Monte Carlo Simulation of the Grafting of Maleic Anhydride onto Polypropylene at Higher Temperature

Yutian Zhu, Lijia An, and Wei Jiang*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun 130022, People's Republic of China

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ABSTRACT: The graft of maleic anhydride (MAH) onto isotactic polypropylene (iPP) initiated by dicumyl peroxide (DCP) at 190 °C was studied by means of the Monte Carlo method. The ceiling temperature theory, i.e., no possibility for the homopolymerization of MAH to occur at higher temperatures, was used in this study. The simulation results show that most MAH monomers were grafted onto the radical chain ends arising from β scission at a lower MAH concentration, whereas the amount of MAH monomers attached to the tertiary carbons was much larger than that grafted onto the radical chain ends at a higher MAH concentration for various DCP concentrations. This conclusion gives a good interpretation for the disagreement on the grafting sites along a PP chain. Moreover, it was found that the grafting degree increased considerably up to a peak value; thereafter, it decreased continuously with increasing MAH concentration. The peak shifted in the lower MAH concentration direction and became lower and lower with increasing DCP concentration. When the DCP concentration was below 0.1 wt %, the peak was hardly observed. Those results are in good agreement with the experiments. On the other hand, the simulation results show that the average grafting number of MAH monomers on per PP chain maintained almost a linear relationship with chain length for various DCP and MAH concentrations. The quantitative relationship among PP molecular weight, DCP, and MAH concentrations was also obtained in this study.

1. Introduction

Manufacturing high-performance polymers is a main goal for both polymer scientists and engineers. The fabrication of multiphase plastics generally offers a route to combine several good properties of individual polymer components. It can be achieved by mixing two or more than two polymers, leading to the formation of polymer blends or composites.[1−3] The combination of the advantageous properties of polypropylene (PP) with those of polar polymers such as nylon has resulted in the development of available PP/polar polymer blends.[4,5] However, PP and polar polymers are thermodynamically immiscible and phase-separated upon blending due to the poor compatibility. Functionalized PP is thus often used to improve the compatibility between PP and polar polymers. Moreover, functionalized PP has some attractive properties such as chromaticity, adhesive capacity, etc. These distinct properties much extended the application fields of PP. Therefore, the functionalization of PP via grafting unsaturated monomers such as maleic anhydride (MAH), acrylic acid, and so on has received much attention in the past decades.[6−17] Many important results related to this topic have been achieved in the past decades. For instance, it has been concluded that there is no possibility for the homopolymerization of MAH to occur at higher temperatures,[14−16] namely, the ceiling temperature theory. However, it is still difficult to obtain the detail information about the grafting process at the molecular level. The precise mechanism of grafted PP with MAH has not been completely clear up to now. For example, Roover et al.[13] suggested that β-secession should have precedence over the MAH grafting reaction, so the MAH will graft on the end of PP backbone. However, Heinen and coworkers[14] proposed that MAH grafted chiefly onto the backbone due to the abundant tertiary hydrogen atoms in PP chains. This controversy on the grafting sites along PP chain has not been well interpreted so far.

On the other hand, it is known that Monte Carlo simulation has proved to be a powerful tool in the study of both polymer physics and polymer chemistry. This technique has been successfully used to study living free-radical polymerizations,[18] free-radical polymerizations,[19−21] emulsion polymerizations,[22,23] and so on.[24,25] Those simulations have given a greater insight into reactive kinetics, complex molecular processes, gel formation, etc. Recently, Liang et al.[26] have employed the Monte Carlo method to study the kinetics of grafting styrene on to *cis*-1,4-polybutadiene. Their simulation results are in good agreement with the experiments. However, to the best of our knowledge, the grafting of MAH onto PP has not been studied by simulation technique so far.

In the present study, the Monte Carlo technique is employed to study the grafting of MAH onto isotactic PP at a higher temperature. The purpose is to give more detail information about the grafting of MAH onto PP and to try to solve the disagreement on the grafting sites along PP chains.

2. Monte Carlo Simulation

2.1. Modeling. The ceiling temperature theory, i.e., no possibility for the homopolymerization of MAH to occur at a higher temperature, combined with the fact that MAH radicals can only dismutationally terminate was used in this study. Based on refs 6−16, a simplified grafting mechanism is given in Figure 1. From Figure 1, the elementary reactions are given in Scheme 1, where PP, $R^{\bullet}$, and R refer to polypropylene chains, a macroradical, and the product of the termination reaction, respectively.

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* Corresponding author: Tel +86-431-5262151; Fax +86-431-5262126; e-mail wjiang@ciac.jl.cn.

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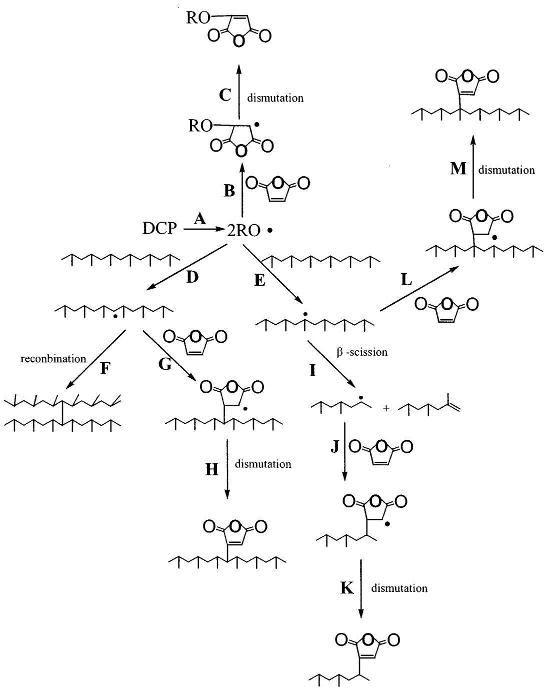
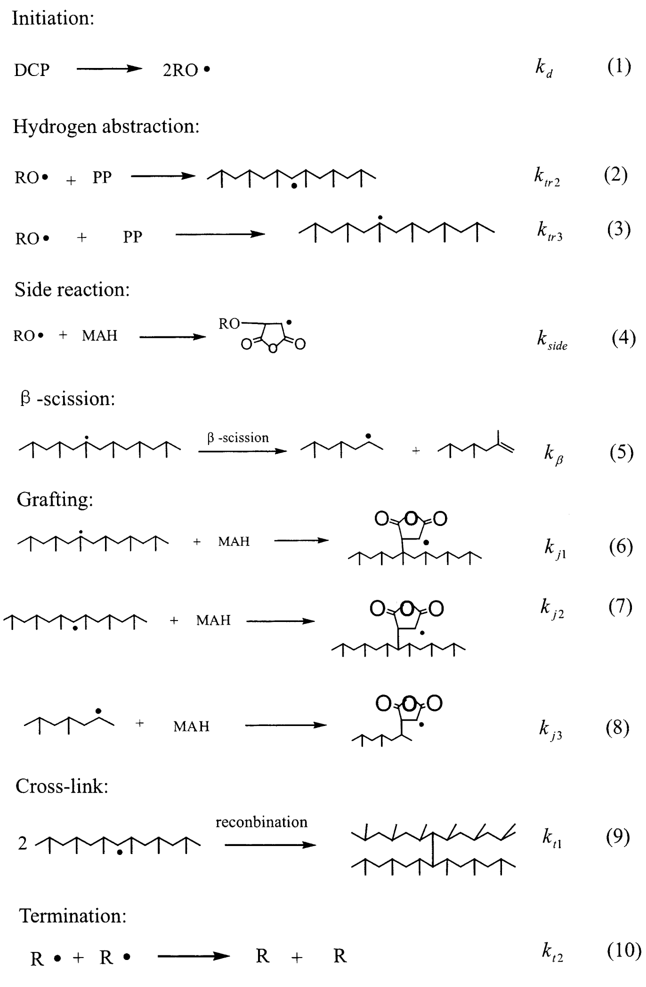


Figure 1. Grafting mechanism of PP-*g*-MAH used in this simulation.

Scheme 1



2.2. Simulation. A total of 10 000 isotactic polypropylene (iPP) chains were initially generated in this simulation. The chain length distribution of 10 000 iPP chains is shown in Figure 2. Their number-average molecular weight (M_n) and weight-average molecular weight (M_w) were 6.5 × 10^4 and 14.1 × 10^4, respectively. The simulated reaction temperature was 190 °C.

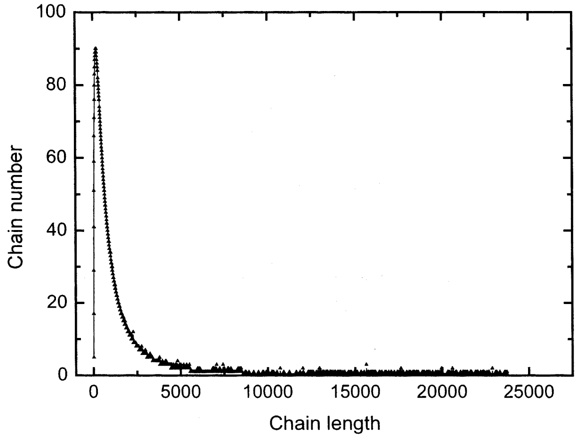


Figure 2. Chain length distribution of the initial 10 000 PP chains.

The principle for the simulation of PP-*g*-MAH was based on Gillespie's algorithm.[27] It was supposed that the reaction system with volume V was spatially homogeneous. As microscopic elementary reaction occurred discretely and stochastically through M reaction channels, the kind of the reaction that took place in a time interval (t, $t + \tau$) could be determined by the uniformly distributed random number in a unit interval, r_1, according to the following relationship:

$$\sum_{\nu=1}^{\mu-1} P_\nu < r_1 \le \sum_{\nu=1}^{\mu} P_\nu \tag{11}$$

$$\tau = (1/a_0)\ln(1/r_2) \tag{12}$$

where r_1 and r_2 are two random numbers, μ is the number of the selected reaction channel, p_ν is the reaction rate probability of reaction ν, τ is the time interval between two successive reactions, and a_0 is the sum of reaction rates, i.e., $a_0 = \sum_{\nu=1}^{M} a_\nu$, where a_ν is the rate of the νth reaction and M is the number of the reaction channels. In the present study, the rates from reaction 1 to reaction 10 are listed as follows:

$$a_1 = k_{\mathrm{d}}^{\mathrm{MC}}[\mathrm{DCP}];\quad a_2 = k_{\mathrm{tr2}}^{\mathrm{MC}}[\mathrm{RO}^\bullet][\mathrm{PP}];\quad a_3 = k_{\mathrm{tr3}}^{\mathrm{MC}}[\mathrm{RO}^\bullet][\mathrm{PP}]$$

$$a_4 = k_{\mathrm{side}}^{\mathrm{MC}}[\mathrm{RO}^\bullet][\mathrm{MAH}];\quad a_5 = k_{\beta}^{\mathrm{MC}}[\mathrm{R3}^\bullet];\quad a_6 = k_{j1}^{\mathrm{MC}}[\mathrm{R3}^\bullet][\mathrm{MAH}]$$

$$a_7 = j_{j2}^{\mathrm{MC}}[\mathrm{R2}^\bullet][\mathrm{MAH}];\quad a_8 = k_{j3}^{\mathrm{MC}}[\mathrm{R}\beta 2^\bullet][\mathrm{MAH}];\quad a_9 = 0.5k_{t1}^{\mathrm{MC}}[\mathrm{R2}^\bullet]^2$$

$$a_{10} = 0.5k_{t2}^{\mathrm{MC}}[\mathrm{R}^\bullet]^2 \tag{13}$$

where [RO$^\bullet$] means the concentration of the radicals dissociated from DCP. [R3$^\bullet$] and [R2$^\bullet$] are the concentrations for the tertiary and the secondary radicals of PP. [Rβ2$^\bullet$] is the concentration of secondary radicals produced in β-scission (reaction 5). [R$^\bullet$] is the total radical concentration in this simulation. From the definition of a_0, it is known that $a_0 = a_1 + a_2 + a_3 + a_4 + a_5 + a_6 + a_7 + a_8 + a_9 + a_{10}$ in this study.

Table 1. Rate Constants Used in the Simulation

k_d (s^{-1})	4.9×10^{-2}	k_{j1} ($L\ mol^{-1}\ s^{-1}$)	1.09×10^4
k_{tr2} ($L\ mol^{-1}\ s^{-1}$)	5.7×10^6	k_{j2} ($L\ mol^{-1}\ s^{-1}$)	1.09×10^4
k_{tr3} ($L\ mol^{-1}\ s^{-1}$)	2.7×10^7	k_{j3} ($L\ mol^{-1}\ s^{-1}$)	1.09×10^4
k_{side} ($L\ mol^{-1}\ s^{-1}$)	2.85×10^6	k_{t1} ($L\ mol^{-1}\ s^{-1}$)	1.99×10^8
k_β (s^{-1})	3000	k_{t1} ($L\ mol^{-1}\ s^{-1}$)	1.99×10^8

As the microscopic elementary reactions occurred in the simulation, the kind of the reaction that took place in a time interval (t, $t + \tau$) could be determined by the probability of each reaction. The following relationship can be obtained:

$$P_v = a_v/a_0 \tag{14}$$

where P_v refers to the νth reaction possibility in the 10 reactions given above. Obviously, the probability given in eq 14 satisfies the normalization condition.

The Monte Carlo rate constant, K^{MC}, is microscopic and can be transformed into the macroscopic experimental constant, K^{exp}, according to the following relationships:

$$K^{MC} = K^{exp} \text{(for first-order reactions)} \tag{15}$$

$$K^{MC} = \frac{K^{exp}}{VN_A} \text{(for second-order reactions)} \tag{16}$$

where N_A is the Avogadro constant and V is the total volume of the system.

The macroscopic rate constants for various reactions are listed in Table 1. Some of them were obtained from the calculation based on the corresponding rate constants at lower temperatures and activation energies, and some of them were obtained by comparing the rate constants with those of similar reactions, whereas some of them had to be reasonably assumed due to the lack of relative information. For k_d, the initiator dissociation constant, a value of 1.05×10^{-4} s^{-1} at 130 °C with the activation energy of 159 kJ mol^{-1} was reported for DCP in ref 28. Using the Arrhenius equation, a value of 4.9×10^{-2} s^{-1} was obtained for k_d at 190 °C. With regard to the hydrogen abstraction constants, it was reported that the value[29,30] of k_{tr3} at 300 K was 2.7×10^5 L mol^{-1} s^{-1}, but no experimental datum of the activation energy could be referenced. However, it was reported that the reactivity ratio among primary, secondary, and tertiary C−H bonds was about 1:12:44 for the *tert*-butoxy radical.[31] Therefore, we neglected the primary C−H bond hydrogen abstraction and calculated the value of k_{tr2} at 300 K to be 5.7×10^4 L mol^{-1} s^{-1}. In this study, we assumed that the values of k_{tr2} and k_{tr3} at 190 °C were 100 times those of them at 300 K. So we obtained that the values of k_{tr2} and k_{tr3} were 5.7×10^6 L mol^{-1} s^{-1} and 2.7×10^7 L mol^{-1} s^{-1}, respectively. There has been no experimental data reported for the grafting rate constants k_{j1}, k_{j2}, k_{j3} and the termination rate constant k_{t2} in the process of PP-*g*-MAH. Therefore, we have to reference the values[28] for the ethylene reaction with polyethylene at 190 °C. It is approximately assumed that the grafting rate constants (k_{j1}, k_{j2}, k_{j3}) are of the same value of 1.09×10^4 L mol^{-1} s^{-1} and k_{t1} and k_{t2} are of the same value of 1.99×10^8 L mol^{-1} s^{-1} in this study. For k_{side} and k_β, no precise values of k_{side} and k_β can be found. The β-scission is an intramolecular reaction and seems to be predominant at higher temperatures in the presence of the organic peroxide.[32−35] As the β-scission reaction is a first-order reaction, a small rate constant means a quick microscopic reaction. In this simulation we assumed that k_β was 3000 s^{-1} and k_{side} was 2.85×10^6 L mol^{-1} s^{-1}. In the following section, it can be found that those values result in a good agreement with the experimental data.

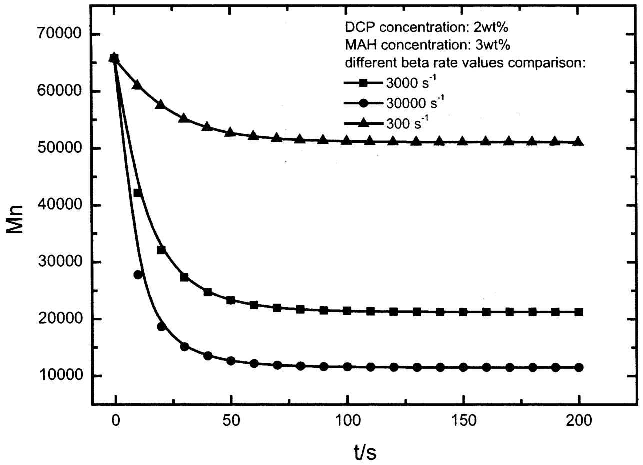


Figure 3. Number-average molecular weight (M_n) of PP with reaction time for various values of β scission.

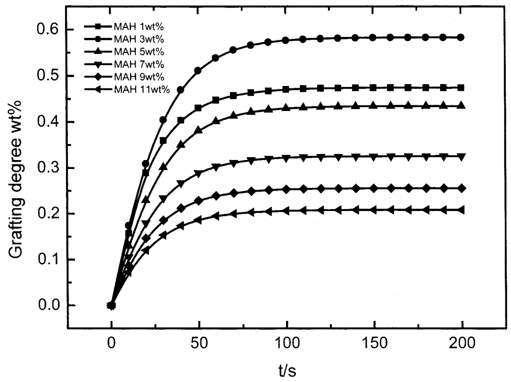


Figure 4. Variations of the grafting degree of MAH with reaction time.

3. Results and Discussion

First, different values ($k_\beta = 300$ s^{-1}, $k_\beta = 3000$ s^{-1}, and $k_\beta = 30\,000$ s^{-1}) were used to evaluate the effect of the value of k_β on the M_n of PP. From Figure 3, it is known that the M_n of PP at 2 wt % DCP and 3 wt % MAH concentrations is considerably high if $k_\beta = 300$ s^{-1}. However, the M_n of PP at the same DCP and MAH concentrations is extremely low if $k_\beta = 30\,000$ s^{-1}. Those results from $k_\beta = 300$ s^{-1} and $k_\beta = 30\,000$ s^{-1} much deviated from the experimental data,[16] whereas the result from $k_\beta = 3000$ s^{-1} did not. Therefore, we set $k_\beta = 3000$ s^{-1} in this study (see Table 1). A similar method was employed to assume the value of k_{side}.

Figure 4 and Figure 5 show the variations of the grafting degree of MAH and number-average molecular weight of PP with reaction time for 2 wt % DCP concentration, respectively. The grafting degree of MAH is defined as W_{MAH}/W_{total}, where W_{MAH} is the weight of grafted MAH and W_{total} is the total weight of PP and grafted MAH. From Figure 4 it is seen that the grafting degree of MAH increases considerably with increasing reaction time up to about 100 s; thereafter, it almost remains unchanged with increasing reaction time. Those results are in agreement with the experiment of Jaehyug et al.,[36] in which the grafting degree of MAH

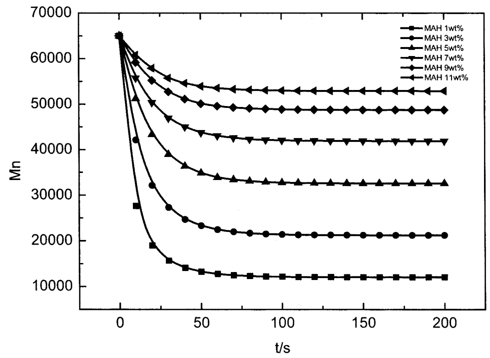


Figure 5. Number-average molecular weight (M_n) of PP with reaction time.

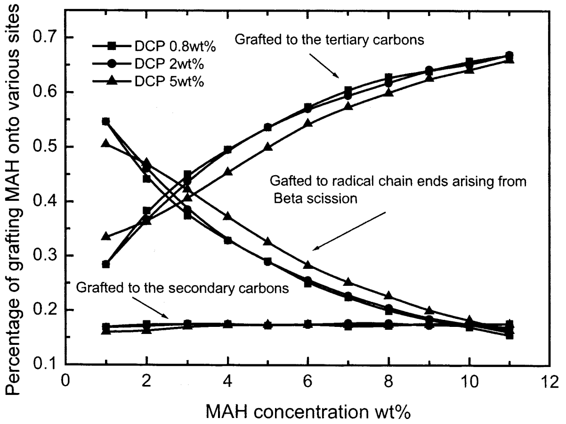


Figure 6. Variation of the percentage of grafting MAH onto various sites with the concentration of MAH.

reached to a flat value after 2 min for melt grafting of MAH onto PP. This agreement implies that the rate values used in the study (Table 1) are reasonable. On the other hand, the M_n of PP decreases markedly with increasing reaction time up to about 100 s; thereafter, it almost remains unchanged with increasing reaction time (Figure 5). The results of both Figure 4 and Figure 5 suggest that the chemical reactions for the grafting at higher temperatures almost terminate at 100 s if the thermal degradation is neglected. Therefore, all the discussion below is for the results at 200 s in order to make it sure that the reactions have been completed.

In general, it is known that MAH monomers can be grafted onto the three sites of a PP chain, i.e., the secondary carbons, the tertiary carbons, and the radical chain ends arising from β scission as shown in Figure 1. The percentages of grafting MAH onto various sites are shown in Figure 6. As expected, the percentage of grafting MAH onto the secondary carbons is the lowest one (about 17%) and almost remains unchanged with the change of DCP and MAH concentrations. However, the percentage of grafting MAH onto the tertiary carbons increases considerably with increasing MAH concentration for various DCP fractions. Contrarily, the percentage of grafting MAH onto the radical chain ends arising from β scission decreases with increasing MAH concentration. Those simulation results give a well interpretation for the controversy on the grafting sites along a PP chain. In the experiment of Heinen et al.,[14] the MAH concentration used was 5 wt %, under which it was known that the most MAH monomers were grafted onto the tertiary carbons from Figure 6. However, most MAH concentrations used were less than 1 wt % in the experiment of Roover et al.[13] Consequently, it leads to that the amount of MAH monomers attached onto the radical chain ends arising from β scission is higher than that of those attached onto the tertiary carbons.

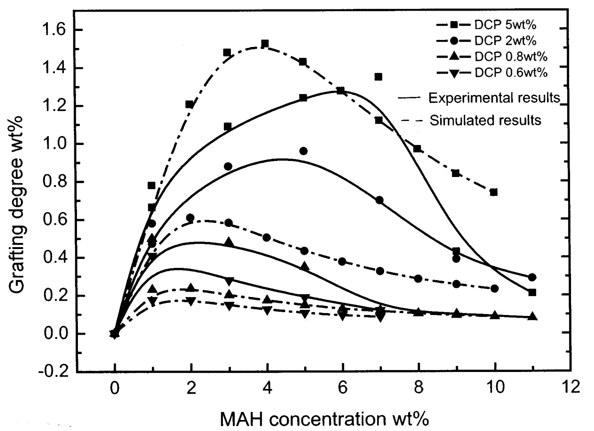


Figure 7. Variation of the grafting degree of MAH onto PP with MAH concentration.

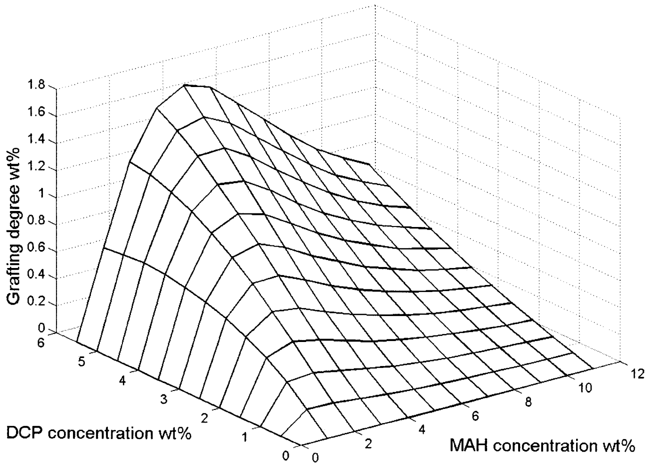


Figure 8. Three-dimensional diagram showing the relationship among grafting degree and MAH and DCP concentrations.

Figure 7 shows the variation of the grafting degree of MAH onto PP chain with the change of MAH concentration for some typical DCP concentrations. For the purpose of comparison, the experimental data by Shi and Yin et al. were also plotted in Figure 7. It is found from Figure 7 that the grafting degree increases considerably up to a peak value; thereafter, it drops continuously with increasing MAH concentration. The peak shifts in the lower MAH concentration direction with decreasing DCP concentration. However, this grafting degree peak becomes lower and lower with decreasing DCP concentration. Those results are in agreement with the experiment by Shi and Yin et al.[16] Furthermore, MAH and DCP concentrations' dependence of the grafting degree in a wider range is shown in Figure 8. The results show that the grafting degree peak cannot be obviously observed anymore when the DCP concentration is below 0.5 wt %. Similar results were observed in the melt grafting of MAH onto a PP chain.[37,38]

Figure 9a–c shows the variation of grafting number of MAH monomers onto PP chains with the chain length at 2 wt % DCP concentration. It is found from Figure 9 that the grafting number of MAH monomers onto the longer chains increases markedly with increasing MAH

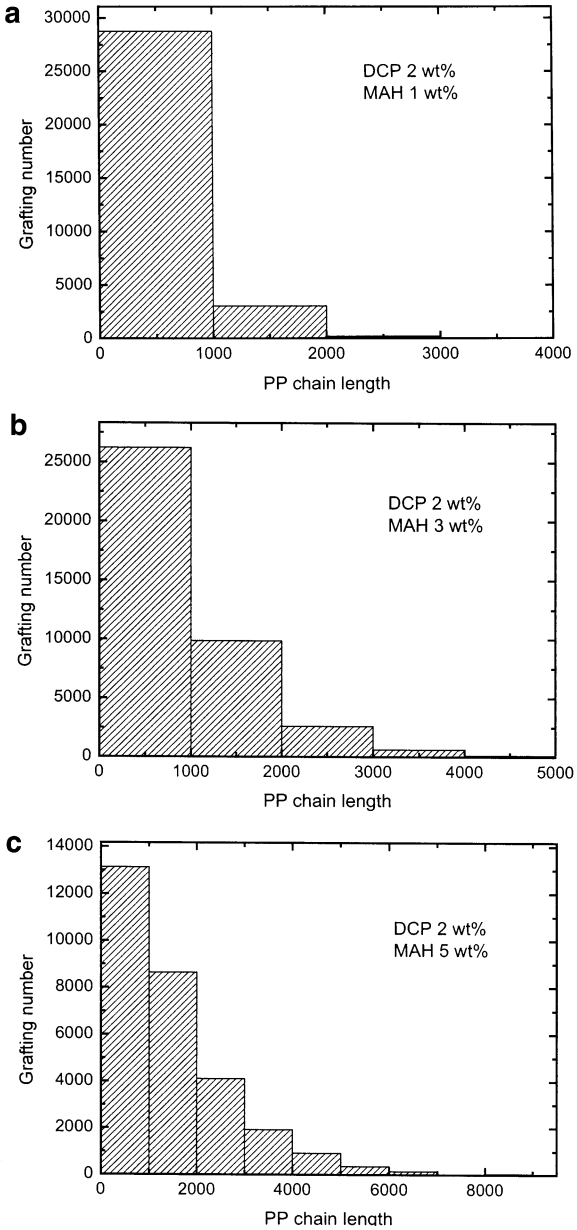


Figure 9. Variation of grafting number of MAH monomers with PP chain length at 2 wt % DCP concentration.

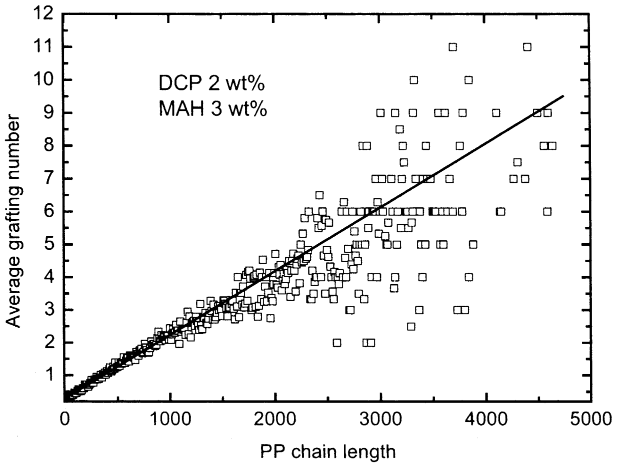


Figure 10. Variation of average grafting number of MAH monomer on each PP chain with chain length.

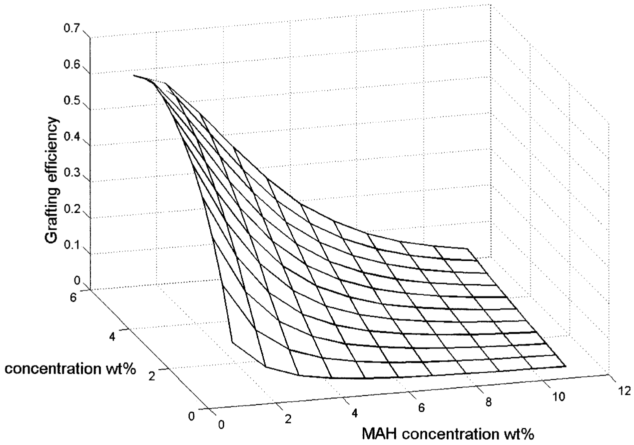


Figure 11. Three-dimensional diagram showing the relationship among the grafting efficiency and the concentrations of DCP and MAH.

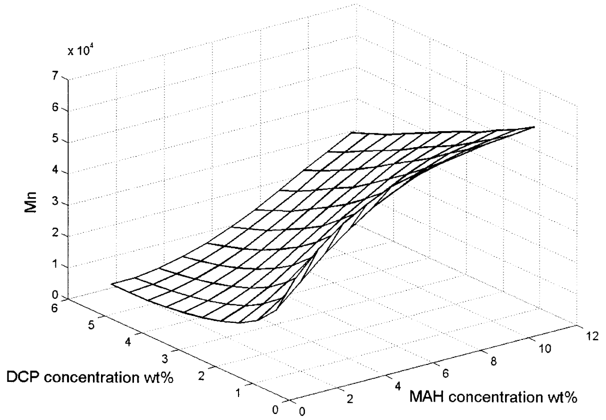


Figure 12. Variation of the number-average molecular weight (M_n) of PP with the concentrations of DCP and MAH.

concentration. Although the grafting number of MAH monomers onto the longer chains is obviously less than that on the shorter chains due to the degradation of PP, the average grafting number of MAH per chain increases continuously with increasing PP chain length as shown in Figure 10. Their correlation can be approximately considered as a linear relationship.

Besides grafting degree, grafting efficiency is another important character generally used. Figure 11 is a three-dimensional diagram showing the relationship among the grafting efficiency and the concentrations of DCP and MAH. The definition of grafting efficiency is the ratio of the weight of grafted MAH to the total weight of MAH used. From Figure 11, it is known that a lower MAH concentration and a higher DCP concentration both result in a higher grafting efficiency. However, the result leads to a lower grafting degree (see Figure 8) and a serious degradation of PP as seen below.

It is generally known that the introduction of DCP can lead to the degradation of PP at higher temperatures. Figure 12 shows the variation of the number-average molecular weight of PP with the change of the concentrations of DCP and MAH. As known, the PP degrades considerably with increasing DCP concentration. Moreover, the results imply that the concentration of MAH is also a key factor that dominates the M_n of PP. Higher concentration of MAH can stop PP from its serious chemical decomposition. In addition, Figure 13 shows the molecular weight distribution of PP for

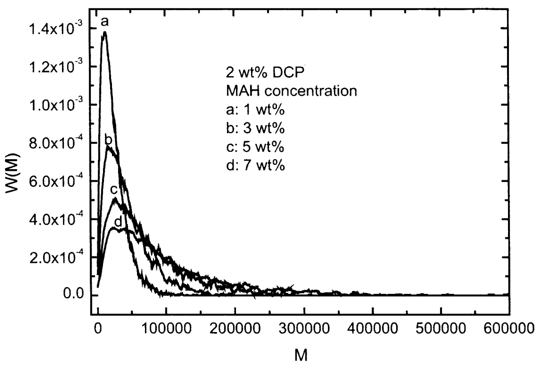


Figure 13. Effect of MAH concentration on the molecular weight distribution of PP for 2 wt % DCP concentration.

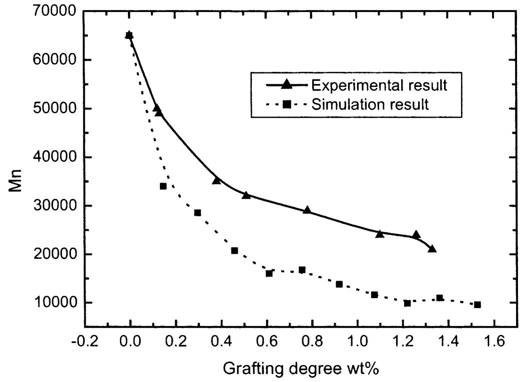


Figure 14. Variation of PP number-average molecular weight with the maximum grafting degree of MAH.

various MAH contents at 2 wt % DCP concentration. The results indicate that the molecular weight distribution becomes wider and wider with increasing the concentration of MAH, and the peak of the distribution shifts in the higher molecular weight direction.

Finally, Figure 14 gives the variation of PP number-average molecular weight with the change of the maximum grafting degree of MAH. For the purpose of comparison, the experimental data by Shi and Yin et al.[16] are also plotted in Figure 14. It is found from Figure 14 that the experimental data are somewhat higher than those of the simulation. However, both of them show that the M_n drops considerably with increasing the grafting degree up to about 0.5 wt %; thereafter, it decreases slowly.

4. Conclusions

Monte Carlo simulation was successfully used to study the grafting of maleic anhydride (MAH) onto isotactic polypropylene initiated by dicumyl peroxide (DCP) at a higher temperature. As a main result, it was concluded that most MAHs monomers were grafted onto the radical chain ends arising from β scission at a lower MAH concentration, whereas the amount of MAH monomers attached to the tertiary carbons was much larger than that grafted onto the radical chain ends at a higher MAH concentration for various DCP weight fractions. This conclusion well interprets the disagreement for the MAH grafted on the PP chain sites along a PP chain. In addition, the simulation results indicated that the grafting degree increased considerably up to a peak value; thereafter, it decreased continuously with increasing MAH concentration. The peak shifted in the lower MAH concentration direction with decreasing DCP concentration. Furthermore, the results show that the average grafting number of MAH on per PP chain remained almost a linear relationship with the chain length for various DCP and MAH concentrations. On the other hand, it was obtained that the molecular weight of PP dropped sharply with decreasing the concentration of MAH, and the molecular weight distribution became wider and wider with increasing the concentration of MAH.

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