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ORIGINAL PAPER

Synthesis and reaction kinetics model of suspension phase grafting polypropylene with dual monomers

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Abstract The grafting polymerization of maleic anhydride (MAH) and styrene (St) onto PP was carried out in suspension phase. Infrared (IR) spectra and ^{1}H-NMR spectra confirmed that MAH and St were successfully grafted onto the PP backbone. The influences, such as monomers concentration, reaction temperature, initiator concentration and reaction time, on the grafting polymerization rate were also studied, and then the polymerization model was obtained to describe the polymerization regularities. The results showed that the model was adequate to reflect the courses, and diffusion and equilibrium adsorption played an important role in suspension polymerization.

Keywords Grafting polymerization · Suspension phase · Model · Diffusion equilibrium · Adsorption

Introduction

Recently, chemical modification of polypropylene has been widely studied, to expand the applications of polypropylene and generate value-added materials with improved mechanical, thermal, and chemical properties. The chemical modification of polypropylene was performed via reactions in a melt, in a solution, or in a suspension phase [1–4]. The modification of polypropylene in suspension phase was a promising new approach because of lower costs and easier operations. However, the most important advantage was the fact that the degradation reaction was reduced with lower reaction temperature [5].

Suspension polymerization was first developed by Hoffman and Delbruch in 1909 [6]. In suspension polymerization the initiator was soluble in the monomer

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phase, which was dispersed into the dispersion medium (usually water) to form droplets. Polymerization proceeded in the droplet phase, in order to prevent settling or creaming, agitation was normally continued throughout the course of the reaction [7–9].

Goncalves produced structured particles through seed suspension polymerization and discussed the mechanism involved in secondary particle formation [10]. Cartier and Hu reported that the grafting percent was improved greatly with the existence of styrene (St), during the course of glycidyl methacrylate (GMA) grafted onto PP [11]. Zhang and Guo proposed reaction mechanism of co-monomer grafted onto PP [12]. Despite all the extensive works on the modification of PP, there were few investigations about the preparation of grafting polymer through suspension polymerization and the effect of diffusion and adsorption on its process.

In this work, suspension polymerization was applied to prepare the PP-g-MAH-St copolymers. During the dispersion, monomers and other agents transferred from liquid phase to the surface of the PP grains, diffused in the pores of the PP grains, and then diffused in the amorphous phase [5, 13, 14]. The influences of various factors on the grafting polymerization rate were also studied. Further, diffusion and adsorption of radical initiators and monomers, and kinetics of the propagation and termination reactions were discussed in the suspension phase. The diffusion–adsorption chemical reaction mechanism and the corresponding model for suspension polymerization were proposed to describe the polymerization regularities.

Experimental section

Materials

Benzoyl peroxide (BPO) (Sinopharm Group) was first dissolved in chloroform, and then recrystallized from cold methanol and dried before use. Styrene (St) was prepared by distillation. Chloroform, methanol, maleic anhydride (MAH), and polyvinyl alcohol (PVA) were used as supplied. Water used in all reactions was double de-ionized water obtained from a purification system.

Suspension polymerization

The polymerizations were performed in a 250 mL glass reactor, equipped with a reflux condenser, a nitrogen purge inlet and a magnetic stirrer under various processing conditions (the detailed reactive conditions were showed in Figs. 5, 6, 7, 8, 9). In a typical process, appropriate amount of PP, MAH, St, BPO, PVA, and water were introduced into a glass reactor. Then the mixture was dispersed using ultrasound for 1.5 h, the reactions occurred at 90 °C for 6 h an inert atmosphere was maintained throughout the reactions. All obtained polymers were washed by Soxhlet extractions with acetone for a day.

Measurement and characterization

The Fourier transform-infrared (FT-IR) spectra of PP and PP-g-MAH-St were recorded with a Perkin–Elmer Lambda 900 FT-IR spectrometer by using KBr pellets. ^{1}H-NMR spectra were recorded on a Bruker Advance III-400 spectrometer using polymer solutions in deuterated benzene at room temperature.

DSC measurements were made on a NETZSCH DTA-404PC thermal system. The samples were scanned from 30 to 205 °C at a heating rate of 10 °C/min.

$$\text{Grafting percent (GP)} = m\,(\text{addition})/m\,(\text{raw PP}) * 100\%$$

$$\text{Grafting rate } (R_\text{g}) = m(\text{addition})/M * t * V$$

While the reaction time (t) and the volume of mixture (V) were fixed, GP could be used to describe R_g.

Theory basis

During the heterogeneous reaction, diffusion–adsorption reaction mechanism could be described as follows: substances participating in chemical reactions were first transferred from liquid phase to the external surface of reaction phase (external mass transfer); then transferred to the interior of reaction phase (internal mass transfer). The most important difference between them was the fact that chemical reaction occurred in the internal mass transfer [15–17].

The processes of external and internal mass transfer were in series. When chemical reaction dominated the whole course, the process was disposed according to the regulations of homogeneous reaction; or according to the ones of mass transfer. Therefore, the models for suspension polymerization were established [15–17].

Model of diffusion–adsorption in domain

When diffusion–adsorption was in domain, the dynamical model was obtained according to the mass transfer, at the pseudostable state [18–20].

$$R_\text{g} = k\prod_i c_\text{is}^n = k_\text{l}a\prod_i (c_\text{ib} - c_\text{is}) \tag{1}$$

$$k_\text{l} = A' \exp(-E_\text{l}/RT) \tag{2}$$

The grafting rate equation was gained from (1) and (2)

$$R_\text{g} = A\exp(-E_\text{a}/RT)[\text{MAH}][\text{St}][\text{BPO}] \tag{3}$$

In these expressions, c_ib and c_is were the substance concentration in water and at surface of PP, respectively; k_l was the coefficient of liquid mass transfer and the function of temperature.

Model of chemical reaction in domain

Suspension polymerization occurred in the amorphous phase. Some hypothesizes were proposed as below: (1) grafting polymerization occurred at the active points between MAH and St, copolymers with nearly alternant monomers were obtained when the mol ratio between St and MAH was <0.8 [21] and (2) a pseudomonomer (M) instead of MAH-St was given in Fig. 1.

On the basis of the above supposes, the reaction mechanism was described in Table 1.

Based on the above mechanism, some calculations were carried out as follows:

$$R_i = R_t \tag{4}$$

$$2k_\mathrm{d}[I] = 2\left([\mathrm{PPM}_x{}^\bullet]^2 + [\mathrm{PPM}_x{}^\bullet] * [\mathrm{RM}_y{}^\bullet] + [\mathrm{RM}_y{}^\bullet]^2\right) * k_t \tag{5}$$

$$\mathrm{d}[R^\bullet]/\mathrm{d}t = 0 = 2k_\mathrm{d}[I] - k_{i1}[R^\bullet][M] - k_{i2}[R^\bullet][\mathrm{PP\text{-}H}] \tag{6}$$

$$\mathrm{d}[\mathrm{RM}_y{}^\bullet]/\mathrm{d}t = 0 = k_{i1}[R^\bullet][M] - k_t[\mathrm{PPM}_x{}^\bullet][\mathrm{RM}_y{}^\bullet] - 2k_t[\mathrm{RM}_y{}^\bullet]^2 \tag{7}$$

$$\mathrm{d}[\mathrm{PPM}_x{}^\bullet]/\mathrm{d}t = 0 = k_{i3}[\mathrm{PP}^\bullet][M] - k_t[\mathrm{PPM}_x{}^\bullet][\mathrm{RM}_y{}^\bullet] - 2k_t[\mathrm{PPM}_x]^2 \tag{8}$$

Then, some results were obtained

$$[R^\bullet] = 2k_\mathrm{d}[I]/(k_{i1}[M] + k_{i2}[\mathrm{PP\text{-}H}]) \tag{9}$$

$$[\mathrm{PP}^\bullet] = 2k_\mathrm{d}k_{i2}[I][\mathrm{PP}]/k_{i3}[M](k_{i1}[M] + k_{i2}[\mathrm{PP}]) \tag{10}$$

$$[\mathrm{PPM}_x{}^\bullet] = \sqrt{8k_\mathrm{d}k_{i1}k_{i2}[I][\mathrm{PP}][M]/k_t(k_{i1}[M] + k_{i2}[\mathrm{PP}]) \Big/ \left(k_{i2}[\mathrm{PP}] + 7k_{i1}[M] + \sqrt{(k_{i1}[M] + k_{i2}[\mathrm{PP}])^2 + 12k_{i1}k_{i2}[M][\mathrm{PP}]}\right)} \tag{11}$$

Therefore, the grafting rate can be described in the following expression

$$R_\mathrm{g} = k_{p2}[\mathrm{PPM}^\bullet][M] \tag{12}$$

In these processes, the concentration of PP was a constant; and the rate constant was in accordance with the Arrhenius equation. Then, we incorporated expressions (11) and (12), and made it simpler; finally we got the equation

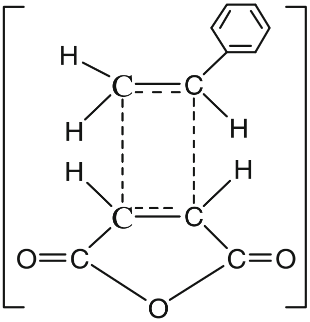

Fig. 1 Structure of pseudomonomer

Table 1 Mechanism of radical grafting reaction

Decomposition of peroxide	$I \xrightarrow{k_\mathrm{d}} 2R^\bullet$
Initiation	$R^\bullet + M \xrightarrow{k_{i1}} \mathrm{RM}^\bullet$
	$R^\bullet + \text{PP-H} \xrightarrow{k_{i2}} \mathrm{PP}^\bullet + \mathrm{RH}$
	$\mathrm{PP}^\bullet + M \xrightarrow{k_{i3}} \mathrm{PPM}^\bullet$
Propagation	$\mathrm{RM}_{(y-1)}{}^\bullet + M \xrightarrow{k_{p1}} \mathrm{RM}_y{}^\bullet$
	$\mathrm{PPM}_{(x-1)}{}^\bullet + M \xrightarrow{k_{p2}} \mathrm{PPM}_x{}^\bullet$
Termination by recombination	$\mathrm{PPM}_x{}^\bullet + \mathrm{RM}_y{}^\bullet \xrightarrow{k_\mathrm{tc}} \mathrm{PPM}_{(x+y)}$
	$\mathrm{PPM}_{x1}{}^\bullet + \mathrm{PPM}_{x2}{}^\bullet \xrightarrow{k_\mathrm{tc}} \mathrm{PPM}_{(x1+x2)}$
	$\mathrm{RM}_{y1}{}^\bullet + \mathrm{RM}_{y2}{}^\bullet \xrightarrow{k_\mathrm{tc}} \mathrm{RM}_{(y1+y2)}$
Termination by disproportion	$\mathrm{PPM}_x{}^\bullet + \mathrm{RM}_y{}^\bullet \xrightarrow{k_\mathrm{td}} \mathrm{PPM}_x + \mathrm{RM}_y$
	$\mathrm{PPM}_{x1}{}^\bullet + \mathrm{PPM}_{x2}{}^\bullet \xrightarrow{k_\mathrm{td}} \mathrm{PPM}_{x1} + \mathrm{PPM}_{x2}$
	$\mathrm{RM}_{y1}{}^\bullet + \mathrm{RM}_{y2}{}^\bullet \xrightarrow{k_\mathrm{td}} \mathrm{RM}_{y1} + \mathrm{RM}_{y2}$

$$R_\mathrm{g} = A\exp(-E_\mathrm{a}/RT)[I]^{1/2}[M]^a \quad (a<1) \tag{13}$$

Results and discussion

Figure 2 showed the IR spectrum of PP and PP-g-MAH-St. Curve (b) exhibited absorptions at 1,873 cm^{-1} [the asymmetric stretching of carbonyl ν_as(C=O)], 1,721 cm^{-1} [the symmetric stretching of carbonyl ν_s(C=O)] implying that MAH was successfully grafted onto the PP backbones [22–24]. On the other hand, Aromatic C=C bands were found at 1,600, 1,500, and 1,450 cm^{-1}, while aromatic C–H absorption was found at 3,070 cm^{-1}, and the bending vibration at 752 cm^{-1}. These implied that St was also grafted [25].

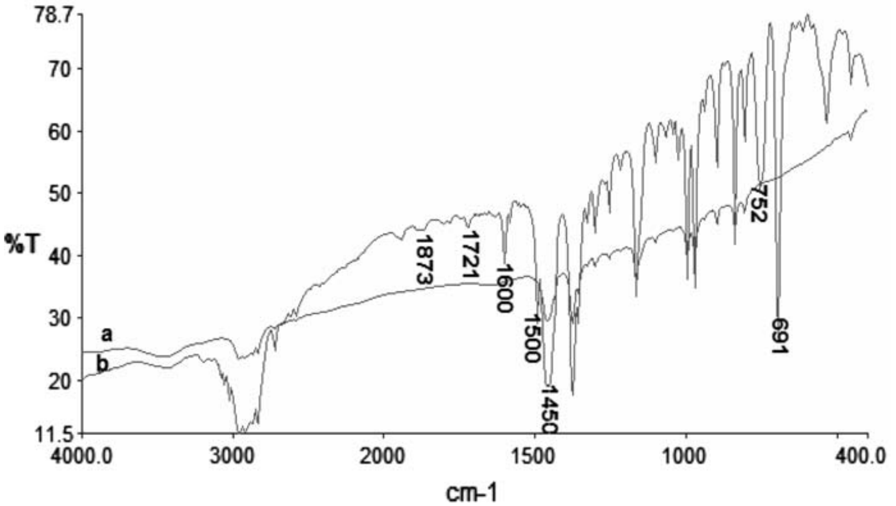

Fig. 2 Infrared spectrum of PP (**a**) and PP-g-MAH-St (**b**)

In order to further confirm that MAH and St were grafted on the PP backbone, the ^{1}H-NMR spectra of pure PP and PP-g-MAH-St were shown in Fig. 3. Compared with the ^{1}H-NMR spectra, it can be seen that the spectrum exhibited characteristic peaks in the range of 6.4–7.0 ppm due to the presence of the aromatic protons and C=C of MAH obtained from disproportion termination. The characteristic peaks in the range of 2.0–2.4 ppm could be assigned to the saturated hydrogen proton on the anhydride ring [26, 27]. From the results of FT-IR and ^{1}H-NMR spectra, it was concluded that MAH and St were successfully grafted on the PP backbone.

DSC curves obtained from the measurement were displaced in Fig. 4. It was clearly seen that there was a broad endothermic peak in PP, which was considered to

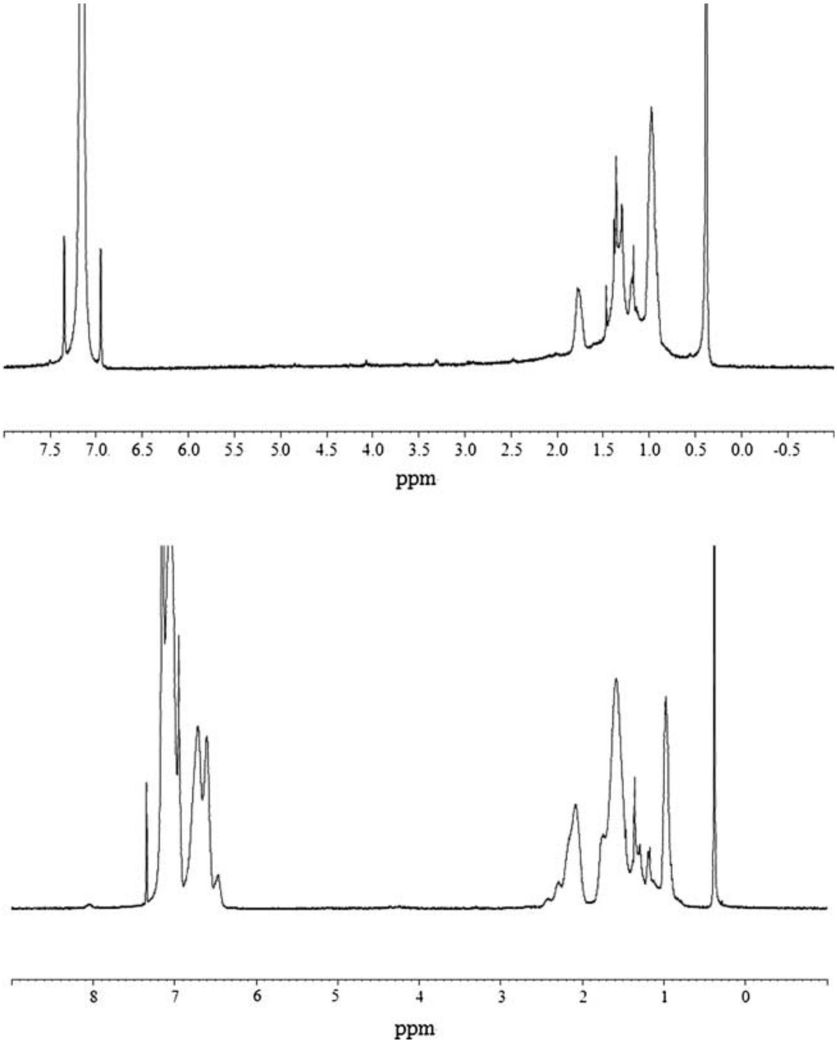

Fig. 3 ^{1}H-NMR spectrum of PP (*above*) and PP-g-MAH-St (*below*)

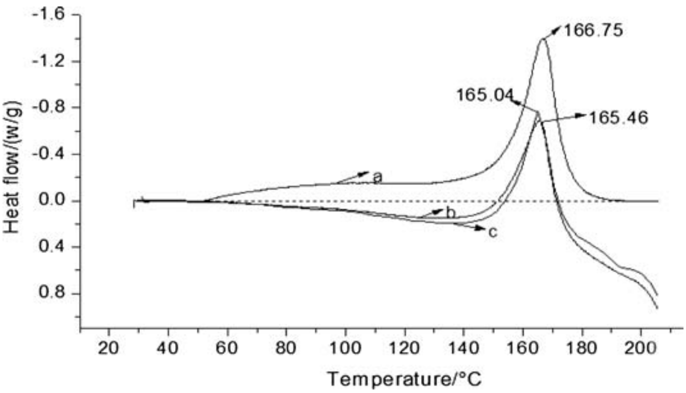

Fig. 4 DSC heating curves for PP (a) and PP-g-MAH-St with different GP (b, c)

correspond to the phase transition from the amorphous phase to crystal form [28]. This result was not found in PP-g-MAH-St polymers. Compared curve (a) with curve (b), (c), it was concluded that the existence of St and MAH in amorphous phase hindered the phase transition and the grafting polymerization mostly occurred in amorphous phase [5, 13, 14].

In order to make sure that the data were accurate, all the experiments were repeated three times at the same conditions, the corresponding results were listed in Table 2.

The effect of initiator concentration on the grafting reaction rate was shown in Fig. 5. It was clearly seen that the rate exhibited a linear increase with increase of the initiator concentration in a certain domains. This could be explained that the number of free radicals, formed by the decomposition of the initiators, increased along with the increasing of the initiator concentration, and further increased the grafting rate. In water phase, the initiator concentration at PP was domain in diffusion and adsorption, the mass transfer rate was an order function of substance concentration, and therefore, the above results were obtained.

Figures 6, 7 showed the influences of monomer concentrations on rate. The similar trends were obtained, due to the rate was governed by the monomer number diffusing throughout the reaction medium and reaching the PP backbones, so the higher initial monomer concentrations increased the probability that MAH and St reacted with PP macroradicals to graft. Besides, monomer acted as a trap for radicals [29], the existence of St could improve the rate due to that its ability supplied electron trapped radicals on the PP backbone as rapidly as possible.

Figure 8 showed the relationship between the rate and temperature, it was found that Arrhenius equation could express the relationship well. From the above analysis, the model was obtained, $R_g = A\,\exp(-E_a/RT)$ [BPO] [MAH] [St]. With the help of reaction kinetics model, grafting polymers of different grafting percent could be obtained.

The model was validated in Fig. 9. With the increase of soaked time, the rate increased to a plateau value described with Langmuir equation. In the process of Langmuir adsorption, the amount of substance at the absorber increased, and then arrived at saturation. The further prolongation of the soaked time was not any useful

Table 2 Results of grafting percent at various conditions and the SD

m(BPO)/m(PP) (%)	Average data	SD	1/*T*	Average data	SD
0.3	12.71	0.16	0.00287	2.47738	0.15
0.5	14.52	0.11	0.00283	2.65395	0.13
0.7	16.33	0.19	0.00279	2.80518	0.09
1.0	18.68	0.13	0.00275	2.92745	0.18

m(MAH)/m(PP) (%)	Average data	SD	*n* (St)/*n* (MAH)	Average data	SD
0.04	3.60	0.075	0.6	6.84	0.15
0.08	7.04	0.20	0.8	9.08	0.13
0.12	10.79	0.13	1	11.58	0.18
0.16	14.39	0.090	1.2	14.27	0.13
0.2	17.17	0.15	1.4	17.15	0.12
0.24	20.33	0.20	1.6	19.07	0.12
0.28	23.91	0.26	1.8	20.78	0.21
0.4	35.64	0.17	2.5	27.75	0.089

Ultrasound time	Average data	Standard deviation
30	14.12	0.09
45	15.61	0.15
60	16.88	0.17
75	18.01	0.13
90	18.63	0.21
105	18.65	0.14
120	18.64	0.19

for rate because of the radical reaction. From these discussions, it was concluded that the model could express the processes of suspension polymerization well and mass transfer between the two phases affect the overall reaction rate.

Conclusion

The PP-g-MAH-St copolymers were successfully synthesized through suspension polymerization. Diffusion and equilibrium adsorption played an important role in suspension phase. During the transport of the components to the reaction sites, the following processes occurred: monomers and other agents transferred from liquid phase to the surface of the PP grains, diffused in the pores and in the amorphous phase of the PP grains and then the grafting polymerization occurred. The corresponding diffusion–adsorption chemical reaction model has proved to be acceptable and mass transfer between the two phases affect the overall reaction rate. In the further work, these processes would be simulated from microcosmic aspect.

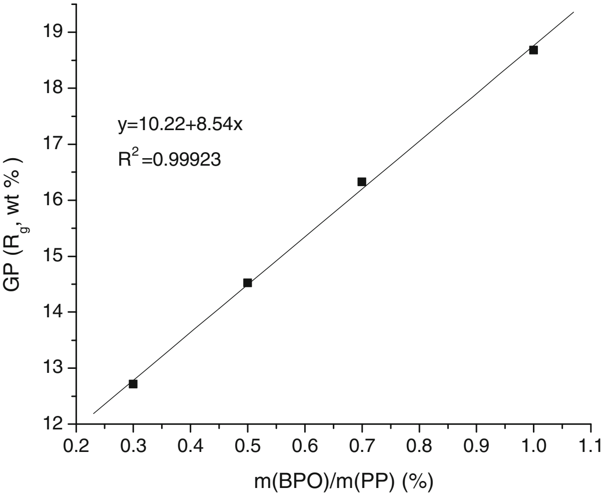

Fig. 5 Effect of BPO concentration on GP (R_g). Amount of PP = 30 g, amount of MAH = 6 g, amount of St = 8.4 g, amount of H_2O = 80 mL, the reactive temperature = 90 °C, the reactive time = 6 h, and the ultrasound time = 1.5 h

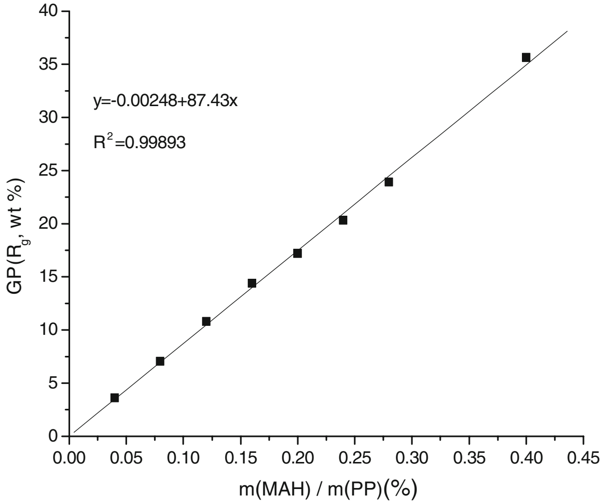

Fig. 6 Effect of MAH concentration on GP (R_g). Amount of PP = 30 g, amount of BPO = 0.3 g, amount of St = 8.4 g, amount of H_2O = 80 mL, the reactive temperature = 90 °C, the reactive time = 6 h, and the ultrasound time = 1.5 h

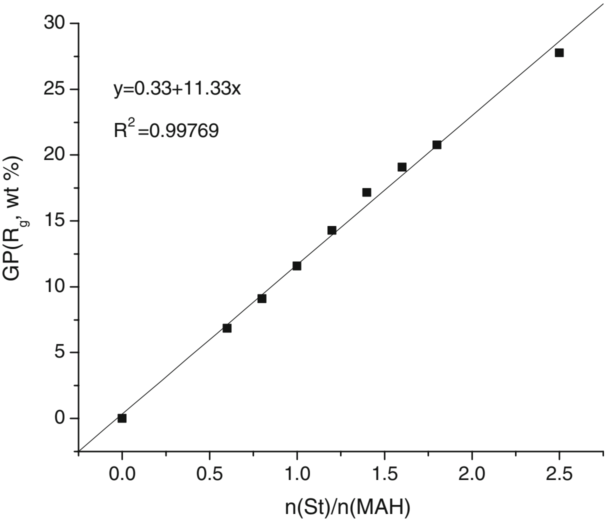

Fig. 7 Effect of St concentration on GP (R_g). Amount of PP = 30 g, amount of MAH = 6 g, amount of BPO = 0.3 g, amount of H_2O = 80 mL, the reactive temperature = 90 °C, the reactive time = 6 h, and the ultrasound time = 1.5 h

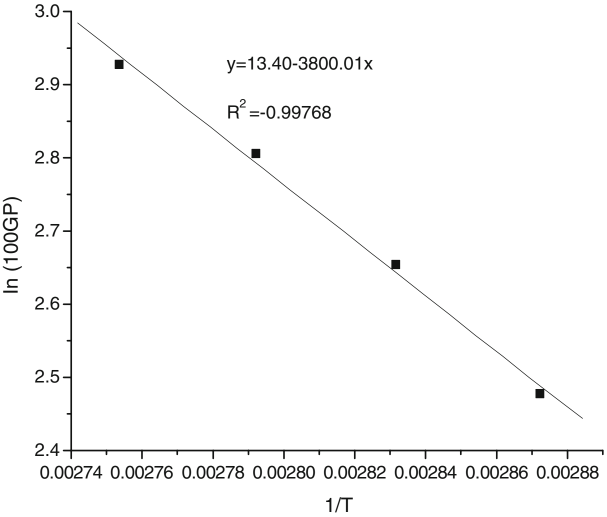

Fig. 8 Effect of reactive temperature on GP (R_g). Amount of PP = 30 g, amount of MAH = 6 g, amount of St = 8.4 g, amount of BPO = 0.3 g, amount of H_2O = 80 mL, the reactive time = 6 h, and the ultrasound time = 1.5 h

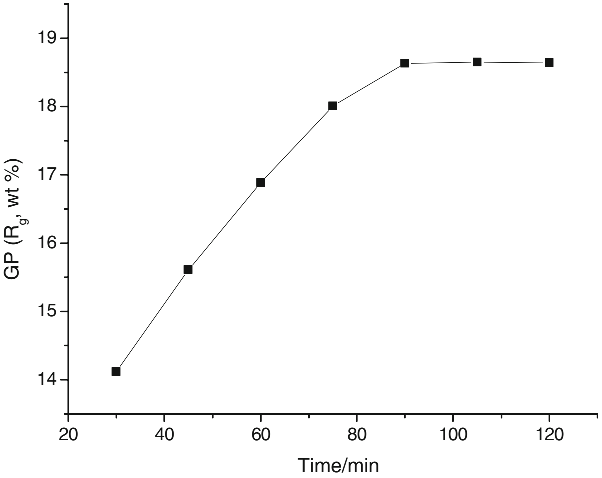

Fig. 9 Effect of ultrasound time on GP (R_g). Amount of PP = 30 g, amount of MAH = 6 g, amount of St = 8.4 g, amount of BPO = 0.3 g, amount of H_2O = 80 mL, the reactive temperature = 90 °C, and the reactive time = 6 h

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