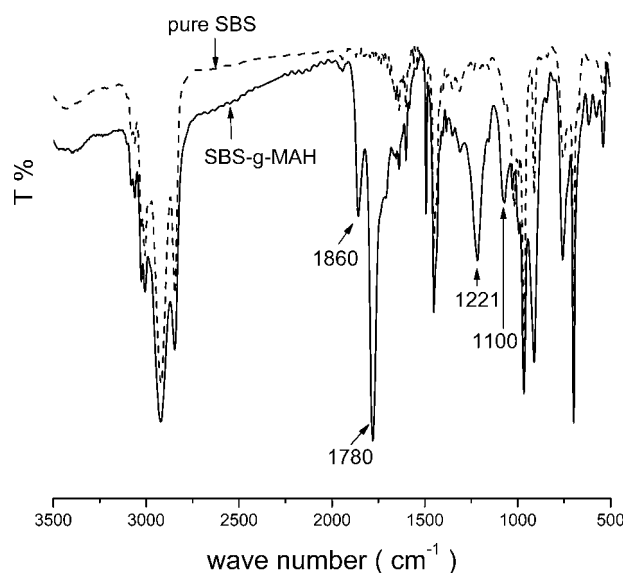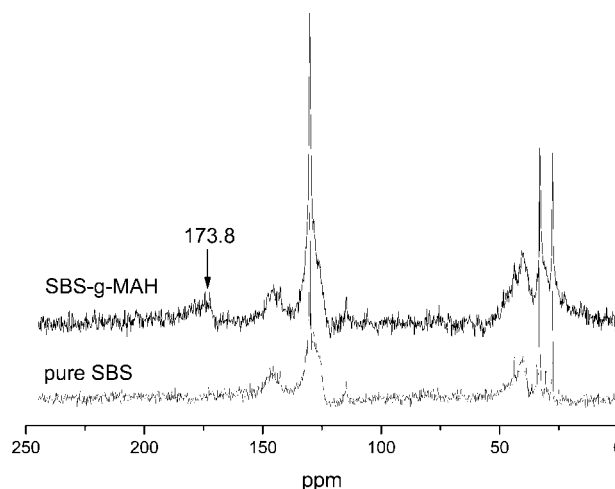
Figure 2 Solid state ^{13}C-NMR spectra of pure SBS and SBS-*g*-MAH.

also mean that the solvothermal process was an effective method to the grafting copolymerization of MAH onto SBS.

Effect of solvent

In traditional solution grafting process, the solvent is the carrier by which monomers are transported to the vicinity of the backbone. Therefore, how to select optimal solvent is very important for grafting polymerization. In general, the choice of solvent depends upon several parameters, including the solubility of monomer in solvent, the swelling properties of the backbone, the miscibility of the solvents if more than one solvent is used, and the generation of free radical in the presence of the solvent, etc.
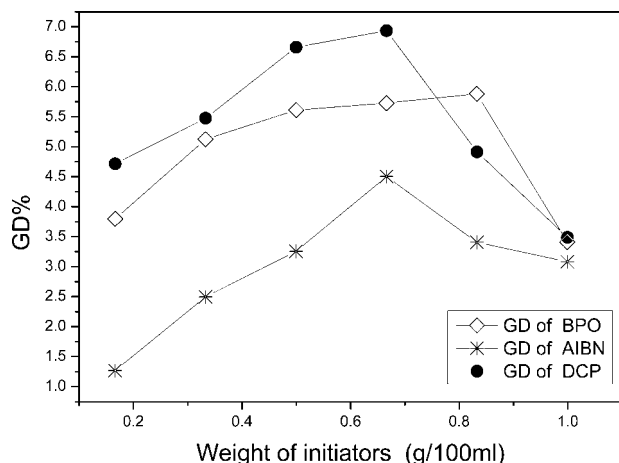
To study the influence of solvent on the grafting polymerization, good solvents like toluene, chloroform, and poor solvent such as acetone for SBS were chosen. The results show that the grafting polymerization can proceed in all solvents and the highest GD was obtained in toluene (Fig. 3). As to toluene and chloroform as solvents, the GD initially increases with increasing BPO loading and then decreases with the increasing BPO. However, GD slightly increases with the increasing BPO in acetone. Although the GD obtained in the poor solvents like acetone is far lower than that of in toluene and chloroform, the grafting polymerization still happened, while it is difficult to happen in the poor solvent in atmospheric pressure according to the traditional solution method. This is because the elevated temperatures and autogenous pressures resulting from heating in sealed autoclave are favorable to increase the solubility and reactivity of polymers, so the grafting polymerization still happened when poor solvents were used.

Figure 1 FTIR spectra of SBS and SBS-*g*-MAH.
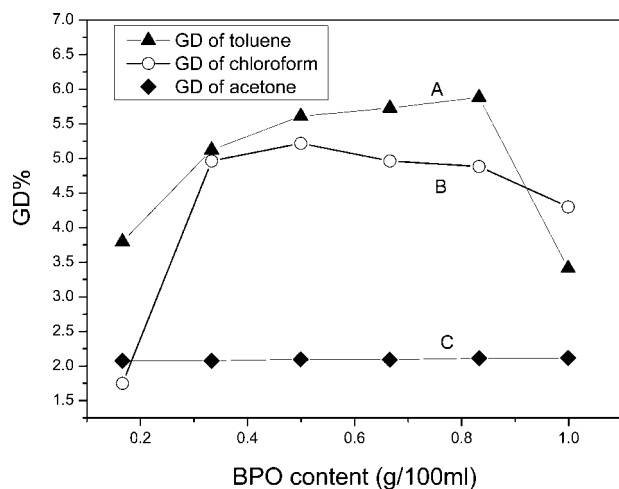
Figure 3 Effect of solvents on the grafting polymerization SBS: 3 g; MAH: 0.3 g. A. Solvent: toluene 30 mL; reaction temperature: 150°C; reaction time: 5 h. B. Solvent: chloroform 30 mL; reaction temperature: 110°C; reaction time: 5 h. C. Solvent: acetone 30 mL; reaction temperature: 120°C; reaction time: 5 h.

Effect of different initiators and their concentration

Besides the radical method, all chemical grafting reactions require an initiator and its nature, concentration, solubility as well as function were needed to be considered. Up to now, various kinds of initiators, such as BPO, AIBN, DCP, etc., have been used and the nature of the initiator has a profound effect on grafting reaction. Figure 4 shows the effects of various initiators and their concentrations on the grafting copolymerization. In this case, the reaction was carried out with 3 g SBS, 0.3 g MAH, 30 mL toluene, and various initiators at 150°C for 5 h, respectively. The results showed that DCP was the most effective initiator among the three initiators for the grafting copolymerization reaction at

TABLE I
The Half-Life of Different Initiators at 150°C

Initiator	$t_{1/2}$ (min)
BPO	0.38
AIBN	0.1
DCP	9.2

150°C. This is because the half-life of BPO and AIBN (shown in Table I) is shorter than that of DCP at high temperature (150°C), and the radical decay of BPO and AIBN was faster and occurred before the well mixing of components, which would decrease the reactive site of MAH molecule and the formed free radical further induces chain scission rather than grafting reaction. Otherwise, long life-time of DCP at high temperature was favorable to the high grafting degree. From Figure 4, we can also find that higher concentration of initiator is not favorable to obtain the high GD when the concentration of initiator reached a certain value because the homopolymer is formed more readily than that of the grafting copolymer. Compared with the GD of SBS-*g*-MAH obtained in melt and in normal solution,[9,30] the GD is much higher. It means that the grafting reaction was easy to carry out in the solvo-thermal conditions. In addition, we can also find that DCP is the best initiator for the grafting copolymerization reaction of maleic anhydride onto SBS and the highest GD was obtained when the initiator concentration was in the range of 0.5–0.7 g/100 mL in toluene.

Effect of MAH concentration

As to the nature of backbone, the reactivity of the monomer concentration has also important effect on grafting reaction. Figure 5 shows that the GD initially increased with the increasing of MAH concentration,

Figure 4 Effect of the various initiators and their concentration on the GD. SBS 3 g; MAH 0.3 g; toluene 30 mL; reactive temperature 150°C; reactive time 5 h.
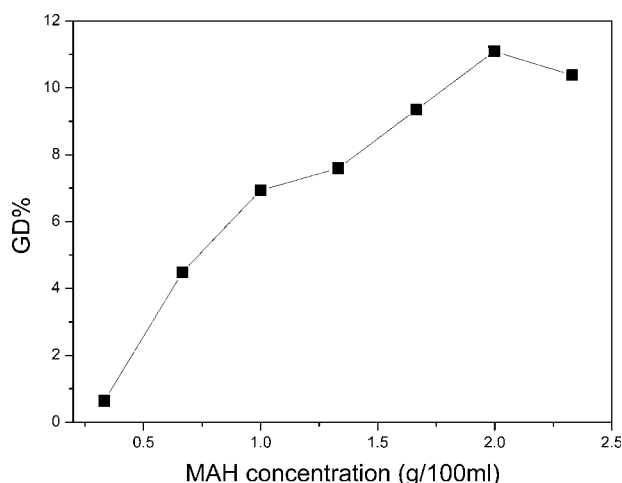

Figure 5 Effect of MAH concentrations on the grafting degree. SBS 3 g; DCP 0.2 g; toluene 30 mL; reactive temperature 150°C; reactive time 5 h.
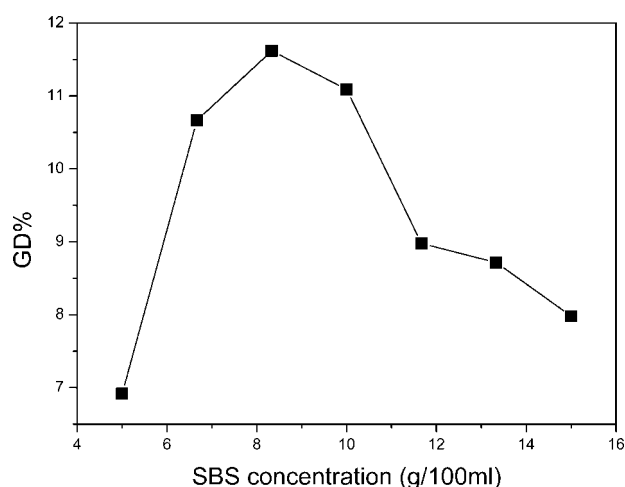
and reached a maximum at 2 g/100 mL, and then decreased with the further increasing of MAH concentration. This is because the extent of grafting reaction is governed by the monomer number diffusing throughout the reaction medium and reaching the polymer backbone, and further acting as a trap for radicals. Otherwise it would have undergone chain scission or crosslinking. But a higher monomer concentration could result in the homopolymerization of MAH and lead to low GD.
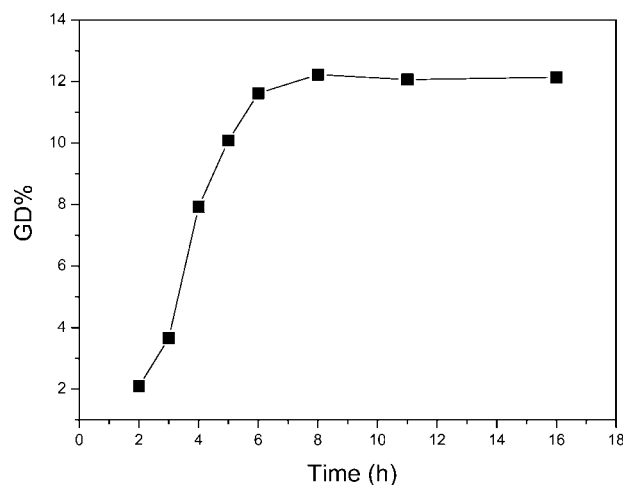
Effect of SBS concentration

The effect of SBS concentration on the grafting polymerization is shown in Figure 6. From which we can see that the highest GD was up to 11.6 wt % when SBS is about 8 g/100 mL. It is well-known that the grafting polymerization was depended on the number of active sites available, and the GD increased with the increasing of grafting site as active centers in SBS, so the GD increased with the increasing of SBS concentration and up to the highest grafting degree when SBS is about 8 g/100 mL. However, if SBS concentration was much higher, the viscosity of reaction medium was remarkably increased, and the diffusion and mobility of MAH and DCP onto SBS backbone became difficult, and further leading to the decreasing of GD.

Effect of reaction time

The grafting reaction time also has great effects on the grafting degree of MAH, and different reaction time in the range of 2–16 h was investigated. Figure 7 shows the relationship between the reaction time and the GD of MAH. We can find that the GD increased rapidly with the prolongation of reaction time up to

Figure 7 Effect of reaction time on the grafting degree. SBS 2.5 g; MAH 0.5 g; DCP 0.167 g; toluene 30 mL; reactive temperature 150°C.

8 h and thereafter reached balance. This could be explained that the grafting reaction is carried out in a sealed vessel, and the reaction solution contained solid polymer is cold in the early stage of the reaction, and a certain time is necessarily needed for the dissolution of polymer and for the reaction system up to reaction temperature, so the grafting copolymerization was difficult to happen and only low GD was obtained in the beginning of the stage. When the reaction time is up to 8 h, the optimal reaction conditions for the grafting reaction were obtained, and as a result the GD was greatly increased and the highest GD was obtained. While the further prolong of the reaction time has not any useful for increasing the GD because all the initiator is used up.[31,32]
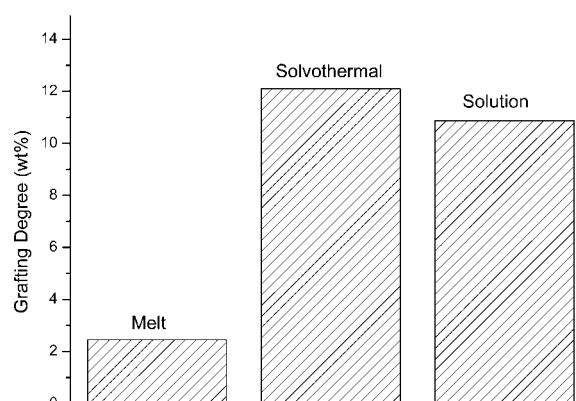
Figure 6 Effect of the concentration of SBS on the grafting polymerization. Toluene 30 mL; reactive temperature 150°C; reactive time 5 h; SBS/MAH/DCP 15/3/1.

Figure 8 Effect of the various methods on the grafting degree. Melt grafting process: SBS 50 g; MAH 5 g; DCP 0.2 g; reacting temperature 160°C. Solvothermal method: SBS 2.5 g; MAH 0.5 g; DCP 0.167 g; toluene 30 mL; reacting temperature 150°C; reacting time 8 h. Solution grafting process: SBS 2.5 g; MAH 0.5 g; DCP 0.167 g; toluene 100 mL; reacting temperature 150°C; reacting time 8 h.

Comparison of the various grafting methods

To compare the effect of the various grafting methods on the grafting reaction, we also prepared several samples by the solvothermal method, the melt grafting, and the solution grafting, respectively. From Figure 8, it can be seen that the GD of the sample prepared by the melt grafting process is less 3%, and by the solution grafting process is about 11%, while by solvothermal method can be up to 12%. These results also indicated, in some way, that the more high grafting degree can be obtained through solvothermal method.

CONCLUSIONS

The SBS-*g*-MAH copolymer was successfully synthesized by solvothermal method, and high GD is obtained. The influence of the reaction parameters on the GD was also investigated. The important results are summarized as follows:

1. 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 due to the special characteristic of solvothermal method. In addition, the toluene is the best solvent for the graft copolymerization of MAH onto SBS.
2. In the grafting polymerization of MAH onto SBS, DCP is the most effective and the GD increased with the increasing of initiator content, MAH concentration and SBS concentration, and reached to a maximum, and then decreased with a further increasing initiator content, MAH concentration and SBS concentration.
3. The GD was initially increased with the increasing of reaction time, and reached to a maximum, and then leveled off.

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