

# The Transient Nature of Maximum Maleic Anhydride Grafting of Polypropylene: A Mechanistic Approach Based on a Consecutive Reaction Model

## Part 1: Batch Solution Process

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**ABSTRACT:** This article reports the chemical modification of an atactic polypropylene performed in solution. To model the process, a Box-Wilson experimental design was used, taking in to consideration the concentrations of maleic anhydride and dycumile peroxide, as well as reaction time, as independent variables. The dynamic character of the process is proposed on the basis of model forecasts supported by experimental results. The proposed kinetic pathway

agrees with the fact that short reaction times are not only sufficient but necessary for the greatest graft yields to be attained, while preventing degradative processes in the system. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1182–1190, 2006.

**Key words:** polypropylenes; grafting; modeling; reaction mechanism; dynamic process

### INTRODUCTION

The chemical modification of polyolefins (especially polypropylene) by the grafting of polar groups such as maleic anhydride, has become widespread over recent decades. The grafting of maleic anhydride (MAH) onto the polymer backbone (which becomes succinic anhydride once attached) confers a certain polarity to the polymer, rendering it very useful as an interfacial agent in polymer-based heterogeneous materials.<sup>1–10</sup> Although these modified polypropylenes have been widely used in commercial applications, the exact nature of the chemical pathways involved in their production is still poorly understood. It is generally accepted, however, that there are competitive reactions in the polymer bulk that give rise mainly to in-chain scission or the degradation of polypropylenes.<sup>11–13</sup> The well-accepted complex nature of the process and its related economic aspects appear to justify the large number of articles on the grafting of polar monomers onto polyolefins (299 references in the review by Xu and Lin,<sup>14</sup> 129 in that by Jois and Harrison,<sup>15</sup> 118 in that by Naqui and Choudhary,<sup>16</sup> and, more recently, 188 in that by Moad<sup>17</sup>).

Initial studies on the grafting of succinic anhydride groups were conducted using isotactic polypropylene.<sup>18,19</sup> More recently, the atactic polymer has been used.<sup>12,20</sup> The possibility of MAH oligomers being grafted onto a polypropylene backbone was thought unlikely by Russell and Kelusky,<sup>21,22</sup> based on ceiling temperature considerations. The present authors thought similarly, based on the reaction between the single succinic groups and resorcinol to yield succinyl-fluorescein grafted groups.<sup>23</sup> Similarly, the hypothesis that the macromolecular reactant is that which controls graft yield, suggested some time ago by Natta et al.<sup>24</sup> when studying the grafting of acrylic groups onto polypropylenes, agrees with the findings of the present authors who used either MAH or *p*-phenylen-bismaleamic acid as polar monomers.<sup>25,26</sup> The proposal that chain scission is mainly responsible for the grafting process disagrees with viscosimetric results that show nonappreciable degradation of the polymeric substrate once modified by either succinic anhydride or succinyl-fluorescein grafted groups.<sup>27</sup>

The present article deals with the chemical modification process, in solution, of an atactic polypropylene by MAH in the presence of the initiator dycumile peroxide. Performing the process in solution allows conditions to be set (mainly in terms of MAH concentration) that are not feasible in molten state processes. A Box-Wilson experimental design with three independent variables (polar monomer concentration, initiator concentration, and reaction time) was used to discuss the results of the polynomial fits obtained.<sup>28–32</sup>

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TABLE I  
Properties of the Atactic Polypropylene Used at Present Work

$M_w$	$M_n$	HI ( $M_w/M_n$ )	DSC					Density ( $\text{g}/\text{cm}^3$ )
			$T_g$ ( $^{\circ}\text{C}$ )	$\Delta H_m$ (J/g)	$T_m$ ( $^{\circ}\text{C}$ )	$\Delta H_c$ (J/g)	$T_c$ ( $^{\circ}\text{C}$ )	
54,000	2,700	20	-22.4	10.6	113.0	-20.1	75.9	0.85

A reaction pathway that takes into account the transient character of the process, which was tested both experimentally and against forecasts of earlier models for different polymer/solvent ratios, is proposed.

## EXPERIMENTAL

### Materials

Atactic polypropylene, a polymerization by-product supplied by Repsol-Química, was used as the starting material. Maleic anhydride (MAH) and dycumile peroxide (Pox) (Perkadox BC), from Panreac and Akzo, respectively, were used as received. To prevent thermo-oxidative degradation of the polypropylene (mainly  $\beta$ -scission) during the process, a 50/50 mixture of Irganox 1010 and Irganox B225 (Ciba-Geigy) was incorporated into the reaction medium as a thermal stabilizer. The modification process was performed using xylene (isomer mixture from Panreac) as a solvent. Table I shows some properties of the atactic polypropylene used.

### Procedures and characterization

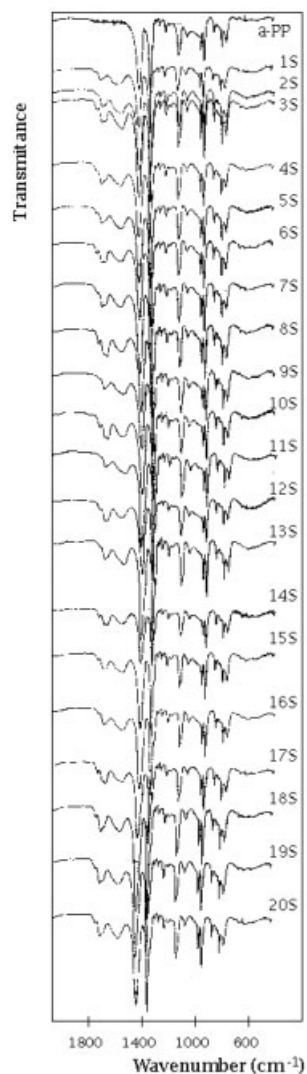
The batch solution chemical modification process was conducted in a conventional glass flask equipped with a reflux column. The reaction temperature was that of the boiling solvent ( $140^{\circ}\text{C}$ ), and the reaction volume was 750 mL. The control factors of the process were determined by following the three independent variables (reactant and initiator concentrations and reaction time) from a Box-Wilson experimental worksheet (Table II). First, the polymer was dissolved in boiling xylene (1/30 (w/w) polymer/solvent ratio) to which 0.1% (w/w) of the thermal stabilizers had previously been added. The preheated xylene-dissolved MAH was then incorporated into the reactor, followed 1 min later by the peroxide prepared in the same way. This moment was taken as the reaction start time. Once the set reaction times had elapsed, the solution was rapidly precipitated in cool methanol, filtered, and the polymer recovered and dried for further characterization. A series of additional experiments were performed by changing the polymer/solvent ratio to 1/5. To ensure that there was no free MAH in the grafted polymer bulk, a series of randomly chosen samples were washed and characterized as described above. No differences in grafting values were appreciated.

The modified polypropylenes obtained were first qualitatively characterized by FT-IR spectroscopy. Infrared spectra were recorded using a Spectrum One FT-IR spectrophotometer (Perkin-Elmer) employing the KBr pellet technique (4 mg Polymer/170 mg KBr). Tests were performed at 32 scans and  $2\text{ cm}^{-1}$ . Figure 1 shows the FT-IR spectra in the  $600\text{--}1800\text{ cm}^{-1}$  range corresponding to the original atactic polypropylene and of each of the modified polymers with their different levels of grafting (amount of succinic anhydride grafted onto the polymer backbone). The presence of grafted succinic groups was concluded owing to bands between  $1700$  and  $1800\text{ cm}^{-1}$ . These were present in all the modified samples but not in the unmodified sample.

Grafting levels were determined by an improved hot titration method.<sup>18,20,33,34</sup> One gram of polymer was dissolved for 60 min in 150 mL of a refluxed xylene-butyl alcohol-water mixture. The hot solution was titrated, not allowing it to cool, with 0.05N ethanolic potasse using thymol blue as an indicator. Excess KOH was then added and the deep blue colored solution back-titrated to a yellow end point by the addition of 0.05N isopropanolic HCl to the hot solution. Results are

TABLE II  
Grafting Values Obtained by Chemical Modification of Atactic Polypropylene for the Box-Wilson Experimental Worksheet Used at Present Work

Exp.	Controlled factors			Graft (%)
	[POx] (%)	[MAH] (%)	Time (min)	
1S	1.00	15.0	5.0	0.38
2S	3.50	15.0	5.0	0.59
3S	1.00	40.0	5.0	0.87
4S	3.50	40.0	5.0	1.31
5S	1.00	15.0	15.0	0.41
6S	3.50	15.0	15.0	0.43
7S	1.00	40.0	15.0	0.92
8S	3.50	40.0	15.0	0.77
9S	0.15	27.5	10.0	0.70
10S	4.35	27.5	10.0	1.04
11S	2.25	6.5	10.0	0.23
12S	2.25	48.5	10.0	1.40
13S	2.25	27.5	1.6	0.65
14S	2.25	27.5	18.4	0.78
15S	2.25	27.5	10.0	0.63
16S	2.25	27.5	10.0	0.69
17S	2.25	27.5	10.0	0.62
18S	2.25	27.5	10.0	0.63
19S	2.25	27.5	10.0	0.68
20S	2.25	27.5	10.0	0.63



**Figure 1** FT-IR spectra for both the neat and the grafted atactic polypropylenes concerning the Box-Wilson experimental worksheet.

expressed as weight percent. In this way, neglectable values were obtained for the original polymer.

## RESULTS AND DISCUSSION

### Polynomial fits and analysis of variance

Table II shows the experimental grafting values obtained by following the Box-Wilson design with three

**TABLE IV**  
Statistical Parameters of the Analysis of Variance (ANOVA)

$r^2$	0.97
Sum of square mean	0.0255
Pure error	0.0009
Confidence factor (%)	99.8
Deviation due to pure error (%)	0.8

independent variables. These were fitted to a quadratic model by surface response methodology<sup>30</sup> to obtain a polynomial that describes the development of grafting level over the whole experimental space scanned. Table III shows the terms of this polynomial equation. The model shows a ( $r^2$ ) value of 0.97, which is excellent for a quadratic model. The very small pure error values (0.0009) seem to uphold the accuracy of the results. All statistical parameters necessary for the analysis of variance (ANOVA) of the model are shown in Table IV. Accordingly, the system can be fully discussed with respect to model forecasts.

### Influence of reactant and initiator concentrations, and reaction time

Figure 2 shows the grafting when POx is varied for different initial amounts of MAH in the reaction medium, while keeping reaction time constant for each plot. For any fixed reaction time, the more initial MAH in the reaction medium the more grafting occurs. Grafting with POx seems to be different between plots (A)–(D). For reaction times up to 9 min [Figs. 2(A)–2(C)], grafting increases with POx for the indicated initial MAH concentration. Lesser amounts of initial POx (<2%) led to an almost constant grafting yield [Fig. 2(C)]. However, at reaction times over 9 min [Figs. 2(D) and 2(E)], grafting reached a critical point (a minimum) at around 2% initial POx. The range of grafting shown in these figures is reduced when compared with that of Figures 2(A)–2(C). The longest reaction time considered [Fig. 2(F)] causes the reverse of that seen with short reaction times [Figs. 2(A)–2(C)], with a decrease in the grafting level when initial POx is increased up to the 2%. There is then an almost constant grafting value once the 2% of initial POx is

**TABLE III**  
Coefficients of the Response Surface Polynomials

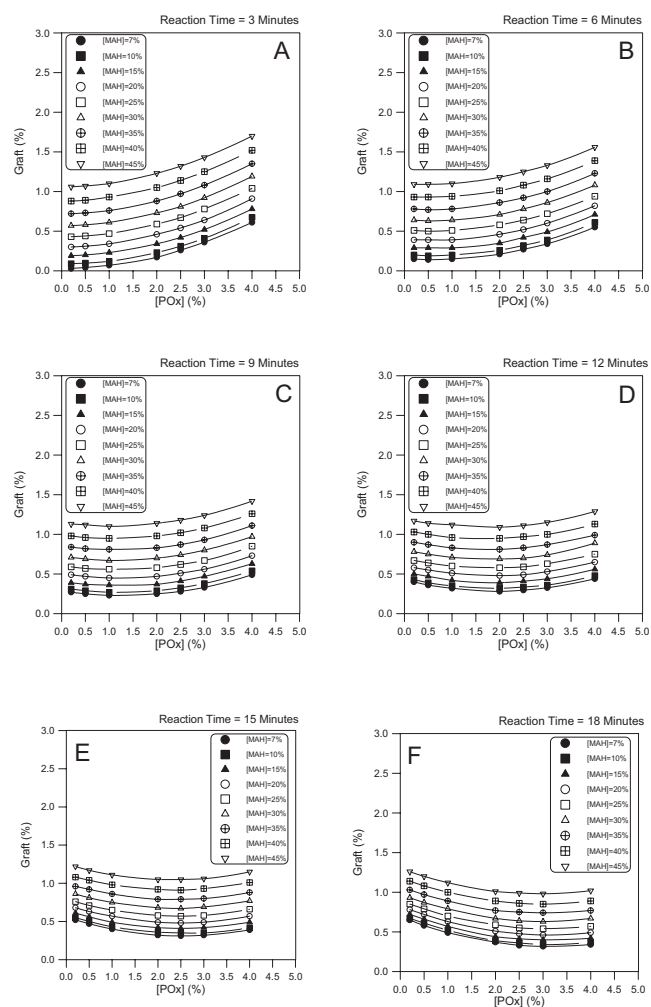
$\{r^2\}$	Independent term	Linear terms			Interaction terms			Quadratic terms		
	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$	$a_7$	$a_8$	$a_9$
0.9705	-0.2159	0.03971	0.01614	0.04645	0.00048	-0.0156	-0.000720	0.03712	0.000247	0.000129

Polynomial equation:  $a_0 + a_1 \times X_1 + a_2 \times X_2 + a_3 \times X_3 + a_4 \times X_1 \times X_2 + a_5 \times X_1 \times X_3 + a_6 \times X_2 \times X_3 + a_7 \times X_1^2 + a_8 \times X_2^2 + a_9 \times X_3^2$

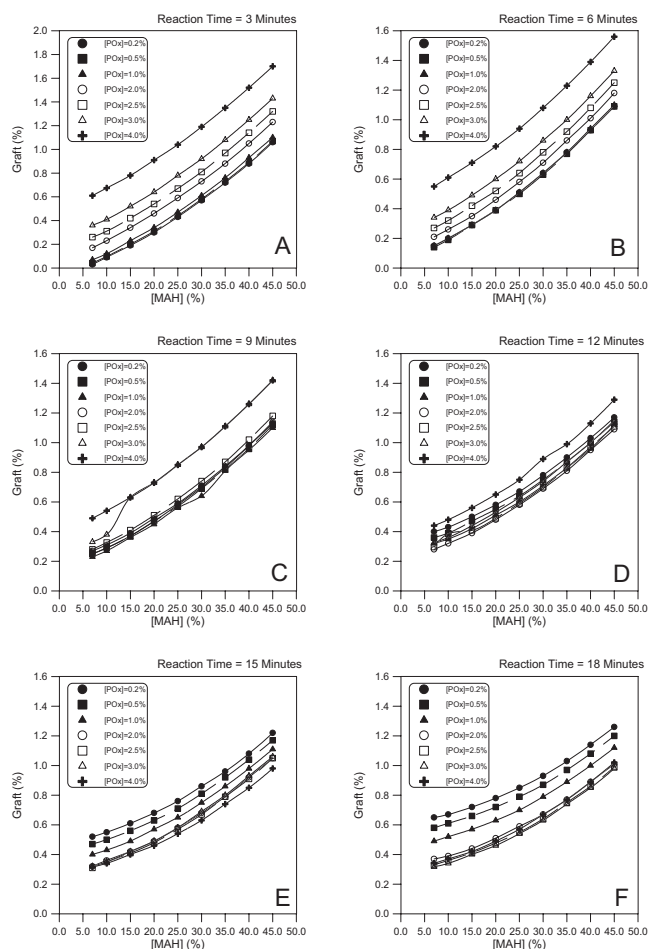
Where  $x_1$  is [POx];  $x_2$  is [MAH];  $x_3$  is reaction time.

surpassed. Further, shorter reaction times result in greater grafting levels with high initial POx, and vice versa. Nevertheless, in all cases the differences in grafting are very small, although significant enough to point to the existence of a critical value for the initiator concentration. This indicates the dynamic character of the chemical modification process.<sup>12,20</sup>

Figure 3 shows the development of grafts as a function of initial MAH concentration for the indicated initial POx values and for the same six different reaction times considered in Figure 2. At 3 min reaction time [Fig. 3(A)], grafting increases almost linearly with initial MAH and POx concentrations. The greatest differences are obtained for initial [POx] values  $>2\%$ . At the 6 min reaction time [Fig. 3(B)], although development is similar, the highest grafting levels reached for initial POx concentrations  $\leq 2\%$  are lower than those in Figure 3(A). For initial POx concentrations below 2%, grafting levels are higher than similar coordinates in Figure 3(A). As reaction time increases up to 9 min [Fig. 3(C)],



**Figure 2** Grafting level vs. initiator concentration at different amounts of initial MAH concentration, at the indicated reaction times (3, 6, 9, 12, 15, and 18 min).



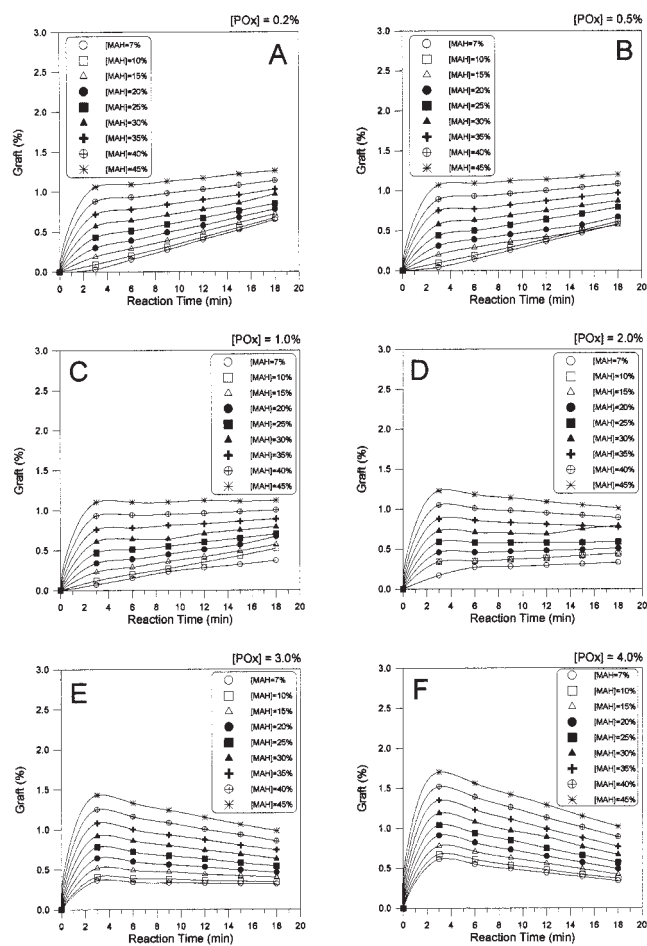
**Figure 3** Grafting level vs. initial MAH concentration at different amounts of initiator concentration, at the indicated reaction times (3, 6, 9, 12, 15, and 18 min).

grafting remains almost in line with rising MAH, but providing similar grafting values irrespective of POx concentration [except for the two highest levels (3 and 4%)]. Grafting variability is less than in Figures 3(A) and 3(B). Moreover, Figure 3(D) shows that only the highest initial POx concentration is able to yield the highest grafting levels. Finally, Figures 3(E) and 3(F), i.e., the longest reaction times, show the reverse behavior. In this case, the lesser the peroxide in the reaction media, the greater the grafting obtained. It must also be noticed that for  $\geq 2\%$  levels of POx, the grafting values are almost identical.

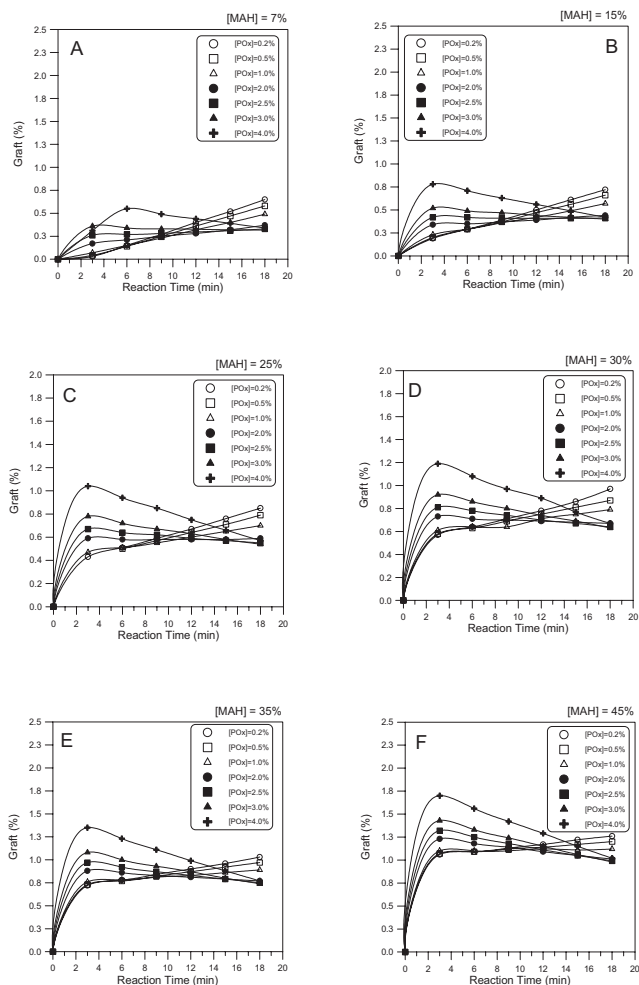
Plotting grafting against reaction time at the indicated levels of either POx (Fig. 4) or MAH (Fig. 5) confirms the oscillatory effect of the initiator concentration on the chemical modification of polypropylene as reported in previous articles.<sup>12,20,25,26</sup> Figure 4 shows the positive effect on grafting caused by an increase in the initial concentrations of both initiator (POx) and polar monomer (MAH), as reported by Minoura et al.<sup>35</sup> Nevertheless, there are differences in the slopes of the curves that pass from being positive to negative for POx levels below and

above 2% respectively. Accordingly, Figure 5 shows that after a certain reaction time ( $\sim 12$  min for present system), the lower the initial POx value, the higher the grafting levels obtained. Reaction time was not taken into account in the early work of Minoura et al.<sup>35</sup> These authors' results were obtained for the mean value of each of the variables considered as independent (reaction time was not one of these). The important role played by reaction time in obtaining the maximum feasible yield in the molten state is discussed elsewhere.<sup>20</sup>

All the above results (Figs. 2–5) show the dynamic or transient character of the process, the maximum grafting level of which is obtained in the first stages of the reaction. This allows the assumption that the process might occur via consecutive reactions ( $A \rightarrow B \rightarrow C$ ), in which the intermediate product (B) would be the desired product (i.e. the grafted product). A series of undesired degradation products would also be formed in quantitative amounts after a certain reaction time.<sup>36,37</sup> Figure 6 shows a schematic representation of this model of consecutive reactions as reported for complex chemical systems.<sup>36,37</sup>



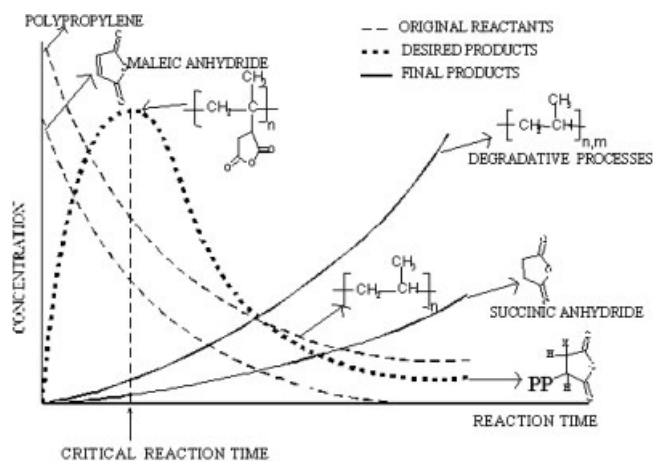
**Figure 4** Grafting level with reaction time at different amounts of initial MAH concentration for the indicated amounts of initiator (0.2, 0.5, 1.0, 2.0, 3.0, and 4.0%).



**Figure 5** Grafting level with reaction time at different amounts of initiator concentration for the indicated amounts of initial MAH concentration (7, 15, 25, 30, 35, and 45%).

### Consecutive reactions model: balance of species involved

The reaction system can be considered homogeneous. From the point of view of a formal kinetic study, this



**Figure 6** Typical reaction scheme of a consecutive reaction model.

system has a very important advantage: the isothermal character of the boiling solvent.

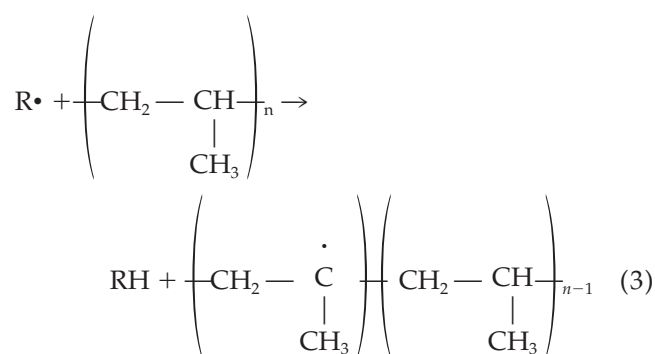
Starting with a radical mechanism, the process can be established as follows. First, decomposition of the initiator, I:



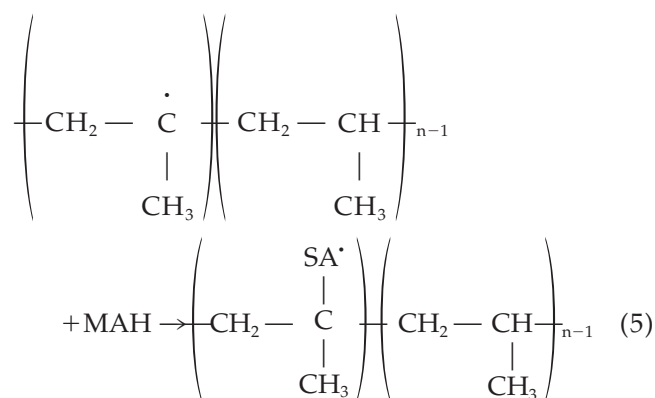
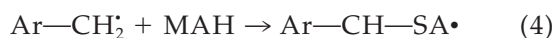
where ( $R\cdot$ ) is the radical generated by the peroxide that is able to interact with either the solvent ( $Ar-CH_3$ ):



or the polymer backbone:



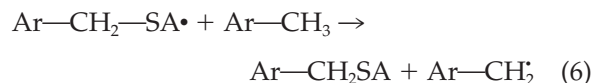
The activated species generated by steps (2) and (3) would then develop as (4) and (5) respectively, reacting with the MAH in the reaction medium to yield the activated succinic anhydride species ( $-SA\cdot$ ) either in the solvent or attached to the polymer backbone.



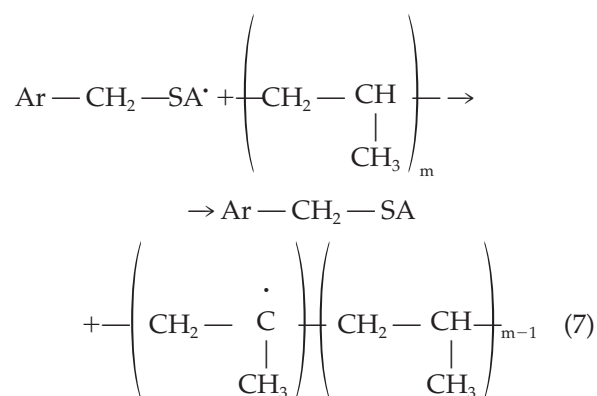
According to our own<sup>12,20</sup> experimental evidence and the early findings of Natta et al.,<sup>24</sup> (the goal being the obtention of the grafted product (a-PP-SA), the contribution of radicals generated on either the secondary carbon atoms (lower reactivity than tertiary atoms) or the single MAH molecules has been neglected. Taking this into consideration, the

species generated by reaction (4) might evolve along three possible paths:

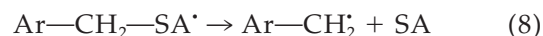
1. By interacting with a nearby solvent molecule:



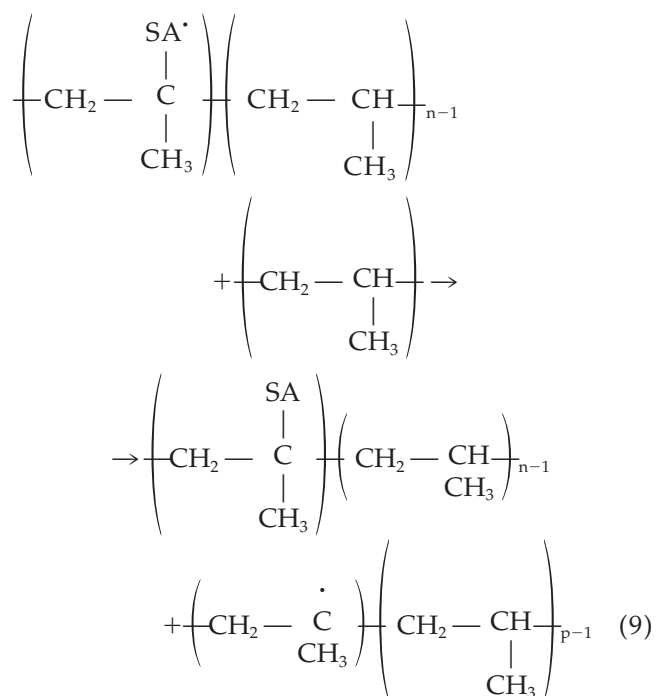
2. By transferring radical activity to a new tertiary carbon atom on the macromolecular reactant would then become a new active center:



3. By returning to the reaction medium, through a decomposition step, as a single succinic anhydride (SA) and becoming a radical identical to that in (2) and later in (4):

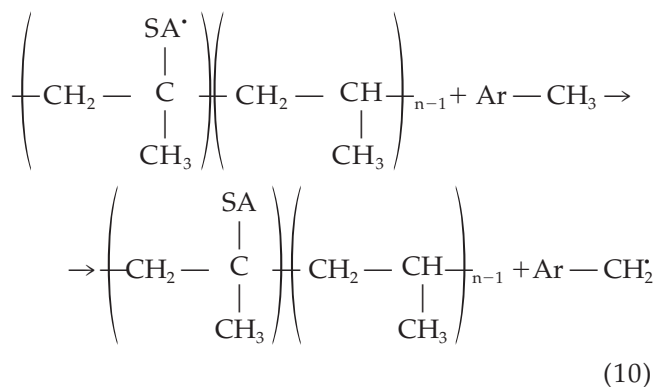


Similarly, the macromolecular radical generated by equation (5) can also evolve by three different reaction paths. First, by reacting with any other segments of the macromolecular substrate to yield a grafted species and a new macroradical:

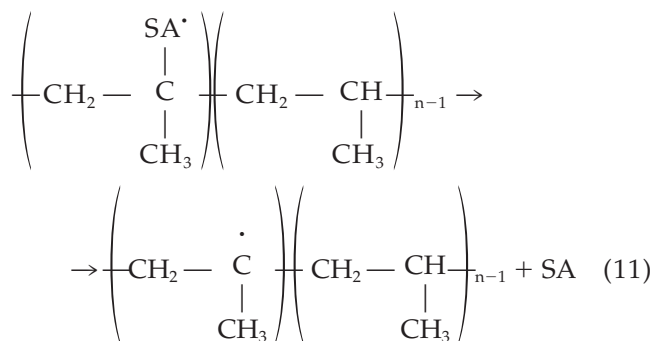


Equation (9) would imply the polymer self-transference of activity by either intra- or interchain transmission, the first of these being sharply affected by the stereoregularity of the polymer.<sup>20</sup>

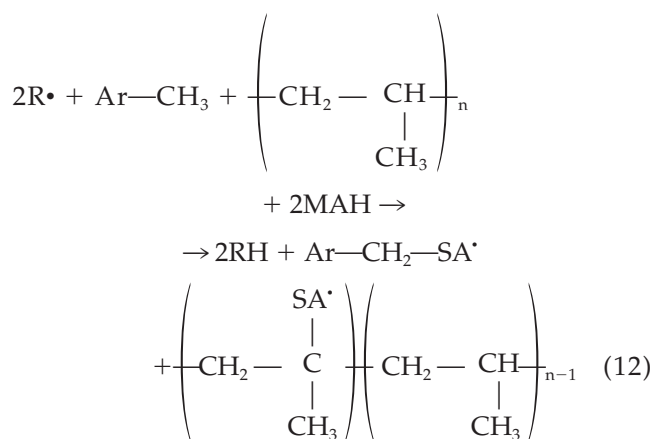
Second, by transferring radicalar activity to the solvent, again yielding grafted polymer:



And third, by transferring reactivity forward to the polymer's own backbone, and restoring a single free succinic anhydride to the reaction medium:

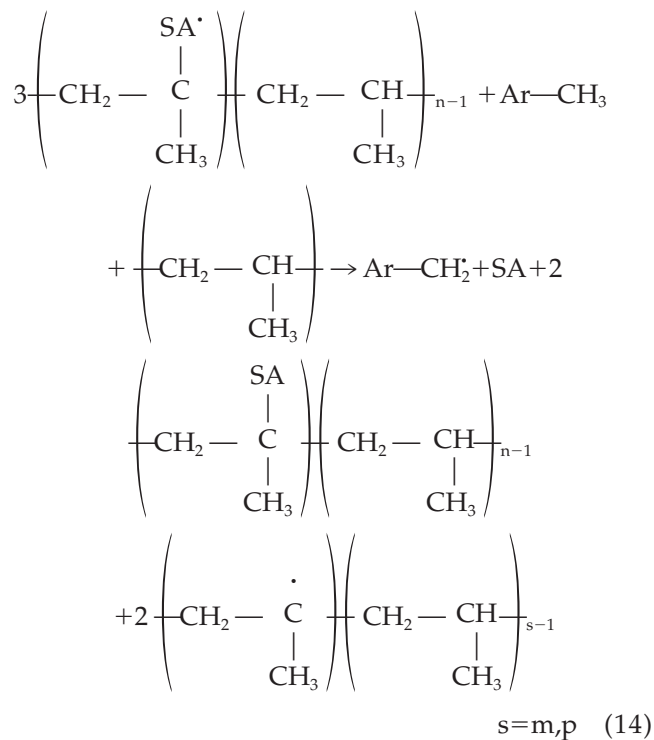
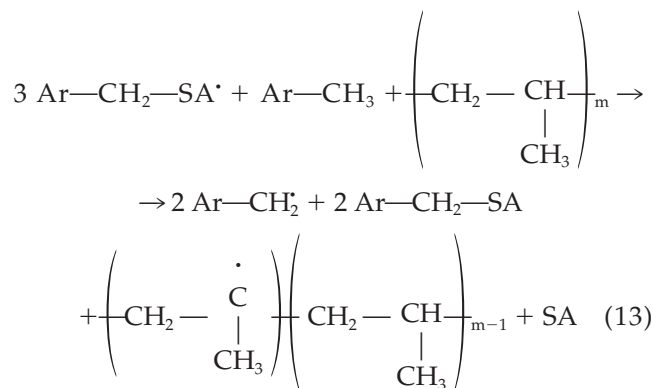


An overall reaction path can be obtained from two partial balances, one for the transient species, the other for the grafted polymer. The first partial balance would result from the addition of (2) to (5), giving:

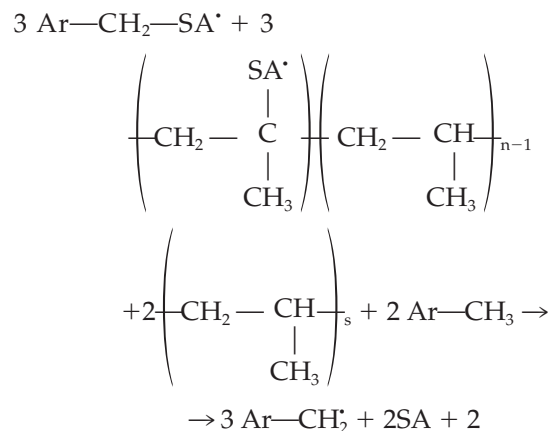


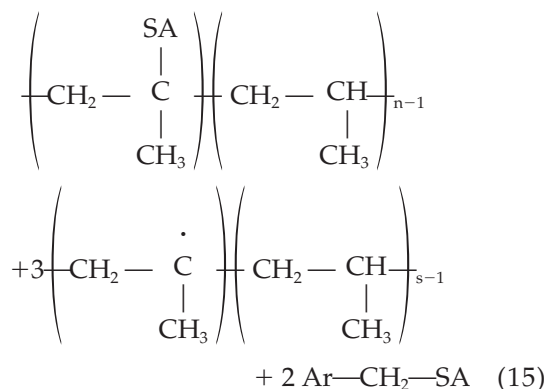
All generated species might be divided into two separate partial balances. One, resulting from the addi-

tion of equations (6) to (8), the other from (9) to (11). These operations result in equations (13) and (14), respectively:

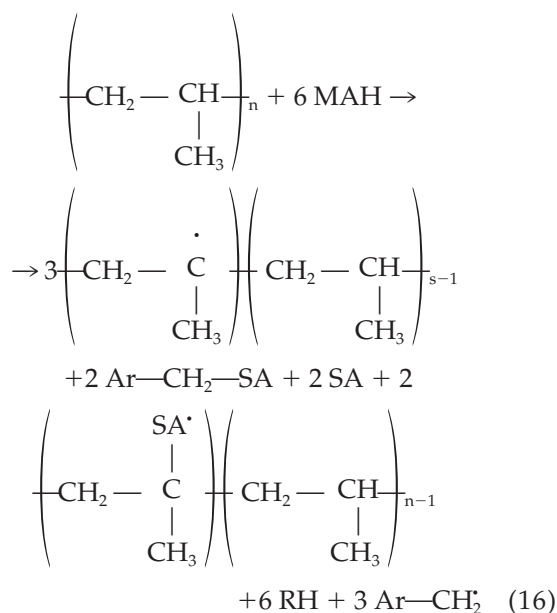


The combination of (13) and (14) would then result in the global balance of the species generated:





The balance of the overall process is obtained from the addition of equations (12) and (15),  $(3 \times (12) + (15))$ , giving rise to equation (16):



Equation (16) contains all the relevant species involved in the chemical modification of polypropylene by a polar monomer, and agrees with a series of remarks associated with findings in previous studies.<sup>12,20,26</sup> This implies the generation of free succinic anhydride (SA) as a reaction by-product and the obtention of the grafted polymer in a ratio of only 2/3 with respect to the remaining radicals active in the polymer bulk (unable to yield grafting reactions and obliged to lose their activity by  $\beta$  scission processes leading to degradation of the polymer). The latter is confirmed by the fact that the reaction proceeds with no loss of efficiency when performed in the presence of radical traps or the thermal stabilizers usually used in polyolefin processing operations.<sup>12,18-20,23,25-27</sup> The low grafting yield obtained, both in terms of the number of bonded polar groups and of conversion levels, is well known from early studies dealing with the role played by the solvent, and because of experimental evidence of higher grafting yields obtained when the procedure occurs in the melt rather than in solution.<sup>14</sup>

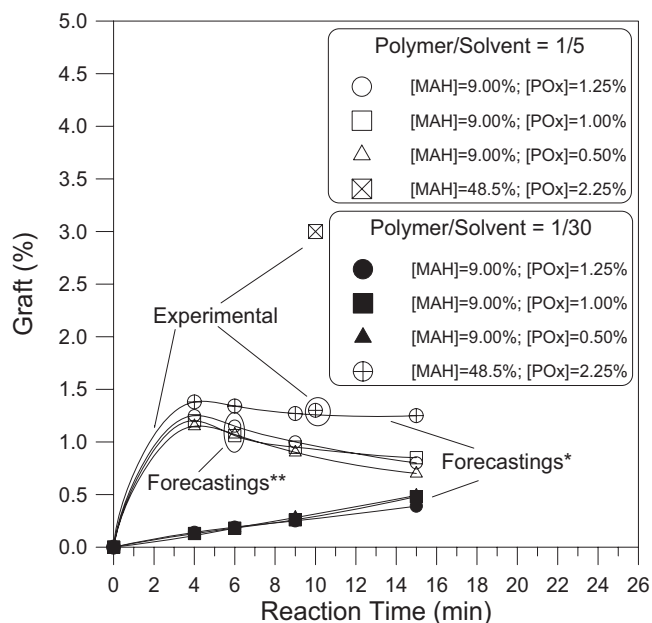


Figure 7 Grafting level vs. reaction time for the indicated reaction conditions. Model forecasts and experimental data.

The proposed kinetic model, based on a pathway of consecutive reactions, can be tested by the data in Figure 7. Forecasts from the Box-Wilson fits for different experimental spaces and reaction conditions are plotted. The almost linear development of grafting with reaction time, observed at the 1/30 polymer/solvent ratio, completely disappears when the polymer concentration increases. Experimental data are also included in Figure 7, and confirm the accuracy of the proposed model. Future work will investigate the unsteady nature of the process as revealed by a molecular probe and a comparative study of the solution and molten state processes.

## CONCLUSIONS

This work proposes a kinetic pathway to explain the findings obtained by the Box-Wilson experimental design methodology (mainly the dynamic character of the process, which indicates the existence of critical grafting values). Accordingly, the balance of the species involved demands consideration of the activity transfer to either the solvent or the macromolecular substrate itself. Such a model agrees with a consecutive reaction mechanism. Its validity, for either solution or molten state processes, is the subject of a forthcoming article in which a molecular probe will be used to check the mechanism.

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