# Mathematical Modeling of the Grafting of Maleic Anhydride onto Polypropylene

*Reinaldo Giudici*

**Summary:** A kinetic model for the free radical grafting of maleic anhydride (MAH) onto polypropylene (PP) was developed. The model is able to predict the effect of MAH and initiator concentrations on the grafting degree as well as the changes in the polymer molecular weight distribution during the grafting process. Simulation results are validated by comparison with data from different sources, showing that the model is able to represent reasonably the main trends of the experimentally measured variables both in batch (internal mixer, static film) and in continuous processing (twin-screw extruder), under different conditions. Model predictions are also compared well with a Monte Carlo simulation previously presented in the literature for the same process.

**Keywords:** grafting; kinetic model; maleic anhydride; modeling; polypropylene

## Introduction

The functionalization of polypropylene (PP) with polar monomers such as maleic anhydride (MAH) by reactive extrusion has received much attention in the past decades. By this method, some properties of PP such as polarity, chromaticity, adhesion with metal, glass or ceramic, and compatibility with polyamides and polyesters could be greatly improved.[1]

Maleation of PP involves grafting of MAH onto polypropylene in the presence of organic peroxides whose decomposition acts as a source of free radicals. This process has been studied experimentally under high temperatures (molten polymer) in batch (torque rheometer, ampoules, films, etc.) and continuous reactors (single-screw and twin-screw extruders, mini-extruders). There are also some studies of grafting in solution. Whatever the case, free radical initiated grafting of PP is accompanied by scission reactions, thus changing the molecular weight distribution and the rheological characteristics of the polymer. Given the number of different variables involved, e.g., peroxide type and concentration, MAH concentration, reaction time, temperature, rotation speed, sequence of reactant feedings, presence of stabilizers, etc., and their interactions, it is difficult to to find the optimal conditions for this process.[2]

Bettini and Agnelli[2,3] studied the maleation of PP in a torque rheometer by changing MAH and peroxide concentration, rotation speed and reaction time according to a factorial design of experiments. They measured the amount of grafted MAH and the melt index of the polymer, and analyzed the results in terms of a surface response empirical model. Martinez et al.[4,5] studied the process both in melt and in solution (in xylene) according to a Box-Wilson type expanded factorial design, changing MAH and peroxide concentrations and reaction time. The results for degree of grafting were analyzed by surface response methodology. Machado et al.[6,7] studied the process in a continuous twin-screw extruder and measured the degree of grafting and dynamic viscosity for samples taken along the extruder. Shi et al.[8] measured grafting degree and MWD of PP maleated in a twin-screw

---

Universidade de São Paulo, Escola Politécnica, Depto. de Engenharia Química, PO Box 61548, CEP 05424-900, São Paulo, SP, Brasil
Fax: (55+11)38132380; E-mail: rgiudici@usp.br

extruder. They also tried to characterize the chemical structures found in the grafted polymer by electrospray ionization-mass spectrometer (ESI-MS) and used this information to propose a tentative mechanism for the process. Heine et al.[9] used C13-NMR to characterize different polyolefins grafted with MAH, and discussed possible mechanism steps to explain the observed structures. Trolez et al.[10] analyzed experimental data of grafting of MAH onto PP showing that the number of grafted chains are higher than the number of radicals generated by peroxide decomposition, that would be an evidence of the occurrence of chain transfer reactions between grafted radicals and polymer molecules. Severini et al.[11] studied grafting of MAH in vapor phase onto PP films and measured polymer MWD and characterized the chemical structures by infrared spectroscopy (IR-ATR). Almost all previously cited work discussed the possible steps involved in the grafting mechanism in order to explain the experimental observations.[2,3,6–11] In general, the occurrence of the following reaction steps is admitted: initiator decomposition, hydrogen abstraction, beta-scission of the radicals generated by hydrogen abstraction, reaction of MAH with the radical, chain transfer to polymer molecules. It is also well accepted that there is no possibility for the homopolymerization of MAH to occur at higher temperatures, due to the ceiling temperature (i.e., MAH propagation is thermodynamically disfavored at high temperatures). Furthermore, it is well known the strong tendency of the PP radicals generated by H-abstraction undergo beta-scission, thus reducing the molecular weight (as in the process to produce controlled rheology PP).

On the other hand, there are also some controversial issues. Bettini and Agnelli[2] performed comparative experiments with and without adding MAH under similar conditions and observed higher melt indexes (i.e., lower molecular weights) in the samples processed in the presence of MAH. Similarly, Machado et al.[7] observed stronger decreases in dynamic viscosity for maleated PP than for PP processed with only peroxide, again indicating the synergistic effect of MAH grafting and scission. On the other way, Severini et al.[11] observed higher degree of degradation in PP processed without MAH. Ho et al.[12] found out that at low concentrations of MAH and initiator (dicumil peroxide, DCP), the presence of MAH could enhance the degradadtion of PP during processing, but the PP degradation can be also reduced at higher MAH concentrations. These differences have been ascribed to the differences in processing conditions.

Although several works have discussed the possible reactions of the mechanism of MAH grafing onto PP, that could qualitatively explain the experimental observations, there are comparatively few published works regarding the modeling and simulation of this process focused in a quantitative, rather than only qualitative, interpretation of the results. Cha and White.[13] presented a kinetic scheme in which the following steps are considered: (a) initiator decomposition; (b) hydrogen abstraction from both ungrafted and grafted polymer chains; (c) grafting of MAH; (d) reaction of polymeric radicals with impurities; (e) termination between polymeric radicals. This kinetic scheme, however, is not able to explain the occurrence of a maximum in the degree of grafting as a function of MAH concentration for a given peroxide concentration, as observed experimentally. In addition, scission step (responsible for the decreasing in the polymer molecular weight) is not considered in this scheme, although also observed experimentally.

A more comprehensive kinetic scheme and simulation model was proposed in the work by Zhu et al.[1] They considered the following steps: (1) peroxide decomposition forming primary radicals; (2) hydrogen abstraction by the primary radical from either tertiary or secondary carbon of PP, given tertiary and secondary backbone radicals, respectively; (3) consumption of MAH by side reaction with primary radicals; (4) beta-scission of tertiary radicals, forming chain-end radicals; (5) grafting of MAH onto tertiary, secondary, and chain-end radicals; (6) termination by combination of two secondary radicals, forming crosslinkings; (7) termination by disproportionation between any two radicals. They simulated the grafting process using a Monte Carlo algorithm in which a large number of initial polymer chains (10,000) is considered, and the occurrence of the different reaction events is decided by comparing randomly generated numbers and the probability of each reaction based on the rate constants and concentrations. Their simulation results were successfully compared with the experimental data of isotactic PP maleation reported by Shi et al.[8]

Monte Carlo simulation, such as that used in the work of Zhu et al.,[1] is a powerful simulation tool that is able to predict the individual structure of each polymer chain, but at a cost of much larger computational effort than that of a deterministic simulation. For computationally more intensive applications, such as those required in process optimization and control, deterministic models based on solving mass balance equations are definitely preferred. The present work aims at presenting a deterministic simulation model for the grafting of MAH onto PP that is able to correctly represent the trends of the main process variables and to provide meaningful quantitative predictions. The kinetic scheme considered is similar (but not exactly equal) to that used in Zhu et al.[1] and other previously published works. The model results are validated by comparison of experimental data from different authors.

## Model Development

The following reaction steps are considered in the mechanism:

(1) Initiator (peroxide) decomposition, forming primary radicals (initiator fragments)

$$I \xrightarrow{k_d} (2f)R_o^\bullet \tag{i}$$

(2) Hydrogen abstraction (chain transfer to polymer), forming backbone radicals:

$$R_0^\bullet + P_s \xrightarrow{k_{fp,0}} S + R_r^{b\bullet} \tag{ii}$$

$$R_r^{b\bullet} + P_s \xrightarrow{k_{fp}} P_r + R_r^{b\bullet} \tag{iii}$$

$$R_r^{e\bullet} + P_s \xrightarrow{k_{fp}} P_r + R_r^{b\bullet} \tag{iv}$$

(3) Beta-scission of backbone radicals, forming a dead chain and a chain-end radical:

$$R_r^{b\bullet} \xrightarrow{k_{cs}} R_s^{e\bullet} + P_{r-s} \tag{v}$$

(4) Grafting of maleic anhydride (A), forming grafted radicals:

$$R_o^\bullet + A \xrightarrow{k_{a,0}} R_o^{A\bullet} \tag{vi}$$

$$R_r^{b\bullet} + A \xrightarrow{k_a} R_r^{Ab\bullet} \tag{vii}$$

$$R_r^{e\bullet} + A \xrightarrow{k_a} R_r^{Ae\bullet} \tag{viii}$$

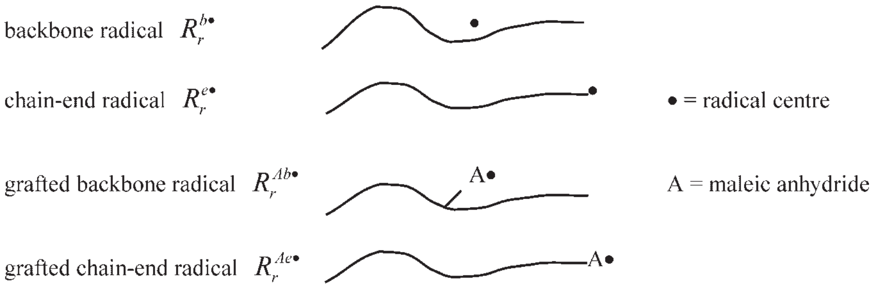

***Figure 1.***
Pictorial representation of radical types.[14]

(5) Chain transfer of the grafted radicals to polymer chains:

$$\begin{pmatrix} R_o^{A\bullet} \\ R_r^{Ab\bullet} \\ R_r^{Ae\bullet} \end{pmatrix} + P_s \xrightarrow{k_{fp'}} \begin{pmatrix} S \\ P_r \end{pmatrix} + R_r^b \tag{ix}$$

(6) Termination between two radicals of any type:

$$\begin{pmatrix} R_o^{\bullet} \\ R_r^{b\bullet} \\ R_r^{e\bullet} \\ R_o^{A\bullet} \\ R_r^{Ab\bullet} \\ R_r^{Ae\bullet} \end{pmatrix} + \begin{pmatrix} R_o^{\bullet} & R_s^{b\bullet} & R_s^{e\bullet} & R_o^{A\bullet} & R_s^{Ab\bullet} & R_s^{Ae\bullet} \end{pmatrix} \xrightarrow{k_t} \begin{pmatrix} S \\ P_r + P_s \\ P_{r+s} \end{pmatrix} \tag{x}$$

The notation adopted and the main steps of this kinetic scheme are most based on the work of Hamielec et al.[14,15] Figure 1 shows a pictorial representation of the different polymeric radical types considered.

Differently from the work of Zhu et al.,[1] the proposed model does not distinguish between hydrogen abstraction in secondary and tertiary carbon of a PP chain. This consideration allows for some model simplification and was adopted because these events does not strongly affect the MWD and the grafting degree. Considering this kinetic scheme, and taking into account the pseudo-steady-state hypothesis for all free radical species, the following mole balances for a batch reactor can be written:

initiator $$\frac{dI}{dt} = -k_d I \tag{1}$$

free MAH

$$\frac{dA}{dt} = -k_{a,0} A R_o - k_a A (Y_{0e} + Y_{0b}) \tag{2}$$

grafted MAH

$$\frac{dA_g}{dt} = +k_a A (Y_{0e} + Y_{0b}) \tag{3}$$

$$\begin{aligned} 0 &= \frac{dR_o}{dt} \\ &= +2fk_d I - k_{fp,0} Q_1 R_o - k_a A R_o \\ &\quad - k_t R_o R_{tot} \end{aligned} \tag{4}$$

$$\begin{aligned} 0 &= \frac{dR_r^b}{dt} \\ &= .k_{fp,0} R_o r P_r + k_{fp} Y_{0b} r P_r + k_{fp} Y_{0e} r P_r \\ &\quad + k_{fp'} r P_r (R_{Ao} + Y_{0Ab} + Y_{0Ae}) \\ &\quad - k_{fp} R_r^b Q_1 - k_{cs} R_r^b - k_a A R_r^b - k_t R_r^b R_{tot} \end{aligned} \tag{5}$$

$$\begin{aligned} 0 &= \frac{dR_r^e}{dt} \\ &= +k_{cs} \sum_{s=r+1}^{\infty} \frac{R_s^b}{s} - k_{fp} R_r^e Q_1 - k_a A R_r^e \\ &\quad - k_t R_r^e R_{tot} \end{aligned} \tag{6}$$

$$\begin{aligned} 0 &= \frac{dR_{Ao}}{dt} \\ &= +k_{a,0} A R_{Ao} - k_{fp'} Q_1 R_{Ao} \\ &\quad - k_t R_{Ao} R_{tot} \end{aligned} \tag{7}$$

$$\begin{aligned} 0 &= \frac{dR_r^{Ab}}{dt} \\ &= +k_a A R_r^b - k_{fp'} Q_1 R_r^{Ab} \\ &\quad - k_t R_r^{Ab} R_{tot} \end{aligned} \tag{8}$$

$$\begin{aligned} 0 &= \frac{dR_r^{Ae}}{dt} \\ &= +k_a A R_r^e - k_{fp'} Q_1 R_r^{Ae} - k_t R_r^{Ae} R_{tot} \end{aligned} \tag{9}$$

$$\begin{aligned} \frac{dP_r}{dt} &= -k_{fp,0} R_o r P_r - k_{fp} Y_{0b} r P_r - k_{fp} Y_{0e} r P_r \\ &\quad - k_{fp'} (R_{Ao} + Y_{0Ab} + Y_{0Ae}) r P_r \\ &\quad + k_{cs} \sum_{s=r+1}^{\infty} \frac{R_s^b}{s} + k_{fp} Q_1 (R_r^b + R_r^e) \\ &\quad + k_{fp'} Q_1 (R_r^{Ab} + R_r^{Ae}) + k_t (R_r^b + R_r^e \\ &\quad + R_r^{Ab} + R_r^{Ae}) R_{tot} \end{aligned} \tag{10}$$

where $A_g$ is grafted MAH, A is the free (unreacted) MAH, I is the initiator (peroxide), $Rrk$ is a k-type radical of size r, $Q_1$ is the first moment of polymer chains (=total number of monomeric units in the polymer chains per unit volume of PP) defined by:

$$Q_1 = \sum_{r=1}^{\infty} rP_r \tag{11}$$

Termination by disproportionation (rather than by combination) is assumed in Equation (10). The zero-moment for the different radical types are defined as:

$$Y_{0b} = \sum_{r=1}^{\infty} R_r^b \qquad Y_{0e} = \sum_{r=1}^{\infty} R_r^e$$
$$Y_{0Ab} = \sum_{r=1}^{\infty} R_r^{Ab} \tag{12}$$
$$Y_{0Ae} = \sum_{r=1}^{\infty} R_r^{Ae}$$

and the total radical concentration is

$$R_{tot} = R_o + Y_{0b} + Y_{0e} + R_{Ao} + Y_{0Ab} + Y_{0Ae} \tag{13}$$

Using (12) in Equation (5), (6), (8) and (9), results:

$$0 = \frac{dY_{0b}}{dt} = k_{fp,0}Q_1R_o + k_{fp}Q_1Y_{0e} + k_{fp'}Q_1(R_{Ao} + Y_{0Ab} + Y_{0Ae}) - k_{cs}Y_{0b} - k_aAY_{0b} - k_tY_{0b}R_{tot} \tag{14}$$

$$0 = \frac{dY_{0e}}{dt} = +k_{cs}Y_{0b} - k_{fp}Q_1Y_{0e} - k_aAY_{0e} - k_tY_{0e}R_{tot} \tag{15}$$

$$0 = \frac{dY_{0Ab}}{dt} = +k_aAY_{0b} - k_{fp'}Q_1Y_{0Ab} - k_tY_{0Ab}R_{tot} \tag{16}$$

$$0 = \frac{dY_{0Ae}}{dt} = +k_aAY_{0e} - k_{fp'}Q_1Y_{0Ae} - k_tY_{0Ae}R_{tot} \tag{17}$$

Combining Equation (4), (7), and (14) to (17), the total radical concentration is:

$$R_{tot} = R_o + Y_{0b} + Y_{0e} + R_{Ao} + Y_{0Ab} + Y_{0Ae} = \sqrt{\frac{2fk_dI}{k_t}} \tag{18}$$

The degree of grafting (% wt) is calculated as:

$$\text{grafting degree} = \frac{98A_g}{42Q_1} \tag{19}$$

where 98 and 42 are the molecular weights of MAH and of PP monomeric unit.

In order to calculate the degree of grafting, it suffices to solve the following subset of equations: ordinary differential Equation (1), (2) and (3), and algebraic Equation (4), (7), (14)–(18). A standard fourth-order variable-step Runge-Kutta-Gill method was used to solve numerically the ODE system and the algebraic equations are used to calculate the concentration of the different radical types at each time step.

## Modeling the Molecular Weight Distribution

In order to evaluate the molecular weight distribution of the polymer during the grafting process, it is necessary to solve the balance for the dead polymer species, Equation (10). By combining Equation (5), (6), (8), (9) and (10), results:

$$\frac{dP_r}{dt} = k_{cs}\left(-R_r^b + 2\sum_{s=r+1}^{\infty} \frac{R_s^b}{s}\right) \tag{20}$$

From Equation (5), (14) and (10), the concentration of b-type radicals of size r, $R_r^b$, and the concentration of dead polymer chains of size r, $P_r$ are related by:

$$\frac{R_r^b}{Y_{0b}} = \frac{rP_r}{Q_1} \tag{21}$$

and substituting in (20) gives:

$$\frac{dP_r}{dt} = \frac{k_{cs}Y_{0b}}{Q_1}\left(-rP_r + 2\sum_{s=r+1}^{\infty} P_s\right) \qquad (22)$$

Let one define the degree of scission u by:

$$\frac{du}{dt} = \frac{k_{cs}Y_{0b}}{Q_1} \qquad (23)$$

The degree of scission, u, is the fraction of the initial monomeric units that experienced scission, and is related to the number-average chain length $r_n$ and the initial number-average chain length $r_{no}$ by:

$$u = (1/r_n) - (1/r_{no}) \qquad (24)$$

Equation (25) can be written as:

$$\frac{dP_r}{du} = \left(-rP_r + 2\sum_{s=r+1}^{\infty} P_s\right) \qquad (25)$$

Considering the long chain hypothesis and the continuous variable approximation, one may define the weight fraction of polymer chains with size r, at a degree of scission u, w(r,u) = r $P_r/Q_1$, so that, Equation (28) can be finally rewritten as:

$$\frac{1}{r}\frac{dw(r,u)}{du} = -w(r,u) + 2\int_r^{\infty} \frac{w(s,u)}{s}\,ds \qquad (26)$$

This is the same equation derived by Saito[17,18] for random polymer chain scission by radiation, and also derived by Hamielec et al.[14] and Triacca et al.[19] for visbreaking of polypropylene (free-radical controlled degradation of PP). The analytical solution of this integro-differential equation for a given initial MWD w(r,0) is:[18]

$$w(r,u) = \left\{w(r,0) + ur\int_r^{\infty} \frac{2+u(s-r)}{s}\,w(s,0)\,ds\right\}e^{-ur} \qquad (27)$$

Equation (23) can be solved simultaneously with ODEs (1), (2) and (3) to obtain the degree of scission u at each time. If the initial MWD w(r,0) of the polymer is known, Equation (27) can be used to evaluate the change in MWD during the grafting process and the final MWD. If only the molecular weight averages, rather than the full MWD of the initial polymer, is known, Equation (24) can be used to obtain the number average of the grafted polymer.

Note that the model developed considers the simultaneous occurrence of grafting and scission, and it reduces to the limiting case of pure scission for A = 0 (processing PP with peroxide in the absence of MAH).

## Results and Discussion

In this section the model is tested for a number of different experiments reported in the literature for grafting of MAH onto PP. The values of the kinetic parameters used in the simulations are shown in Table 1, and most of them were obtained by fitting the model results to experimental data from literature[8,13] using least squares criterion and Levenberg-Marquardt optimization method.

### Comparison with Experimental Data Reported by Shi et al.[8]

Shi et al.[8] reported experiments of grafting of MAH onto PP carried out in a corotating twin-screw extruder at 180–190 °C using residence times about 2 minutes, using different amounts of initiator dicumil peroxide (DCP, 0.6–5.0% wt) and maleic anhydride (MAH 0.5–11%wt). Figure 2 presents the comparison of experimental and simulated values of degree of grafting and average molecular weight. An increase in the DCP concentration causes an increase in the grafting degree. The effect of MAH concentration on the grafting degree is complex: for lower values, there is a considerable increase in grafting degree as the amount of MAH increases, up to a peak value; thereafter, it drops continuously with increasing MAH concentration, thus showing an opposite effect. The peak increases for higher DCP concentrations

***Table 1.***
Rate constants used in the simulations.

| Rate constant | Unit | Value (185 °C) | Source | Value (230 °C) | Source |
|---|---|---|---|---|---|
| f | – | 0.6 | adopted | $0.6 \times 2$[a)] | adopted |
| $k_d$ | $s^{-1}$ | $4.9 \times 10^{-2}$ (DCP) | ref. [1] | $6.1 \times 10^{-1}$ (DBHA) | ref. [13] |
| $k_{a,o}$ | $L\ mol^{-1}\ s^{-1}$ | $7.00 \times 10^{+6}$ | NLR | $7.67 \times 10^{+6}$ | NLR |
| $k_a$ | $L\ mol^{-1}\ s^{-1}$ | $2.73 \times 10^{+4}$ | NLR | $2.99 \times 10^{+4}$ | NLR |
| $k_{fp,o}$ | $L\ mol^{-1}\ s^{-1}$ | $2.58 \times 10^{+4}$ | NLR | $3.05 \times 10^{+5}$ | NLR |
| $k_{fp}$ | $L\ mol^{-1}\ s^{-1}$ | $2.58 \times 10^{+3}$ | NLR | $3.05 \times 10^{+5}$ | NLR |
| $k_{cs}$ | $s^{-1}$ | $2.10 \times 10^{+3}$ | NLR | $2.10 \times 10^{+3}$ | NLR |
| $k_{fp'}$ | $L\ mol^{-1}\ s^{-1}$ | 0. | adopted | 0. | adopted |
| $k_t$ | $L\ mol^{-1}\ s^{-1}$ | $1.99 \times 10^{+8}$ | ref. [1] | $2.56 \times 10^{+9}$ | NLR |

DCP = dicumil peroxide DBHA = 2,5-di-methyl-2,5-bis-(t-butylperoxy) hexane;

[a)] DBHA is a bifunctional initiator that contains two peroxide groups per molecule and generates 4 radicals per fragmented initiator molecule. This effect can be account for using an artificially doubled value for the efficiency, or equivalently, by changing the effective stoichiometric coefficient (2f) to (4f) in reaction step (i);

NLR = nonlinear regression (model fitting to experimental data from ref. [8] at 185 °C, Figure 2(a), and from ref. [13] at 230 °C, Figure 4(a)).

and shifts to the higher MAH concentration direction as the DCP concentration is increased. The model is able to represent satisfactorily such complex trends.

Figure 3 presents the joint effects of MAH and DCP concentrations on the degree of grafting and on molecular weight, as three dimensional plots similar to those shown by,[1] showing that the predictions of the present deterministic model are quite similar to those from the Monte Carlo model proposed by Zhu et al.[1] This complex behavior on the effect of MAH concentration can be explained by the mechanism. In terms of the consumption of MAH, reaction steps (vii) and (viii) that are responsible for grafting compete with step (vi) that spends MAH without effectively graft it onto a polymer chain. Besides, steps (vi) and (ii) evidence a competition between MAH and the polymer chains to react with the primary radicals generated

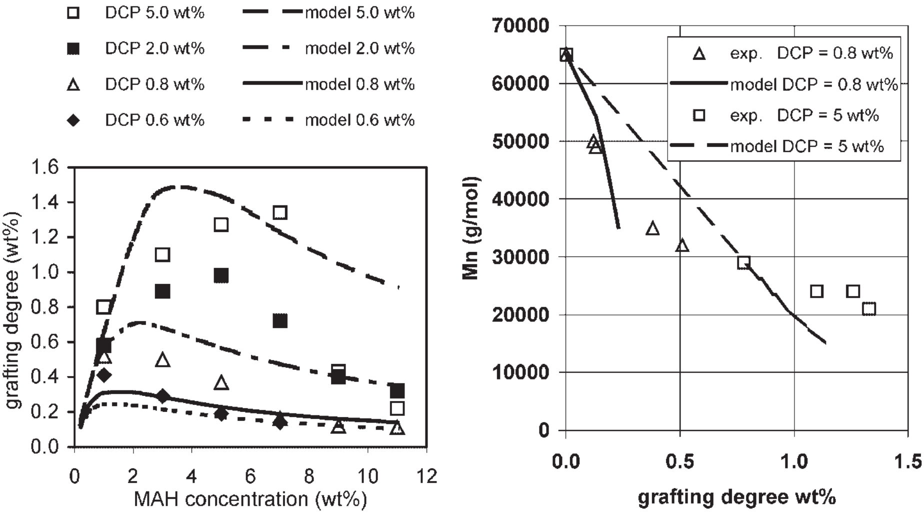

***Figure 2.***
Comparison between model predictions (curves) and experimental data (points) obtained by Shi et al.[8] in co-rotating twin-screw extruder at 180–190 °C, residence time 2 minutes. (a) Effect of initial MAH and DCP concentration in the grafting degree. (b) Number-average molecular weight as a function of grafting degree.

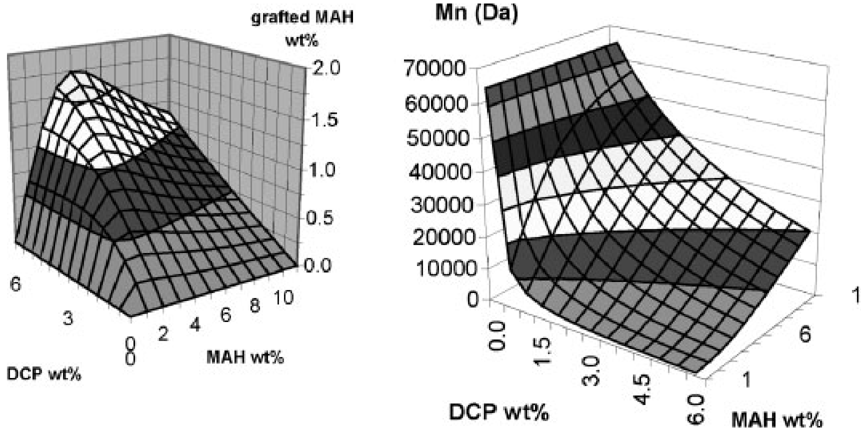

***Figure 3.***
Joint effect of MAH and DCP concentrations on the grafting degree (left) and on the number-average molecular weight (right), as predicted by the proposed model.

by peroxide decomposition. Higher MAH contents favor step (vi) against step (ii), thus reducing the MAH incorporation to the polymer chains; on the other way, for lower MAH concentrations the primary radicals would attack preferentially the polymer chains, increasing the number of polymeric radicals responsible for the grafting reaction. Figure 3 also shows the effect of MAH and DCP concentrations on the number-average molecular weight. In these simulations, an initial polymer with $r_{no} = 65000$ and polydispersity 4.2 was considered, as reported by Shi et al.[8] Under the studied conditions, increasing MAH concentration difficults the occurrence of scission, so that the absence of MAH would favor scission. This reduction in PP degradation caused by the presence of MAH can be interpreted by the mechanism: MAH converts the backbone radicals otherwise prone to scission into a nonscissionable grafted radical (b' type), preventing it from undergo degradation. In this way, grafting is competing with scission process. Figure 2(b) shows the comparison of the model predictions with the experimental data from Shi et al.[8] for number-average molecular weight.

In general, given the similarities between the proposed model and the model presented by Zhu et al.,[1] the quality of the predictions are analogous. Nonetheless, there are some differences in the formulation of these models, not only in some details of the kinetic scheme, but also the simulation approach used (Monte Carlo versus deterministic approch). Monte Carlo simulation such as used by ref. [1] provides more details of individual chain structures, but at a cost of much more demand on computer memory and simulation time. Oppositely, deterministic approach is far more preferred in applications that require repeated simulations, such as optimization and control.

### Comparison with Experimental Data Reported by Cha and White[13]

Cha and White[13] studied grafting of MAH onto PP in both an internal batch mixer (Brabender Plasti-Corder) during 10 minutes and in twin-screw extruder (Japan Steel Works Tex 30), at 230 °C and rotation speed 100 rpm. In the extruder the flow rate was 6 kg/h and the average residence time 185 s. Figure 4(a) presents the experimental results (points) for degree of grafting as a function of initial concentrations of MAH and peroxide (DBHA, 2,5-Di-methyl-2, 5-bis-(t-butylperoxy) hexane, Lupersol 101), for the runs carried out in the internal

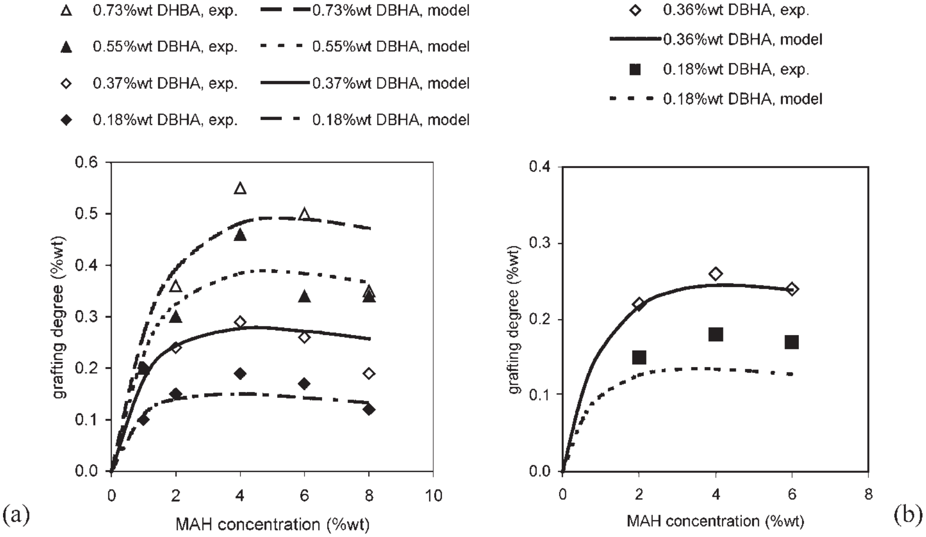

***Figure 4.***

Comparison between model predictions (lines) and experimental data (symbols) from Cha and White[13] obtained in (a) batch internal mixer (230 °C, 100 rpm, batch time 600 s) and obtained in (b) twin-screw extruder (230 °C, 100 rpm, residence time 185 s).

mixer (a) and in twin-screw extruder (b). Simulations results are presented as lines in the same plots. In the model calculations, an ideal plug-flow behavior was assumed for the flow in the extruder, using the residence time in place of the batch time. The model reproduces reasonably the trends of the experimental results, showing the existence of a maximum in these curves. Note that the data of Cha and White[13] were obtained at 230 °C and those of Shi et al.[8] were taken at 185 °C, thus the necessity of using different sets of rate constants, as shown in Table 1.

### Comparison with Experimental Data Reported by Severini et al.[11]

Severini et al.[11] studied the MAH grafting in gaseous phase on to PP films in presence of peroxide at 120 °C. Peroxide was deposited onto the surface of PP films by evaporation of a solution in toluene. These films were put in an oven under nitrogen atmosphere with MAH vapor. MWD curves were measured by gel permeation chromatography (GPC) for the following samples: (1) virgin PP with Mn = 257 000 and Mw = 231 000; (2) PP processed by 30 and 60 minutes using 0.62%wt benzoil peroxide (BPO) and 0.2% wt MAH content; and (3) PP processed by 30 minutes with 0.62%wt benzoil peroxide without MAH. Figure 5(a) shows the comparison between the experimental MWD curves and the corresponding curves simulated using Equation (30) considering the MWD of the virgin PP as the initial distribution. The model correctly predicts the shift of the MWD curves towards the lower molecular weights as a result of the occurrence of scission. However, the quantitative agreement between simulated and experimental MWD curves is not good. This is probably due to a non-perfect mixing of the reactants within the whole polymer film, as the reactants took contact with the film surface, so the diffusion of MAH and BPO into the film may be not complete. The simplest way tho take this segregation into account in the model calculation is to admit that there exist two regions in the processed film: one region that took contact with the reactants and suffered grafting and scission, and another one that did not, so remained as the initial PP. Assuming this simple two-region segregated model, the final MWD of

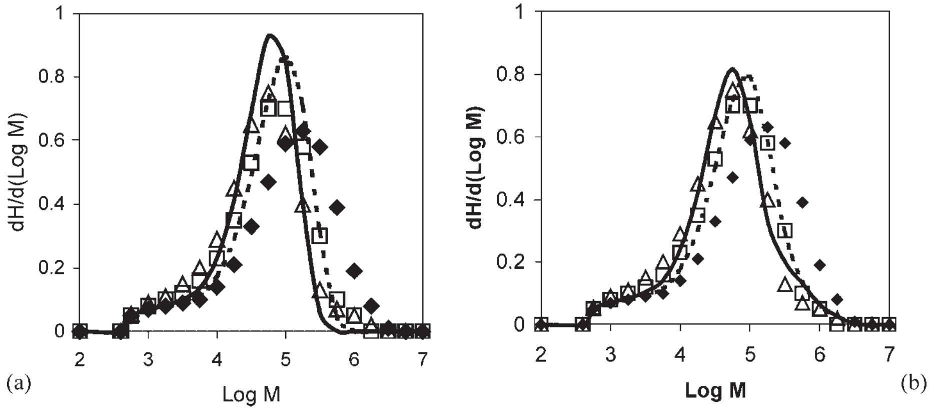

***Figure 5.***
Comparison between model predictions and experimental data from Severini et al.[11] Symbols are experimental data: (◆) virgin PP; (€) maleated PP; (△) PP processed without MAH. Lines are predicted MWD from Equation (27) (left) and from Equation (28) (right): (----) maleated PP; (—) PP processed without MAH.

the whole film will be given by:

$$w(r,u) = yw(r,0) + (1-y) \times \left\{ w(r,0) + ur\int_{r}^{\infty} \frac{2+u(s-r)}{s} w(s,0)ds \right\} e^{-ur} \tag{28}$$

where y is the weight fraction of the film that remained unchanged (undegraded PP) and $(1-y)$ is the fraction of the original polymer that took contact with the reactants and underwent scission (degraded PP). This approach introduces only one additional parameter, the unchanged fraction of the original polymer (y). This very simple segregation model was also used by Iedema et al.[16] and can be seen as a simpler version of the equation used by Soares et al.[20] to simulate bad mixing in visbreaking of PP. Using this simple segregation model, the fitting of the experimental MWD observed by Severini et al.[11] is significantly improved, as shown in Figure 5(b).

In the presence of MAH, the degree of scission was lower than that in the absence of MAH. This shows the effect of degradation hindrance caused by the grafting of MAH. According to the kinetic scheme, step (vii) competes with the scission step (v), and grafted radicals do not undergo scission. Under the absence of MAH, scission may occur at more intense way, resulting in a MWD shifted towards lower molecular weights.

## Conclusions

A kinetic model was proposed and tested to represent the main trends in the process of free radical grafting of maleic anhydride (MAH) onto polypropylene (PP) in melt. The model is able to predict the effect of MAH and peroxide concentrations on the grafting degree as well as the changes in the polymer MWD. The predictions are similar to those from a Monte Carlo model previously reported in the literature[1] for the same process. The proposed deterministic model is based on the numerical solution of mass balances and reaction kinetics, so it is less computationally demanding than a Monte Carlo model. Simulation results were compared with experimental data from different literature data,[8,13] under diverse conditions. Full molecular weight distributions obtained in vapor phase grafting of MAH on PP film[11] was correctly reproduced by the simulation by adopting a simple segregation model.

*Acknowledgements:* The financial support from FAPESP (Fundação de Apoio à Pesquisa do Estado de São Paulo) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) is gratefully acknowledged.

[1] Y. Zhu, L. An, W. Jiang, *Macromolecules* **2003**, *36*, 3714–3720.

[2] S. H. P. Bettini, J. A. M. Agnelli, *J. Appl. Polym. Sci.* **1999**, *74*, 247–255.

[3] S. H. P. Bettini, J. A. M. Agnelli, J. A. M., *J. Appl. Polym. Sci.* **1999**, *74*, 256–263.

[4] J. M. G. Martinez, J. Taranco, O. Laguna, E. P. Collar, *Intern. Polym. Processing* **1994**, *IX*(3), 246–251.

[5] J. M. G. Martinez, J. Taranco, O. Laguna, E. P. Collar, *Intern. Polym. Processing* **1994**, *IX*(4), 346–349.

[6] A. V. Machado, J. A. Covas, M. van Duin, *Polymer* **2001**, *42*, 3649–3655.

[7] A. V. Machado, J. A. Covas, M. van Duin, *J. Appl. Polym. Sci.* **2000**, *38*, 3919–3932.

[8] D. Shi, J. Yang, Z. Yao, H. Wang, W. Jing, J. Yin, G. Costa, *Polymer* **2001**, *42*, 5549–5557.

[9] W. Heinen, C. H. Rosenmoller, C. B. Wenzel, H. J. M. de Groot, J. Lugtenburg, M. van Duin, *Macromolecules* **1996**, *29*, 1151–1157.

[10] Y. Trolez, C. Macosko, A. Boilloux, 6th Annual Meeting of The Polymer Processing Society, Nice, France (1990) *Abstracts*, volume 6, paper 01–16.

[11] F. Severini, M. Pegoraro, L. Yuan, G. Ricca, N. Fanti, *Polymer* **1999**, *40*, 7059–7064.

[12] R. M. Ho, A. C. Su, C. H. Wu, S. I. Chen, *Polymer* **1993**, *34*(15), 3264–3269.

[13] J. Cha, J. L. White, *Polym. Eng. Sci.* **2001**, *41*(7), 1227–1237.

[14] A. E. Hamielec, P. E. Gloor, S. Zhu, Y. Tang, COMPALLOY'91, Proceedings of the 2nd International Congress on Compatibilizers and Reactive Polymer Alloying, Schotland Business Inc., Princenton, NJ **1990**, pp. 85–145.

[15] A. E. Hamielec, P. E. Gloor, S. Zhu, *Can. J. Chem. Eng.* **1991**, *69*, 611–618.

[16] P. D. Iedema, C. Willems, G. van Vliet, W. Bunge, S. M. P. Mutsers, H. C. J. Hoefsloot, *Chem. Eng. Sci.* **2001**, *56*, 3659–3669.

[17] O. Saito, Statistical theories of crosslinking, in: *The radiation chemistry of polymers*, M. Dole, Ed., Academic Press, New York **1972**, pp. 223–261.

[18] O. Saito, *J. Phys. Soc. Japan* **1958**, *13*, 198–206, 1451–1464, 1465–1475.

[19] V. J. Triacca, P. E. Gloor, S. Zhu, A. N. Hrymak, A. E. Hamielec, *Polym. Eng. Sci.* **1993**, *33*(8), 445–454.

[20] J. B. P. Soares, T. Shouli, A. E. Hamielec, *Polym. React. Eng.* **1997**, *5*(1–2), 25–44.