Chemical Modification of Polypropylenes by Maleic Anhydride: Influence of Stereospecificity and Process Conditions

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ABSTRACT: An investigation about the possibilities of atactic polypropylene in order to be chemically modified either in solution or in molten state processes, and further predictions about the reaction conditions' influence in the process, have been carried out. For those purposes the Box–Wilson experimental design method has been used. Besides, in order to check the experimental design polynomials forecasting of the models, additional experiments were performed at different working temperatures, kind of solvent, and stereospecificity of the polymer by comparison of processes carried out on atactic and isotactic polypropylenes. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 483–495, 1998

Key words: functionalization; polypropylenes; stereospecificity; solution; molten state; mechanism; processing conditions

INTRODUCTION

Polypropylene is one of the largest and fastest growing polymers because of its useful properties, wide applicability, and low cost.

The functionalization possibilities of polypropylenes (both atactic and isotactic polymer) by polar monomers as an effective way of increase the polarity of polypropylene, and so its affinity with other polar materials it is often combined to, are interesting. In fact, these kinds of grafted polymers have been widely used to improve interfacial adhesion between the components in polymer blends.[1-8] Also, modified isotactic (i-PP)[9-19] and atactic polypropylenes[20-22] have been extensively used for significant improvement of the mechanical properties of composites based on PP and mineral reinforcements.

Papers describing functionalization in both solution[2,6,18,19,23,24] and molten state[19,20,25-30] have been published. It is something generally accepted that modification reactions are initiated by peroxide radicals transferring their activity to the polymer chain.[31-33] It has been demonstrated the great importance the kind of solvent has on the reaction conversion, even the effect of the isomer of solvent used.[24]

As suggested in Ref. 34 it has been also shown, working on model compounds[35-37] and on polymers too (PE[38,39], i-PP[18,40], and a-PP[20,21]), that maleic anhydride (MAH) units enter in the polymer as single succinic anhydride units.

Following with our works dealing with the chemical modification of polyolefins[21,22,26,31] in this article we present results coming from a two-independent-variables Box–Wilson experimental design used for a-PP modification, in solution and in the melt, and a discussion on the mathematical fits obtained. Besides a number of additional experimental data supporting the model forecastings are discussed.

An atactic polymer is mainly used for several reasons. One of those is the fact that a-PP can be processed at the same temperature in the melt as the solution process is performed when xylene is used as solvent (140°C). The latter let us make a comparison with almost nondependence of working temperature. Another reason, and very important from the industrial point of view, is the fact that modified atactic polypropylene has been demonstrated to improve mechanical properties in PP-based composites.[20,22]

EXPERIMENTAL

Materials

As starting material atactic polymer (a-PP), an industrial waste coming from stereospecific polymerization process of polypropylene, was used. For experimental data an isotactic polypropylene (i-PP) grade, named ISPLEN 050, was employed. Both of them were supplied by Repsol Química. Maleic anhydride (Scharlau/FEROSA) and dycumil peroxide "Perkadox BC" (Akzo) were used as reactant and initiator, respectively. Solvents used at present work were xylene (isomer mixture) from Panreac, and decaline (Scharlau/ FEROSA). In order to prevent termo-oxidative degradation thermal stabilizers were added to the reaction media (Irganox 1010 and Irganox B225 from Ciba-Geigy).

Procedure

Modification reactions on atactic polypropylene were conducted in batch reactors, both in solution and in the melt. In both cases processing temperature was set up at 140°C, corresponding to the xylene boiling temperature. Additional experiments were carried out at 120°C (in the melt) and at 180°C (decaline). Thermal stabilizers (Irganox 1010 and B225) were first added to the polymeric system in order to prevent thermal-induced degradation.

Chemical reactions in the melt were performed in an internal mixer (Rheomix 600) attached to a microprocessor (Rheocord 90 from Haake). Reaction time was considered to be 6 min. Processing operations were as follows: first, when the reactor was at the setup temperature, polypropylene and maleic anhydride were added. After 3 min, when they were well mixed, initiator was added. This moment is considered to be the reaction startup.

Six minutes later the reactor was opened and the reaction mixture cooled in an ice bath. In order to remove nonreacted MAH the polymer was solved in boiling xylene and precipitated into methanol. Modified polymer was then ready to be characterized.

Modification in solution was conducted in a conventional glass reactor equipped with a refluxing column. First, polymer was solved in xylene (polymer/solvent = 1/5), then xylene-solved maleic anhydride was added, and one minute later the peroxide too. This moment is considered zero time for the reaction. After 6 min the solution was precipitated and the polymer recovered was then characterized.

Characterization

In order to characterize the obtained modified polymer first a qualitative study was done by using FTIR. Infrared spectra were recorded on a Nicolet 520 FTIR using the KBr pellet technique imposed for the sample texture. Runs were performed at 32 scan and 4 cm^{-1}. As an example Figure 1 shows FTIR spectra for modified and nonmodified samples.

Quantitative analysis was done by a titration method[18,41,42] as follows. One gram of modified polymer was put in 150 mL refluxing xylene/water/n-butanol mixture for 60 min. The hot solution was then titrated without permitting it to cool with 0.05N ethanolic KOH using thymol blue as indicator. Then an excess of KOH was added and a deep blue color was back-titrated to a yellow endpoint by addition of 0.05N isopropanolic HCl to the hot solution. Results were expressed as weight percentage. As well samples without grafts were titrated, yielding neglected values.

RESULTS AND DISCUSSION

Atactic polypropylene has to be processed at a lower temperature than the isotactic polymer (190°C) due to its structural nature. Chosen temperature was 140°C because it was the higher temperature that material could be processed in the melt; besides, it is the temperature of boiling xylene. This fact would let us make comparisons between solution and molten state processes at the same working temperature.

First, a comparison of the grafting levels reached when modified a-PP for both solution and melt processes were done. For all the experimental work a
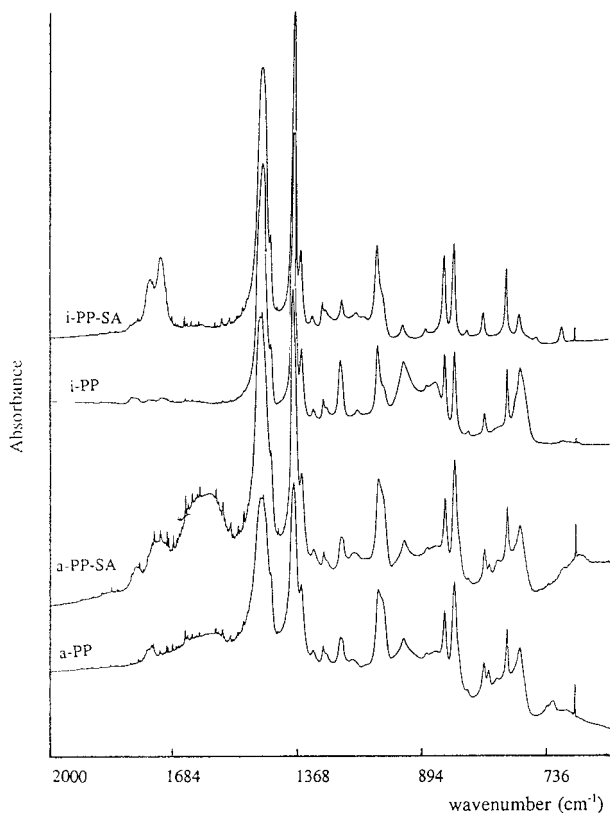
Figure 1   FTIR spectra for both atactic (A) and isotactic (B) polypropylene with and without succinic anhydride grafted groups.

Box–Wilson design was used in order to model the process.[43–50] Table I shows both the experimental design considering two independent variables (initial concentration of maleic anhydride and peroxide) and the results obtained expressed as grafting level (w/w) and as conversion. Those results were fitted to quadratic polynomials in order to have information about the behavior of the system all along the experimental range. Table II compiles the terms of these polynomials. In Table III statistical parameters for analysis of variance (ANOVA) have been resumed. From the latter it can be observed the kind of polynomials obtained from the Box–Wilson experimental design. From Table III it can be concluded there is very little pure error, and then deviation due to pure error. This latter looks to demonstrate the accuracy of the results obtained (with minimal experimental error). In other words, knowing the high value the confidence factor has (nearly 100%), it can be affirmed the process of chemical modification is following a quadratic evolution that is in good agreement with the interfacial phenomenon suggested in Ref. 22. Finally, the value for $\langle r^2 \rangle$ is indicating the mathematical accuracy of the model. It is interesting to observe that values for $\langle r^2 \rangle$ result to be higher for the process in the melt than in that on solution. This latter indicates the existence of some effect not taken into account in the model as it could be the kind of solvent, or the amount of it used. These questions will be discussed later.

Effect of Reaction Media: Solution versus Molten State

In Figures 2–5 grafting and conversion values obtained from polynomials in Table II have been

Table I   Grafting and Conversion Values Obtained by Chemical Modification of Atactic Polypropylene Either in Solution or in Molten State for the Box-Wilson Experimental Worksheet Used at Present

			Solution		Molten State	
Exp.	[POx] (%)	$[MAH]_0$ (%)	$[MAH]_{GRAFT}$ (%)	Conv. (%)	$[MAH]_{GRAFT}$ (%)	Conv. (%)
1	0.70	3.00	1.05	35.00	2.35	78.00
2	3.50	3.00	1.30	43.00	2.45	81.70
3	0.70	15.00	2.10	14.00	2.90	19.30
4	3.50	15.00	1.80	12.00	3.97	26.47
5	0.12	9.00	0.90	10.00	2.20	24.50
6	4.08	9.00	1.42	15.80	4.10	45.20
7	2.10	0.51	0.44	86.00	0.44	86.50
8	2.10	17.50	2.50	14.30	2.00	11.80
9	2.10	9.00	1.20	13.30	4.00	44.44
10	2.10	9.00	1.00	11.10	4.10	45.00
11	2.10	9.00	1.10	12.20	4.20	46.70
12	2.10	9.00	0.98	10.80	4.20	46.70
13	2.10	9.00	0.98	10.80	4.20	46.70

Table II   Coefficients of the Response Surface Polynomials

		Linear Terms			Interaction Terms	Quadratic Terms	
	r^2	a_0	a_1	a_2	a_3	a_4	a_5
Grafting Level							
Solution	0.871	0.6474	−0.0398	−0.008	−0.01637	0.05912	0.007524
Melt	0.917	−0.3643	0.7100	0.6969	0.02887	−0.1489	0.002455
Conversion							
Solution	0.934	70.64	5.557	−11.51	−0.2976	−0.3834	0.4965
Melt	0.969	83.68	9.10	−6.858	0.1033	−1.539	−0.0269

Polynomial Equation: $a_0 + a_1x_1 + a_2x_2 + a_3x_1x_2 + a_4x_1^2 + a_5x_2^2$
$$x_1 = [POx]_0$$
$$x_2 = [MAH]_0$$

plotted. Those figures are exhibiting both grafting level (A) and conversion (B) as a function of peroxide or maleic anhydride initial concentration present in the reaction media for the process of chemical modification in solution.

In Figure 2(A) graft values versus initial MAH concentration in the reaction media have been represented, and in Figure 2(B) conversion versus MAH concentration for different considered constant concentrations of initiator and for a solution process. From Figure 2(A) it can be concluded the higher the peroxide level the higher the graft obtained. This is absolutely true for low levels of MAH in the media but not for values beyond 12% of graftable units, when it seems the grafts obtained seem to get closer to each other with nondependence of the maleic anhydride level present in the media. When discussed in Figure 2(B) we can appreciate that conversion is favored for low levels of MAH in the media. Then when $[MAH]_0$ is higher than 12%, conversion tends to be almost the same or even lower than that at low values for $[MAH]_0$. Otherwise the effect of peroxide is very notable for values of $[MAH]_0$ below 12%. The higher the peroxide concentration the higher reaction conversion agrees to the fact the reaction is performed in solution. In that case although the highest peroxide concentration implies a higher number of radicals onto polypropylene it will also suppose a spectacular increment in number of radicals transferred to the solvent. Some studies have clearly concluded the influence the kind of solvent has on the transference possibilities when working with xylene (different isomers),[23,24] benzene,[23] and decalin.[51] In such studies a high degree of transference to the solvent and even grafting reactions between solvent and polar monomer[51] can be formed. This fact seems to be coincident with the previous findings, i.e., after a maximum MAH initial concentration when adding more and more MAH to the media the excess would have the tendency to react with the molecules having more mobility as they are those of solvent.

Another way to observe the effects obtained before is by representing graft level or conversion versus peroxide concentration [POx] for different constant initial MAH concentrations $[MAH]_0$ (Figs. 3(A and B)). In Figure 3(A) it can be noticed that the higher the $[MAH]_0$ the higher the

Table III   Statistical Parameters of the Analysis of Variance

	r^2	Sum of Squares Mean	Pure Error	Confidence Factor (%)	Deviation due to Pure Error (%)
Grafting level					
Solution	0.871	0.144	0.090	98.9	2.8
Melt	0.917	0.454	0.010	99.5	1.3
Conversion					
Solution	0.934	122.236	1.193	99.6	0.9
Melt	0.969	75.475	1.277	99.8	1.1
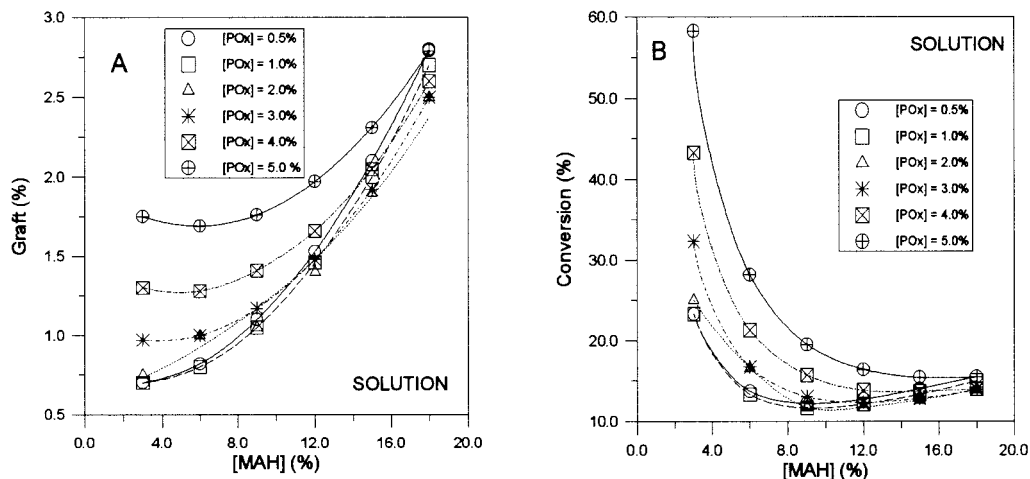
Figure 2 Evolution of grafting level (A) and conversion (B) versus maleic anhydride initial concentration at different amounts of initiator for a modification process of atactic polypropylene in solution.

grafting level. However grafts tend to suffer only little variations. This may be explained by an excess of radical activity that might be transferred to the solvent. The separation existing between isolines is higher when $[MAH]_0$ is higher, and this effect is more evident at the lowest values of $[POx]$. The latter seems to confirm the important role played for $[MAH]_0$ up to an optimum concentration added to the reactor. When talking about conversion [Fig. 3(B)], as it would be expected, conversions are the highest when $[MAH]_0$ is the lowest, and besides this variable looks to have a very sharp influence for a given peroxide concentration. We can conclude then that when there is a little amount of monomer in the media the peroxide has created such a number of active centers in the polymer that they are suddenly occupied by the polar monomer and then the possibility to lose the activity by reacting to the solvent is minimized. However, when $[MAH]_0$ increases the conversion trends to equilibrate itself, that is, peroxide level becomes less and less important, transference to the solvent gets more and more influence.
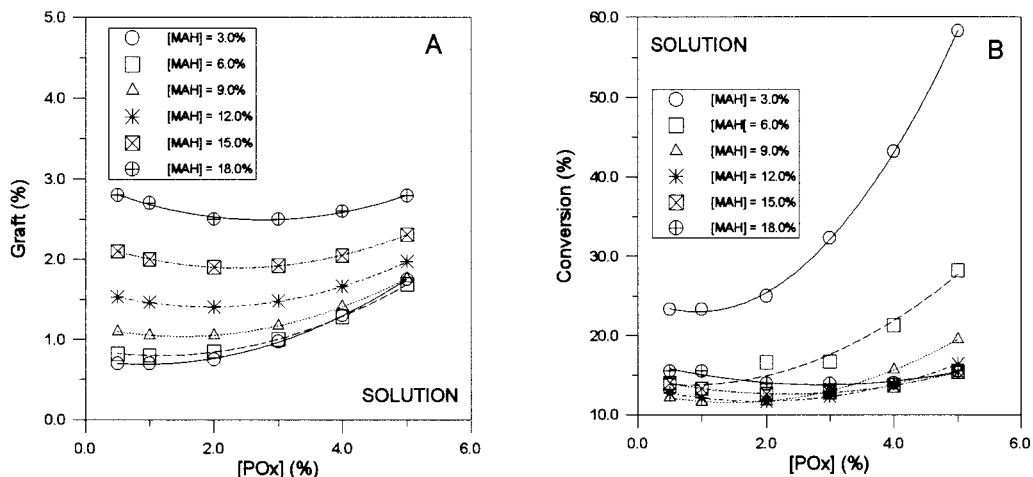
Figure 3 Evolution of grafting level (A) and conversion (B) versus initiator concentration at different amounts of initial maleic anhydride concentration for a modification process of atactic polypropylene in solution.

From all the above-mentioned it may be appreciated that the maximum grafting level was around 2.5% and conversion about 60% when higher. However, in Figures 4 and 5, representing data obtained from a process in the melt, it can be seen that maximum grafts were around 4.5% and the conversion level up to 80%. All these may be explained by the absence of solvents in a molten polymer. That is, when initiator creates radicals they only can be transferred to the polymer, or what is the same, when we are carrying out a functionalization process in the molten state the same polymer can react to MAH acting as a "solvent" for the graftable species at the same time. Then when activity is transferred to the polymer chain which must transfer its activity to the neighborhood, polymer chains are closer to each other than in solution, and then MAH not previously reacted may be bonded now to the backbone of the polymer.

Then, in the molten state (and contrary to what happened in solution) not only the grafting level grows when the level in the media increases, grafting level does also by the additional possibilities to extend the reaction yielding through the transference to the polypropylene "solvent" chains. Obviously this situation must be ending all along the time, and, in fact, may be explained assuming all the radicals existing at a given reaction time (we are studying a dynamical process) they only can be used in the grafting reaction or in the degradation reaction.

It must be noticed in Figure 4(A) that the maximum level of grafting is reached when $[POx]$ values are in a range between 2 and 3%. From higher values an involution in the grafting level is produced. Assuming the nature of the reaction taking place in the polymer bulk it must be expected an optimum of grafting for a certain value of $[MAH]_0$ present. That is what seems to be deduced from the plot in Figure 4(A), being next to 10% in $[MAH]_0$. When studying the conversion plot in Figure 4(B) we conclude in the same sense there is an involution in the system when concentration levels of peroxide are between 2 and 3%. This plot exhibits a linear evolution of conversion when correlated to $[MAH]_0$ except for the highest level of peroxide considered. The latter seems to support the reaction mechanism proposed because it suggests that for radical levels above to a certain value the degradation reaction increases rapidly and then, consequently, the grafting level decreases because of the efficiency loss for grafting of the generated radicals.
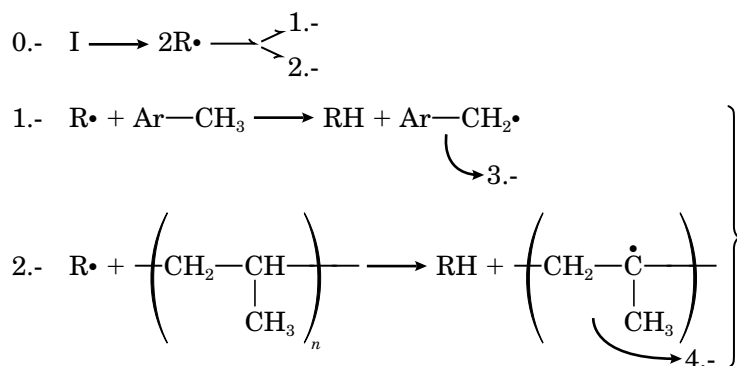
In Figure 5 the evolution of grafts when varying peroxide for different fixed amounts of MAH have been plotted. The same conclusions as in Figure 4 can be extracted. Besides the fact of concluding a maximum graft may be reached for a concentration of maleic anhydride between 9–12%, the evolution of grafting seems to suggest again the interfacial phenomenon governing the process. These results are supporting the interpretation based on solubility aspects in terms of the amount of $[MAH]_0$, which is such that all these molecules cannot be totally solved in the polymer but only a certain number of MAH groups.[30] In fact, when involution is produced we can appreciate a change of slope in curves. By comparison of curves 2 and 5, corresponding to $[MAH]_0$ values of 6% and 15%, respectively, we appreciate that the grafting level of curve 2 is higher than curve 5, until values in the peroxide level next to 3%. The latter would be congruent with the limited solubility assumption of MAH in the polymer bulk.[30]

From values higher than this peroxide concentration the tendency is just the opposite. Now the degradation in the polymer increases rapidly with the percent level of peroxide, then shorter chains appear and so a sharp increase of specific surface and mobility in the system allowing the chains to have higher mobility and, as consequence, higher solubility of maleic anhydride in the polymer, making easier to bond itself to an active center. The same effect can be concluded from curves in Figures 4 and 5. So, Figure 5(B) shows the evolution of conversion as a function of initiator level for different amounts of MAH in the reaction media. Again we can observe, as it would be expected, that conversion is correlated inversely to the MAH level. Besides, a critical value for $[POx]$ is also concluded (2–3%). This plot again confirms the initiator influence concluded before, suggesting the reversible character the grafting reaction has.

All the previously discussed was done in order to check the proposed[22] reaction mechanism for that process which would be valid either for the solution or in the melt process. The present article suggests the processes occurring can be divided in two ways.
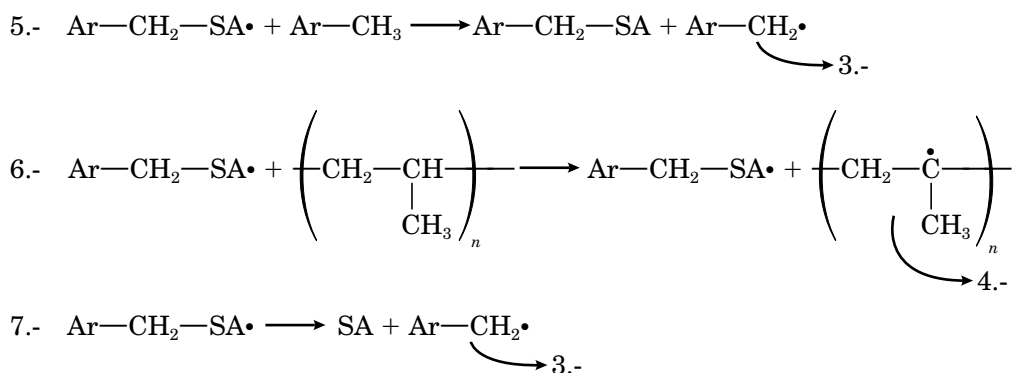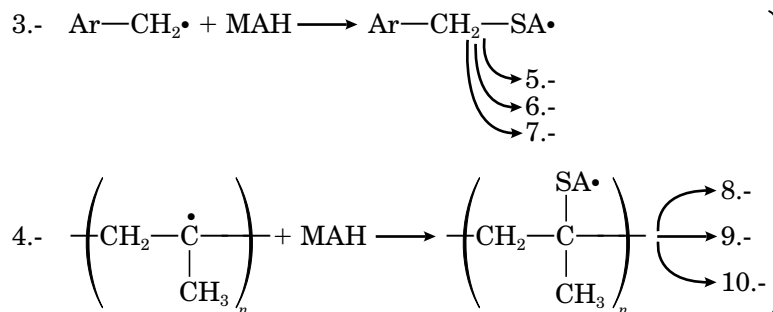
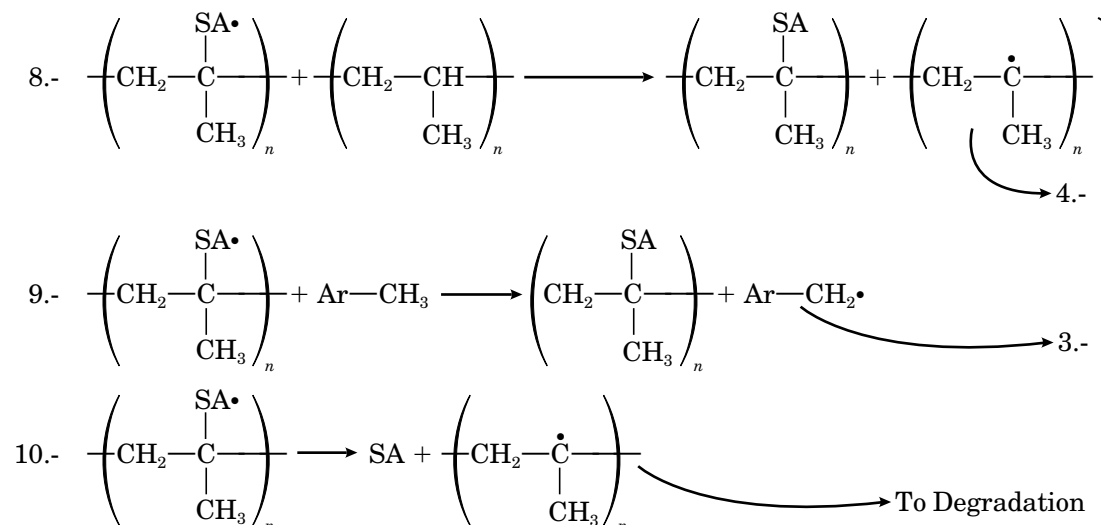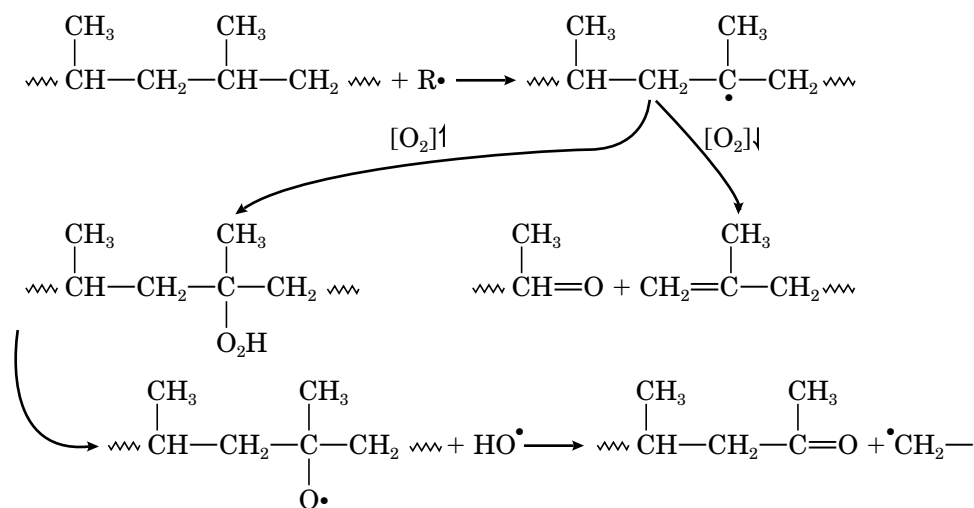On one hand, at the beginning of the reaction we have:

$$0.- \quad I \longrightarrow 2R\bullet \longrightarrow \begin{cases} 1.- \\ 2.- \end{cases}$$

$$1.- \quad R\bullet + Ar-CH_3 \longrightarrow RH + Ar-CH_2\bullet \searrow 3.-$$

$$2.- \quad R\bullet + \left(CH_2-\underset{\underset{CH_3}{|}}{CH}\right)_n \longrightarrow RH + \left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\bullet}{C}}\right)_n \searrow 4.-$$

where:

$Ar-CH_3$ would be solvent molecule and

$\left(CH_2-\underset{\underset{CH_3}{|}}{CH}\right)_n$ would be repetitive unit on the macromolecule backbone.

On the other hand, and in accordance with our findings, we must consider the following species which are generated while time of reaction goes by:

$$3.- \quad Ar-CH_2\bullet + MAH \longrightarrow Ar-CH_2-SA\bullet \begin{cases} 5.- \\ 6.- \\ 7.- \end{cases}$$

$$4.- \quad \left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\bullet}{C}}\right)_n + MAH \longrightarrow \left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{SA\bullet}{|}}{C}}\right)_n \begin{cases} 8.- \\ 9.- \\ 10.- \end{cases}$$

$$5.- \quad Ar-CH_2-SA\bullet + Ar-CH_3 \longrightarrow Ar-CH_2-SA + Ar-CH_2\bullet \searrow 3.-$$

$$6.- \quad Ar-CH_2-SA\bullet + \left(CH_2-\underset{\underset{CH_3}{|}}{CH}\right)_n \longrightarrow Ar-CH_2-SA\bullet + \left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\bullet}{C}}\right)_n \searrow 4.-$$

$$7.- \quad Ar-CH_2-SA\bullet \longrightarrow SA + Ar-CH_2\bullet \searrow 3.-$$

8.- $\left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{SA\bullet}{|}}{C}}\right)_n$ + $\left(CH_2-\underset{\underset{CH_3}{|}}{CH}\right)_n$ $\longrightarrow$ $\left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{SA}{|}}{C}}\right)_n$ + $\left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\bullet}{C}}\right)_n$

$\longrightarrow$ 4.-

9.- $\left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{SA\bullet}{|}}{C}}\right)_n$ + Ar—CH$_3$ $\longrightarrow$ $\left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{SA}{|}}{C}}\right)_n$ + Ar—CH$_2\bullet$

$\longrightarrow$ 3.-

10.- $\left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{SA\bullet}{|}}{C}}\right)_n$ $\longrightarrow$ SA + $\left(CH_2-\underset{\underset{CH_3}{|}}{\overset{\bullet}{C}}\right)_n$

$\longrightarrow$ To Degradation

The degradation reaction scheme is classically written as follows:

$\overset{\sim\sim}{} \overset{}{CH}-CH_2-\underset{}{\overset{\overset{CH_3}{|}}{CH}}-CH_2 \sim\sim$ + R• $\longrightarrow$ $\sim\sim CH-CH_2-\underset{\underset{\bullet}{}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim\sim$

with CH$_3$ on the first CH.

$[O_2]\uparrow$ $[O_2]\downarrow$

$\sim\sim \overset{\overset{CH_3}{|}}{CH}-CH_2-\underset{\underset{O_2H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim\sim$ $\sim\sim \overset{\overset{CH_3}{|}}{CH}=O + CH_2=\underset{}{\overset{\overset{CH_3}{|}}{C}}-CH_2\sim\sim$

$\longrightarrow \sim\sim \overset{\overset{CH_3}{|}}{CH}-CH_2-\underset{\underset{O\bullet}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2 \sim\sim$ + HO$^\bullet$ $\longrightarrow \sim\sim \overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{C}=O + {}^\bullet CH_2-$

where the conditions of the lowest oxygen concentration would be the case of applicability in our experimental runs, either by the presence of the thermal stabilizers or when reactions were conducted under N$_2$ atmosphere.

It must be noted that reactions 1, 3, 5, 6, and 7 would be concerned with the classical transference to the solvent effect,[24] meanwhile the molten state process would be to change the solvent molecule in steps 1, 3, 5, 6, and 7 by another chain of polypropylene. Consequently, 1 is similar to 2, 3 passes to be identical to 4, and 5, 6, and 7 would be the same as 8, 9, and 10, respectively.

Influence of the Kind of Solvent

As mentioned before when we use a solvent in the process of chemical modification it can be assumed that part of the active species to be grafted are going to react to the solvent, and then a lower reaction yielding can be expected if compared to a process carried out in the molten state. In other words, when the reaction takes place in solution a part of MAH is going to the polymer and other to the solvent. However in the melt process part of MAH is going to the polymer and the rest to the polymer acting as "solvent," that is, MAH is
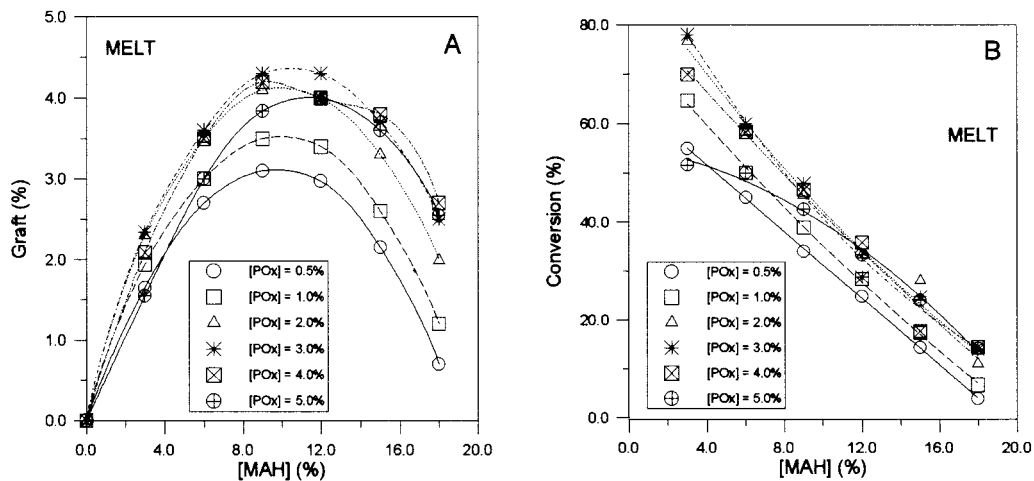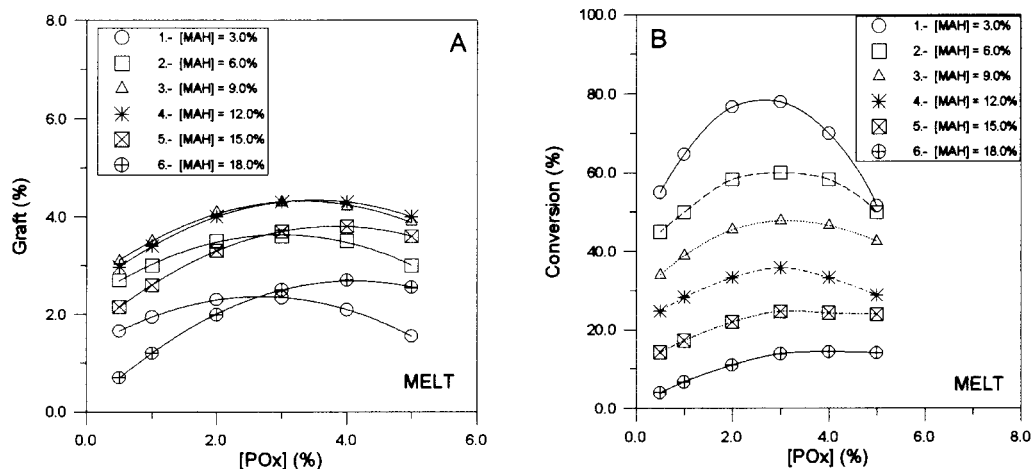
Figure 4 Evolution of grafting level (A) and conversion (B) versus maleic anhydride initial concentration at different amounts of initiator for a modification process of atactic polypropylene in the molten state.

always obliged to react to the polymer. Then higher graft and conversion levels must be obtained when reactions were conducted in the melt as it could be concluded from Figures 2–5.

At this point it would be obvious that not only the solvent present has influence in reaction yielding, but the kind of solvent, too. There are works in literature reporting differences between grafting reactions carried out in different isomers of xylene,[24] different behavior of benzene and xylene,[23] and the great capability shown for decaline to get activity and grafts from the reaction media.[51]

In these terms Table IV compiles the results obtained at the indicated reaction conditions. It could be observed that, despite the favorable effect it ought to suppose the higher reaction temperature, the grafting level obtained by using decaline as solvent was almost twice lower than that obtained by using xylene. As it has been mentioned before if we remember the statistical parameters of the fits from the experimental runs, which were compiled in Table III, we appreciate the accuracy (excellent in both cases) is better for the data coming from the process in the melt than for the performed in solution. This aspect can be easily ex-

Figure 5 Evolution of grafting level (A) and conversion (B) versus initiator concentration at different amounts of initial maleic anhydride concentration for a modification process of atactic polypropylene in the molten state.
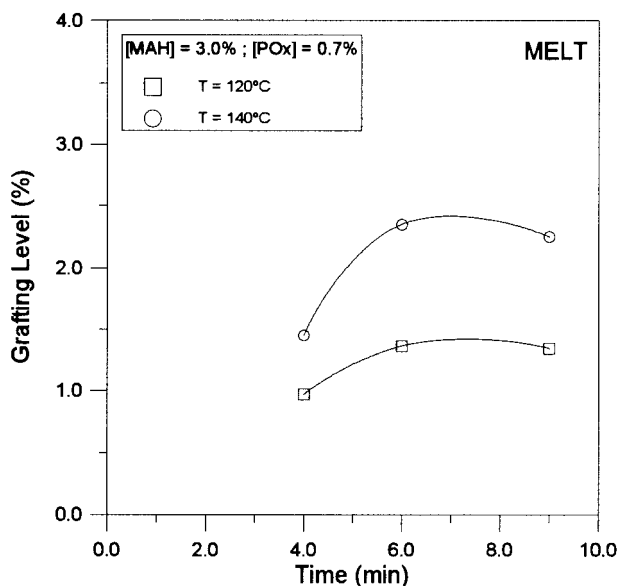
Figure 6 Evolution of grafting level with reaction time at 120 and 140°C as working temperature (a-PP in the melt) at the given reaction conditions.

plained now by the fact the models have been built up by not including parameters associated with the kind and influence of solvent used. This latter looks, then, to suggest the solvent plays an important role in the reaction yielding we are supporting, mainly in the sense to cause a decrease in the maximum grafting feasible in the modified polymer.

Effect of Working Temperature

In order to study the effect that temperature plays in the process we performed two experimental sets for modifying atactic polypropylene in the melt at two different working temperatures (120 and 140°C) and the same concentrations of reactives ([MAH] = 3%; [POx] = 0.7%). In Figure 6 grafting values versus reaction time have been plotted and, as expected, grafting levels are higher at 140 than at 120°C. This agrees with the fact that at 120°C the activity of the dycumil

peroxide decreases almost 40% if compared with that at 140°C,[22,52,53] and in fact, decrements of 32, 37, and 37% in conversion at 4, 6, and 9 minutes, respectively, are obtained. From that the favorable effect that temperature has on the reaction yielding, when it is only this variable what changes, could be concluded. However, when we compare two processes (melt and solution) being performed at the same temperature (140°C) (Figs. 2–5) we can appreciate again the solvent influence is very high, and even in the case of working at higher temperatures (Table IV) the effect of solvent has more negative influence on the grafting level than the temperature-favorable effect had.

Reaction Time Dependence

Up to now, in isochrona experiments, we have compared grafting or conversion values of polypropylenes coming from batches obtained at six minutes of reaction time. This latter was chosen because, according our previous experiences[18,19,22] it is where the maximum of succinic anhydride grafted into the polymer could be reached. Besides, we proposed that for higher values of reaction time the degradation reactions in the polymer bulk begin to be more and more important. Obviously, when trying to check the above-mentioned possibilities first step would be the study of the grafting evolution all along the reaction time. On the other hand, we cannot forget that transference processes involved in the termination step have not only intermolecular character, that is, only concerning the solvent molecules (either those of classical solvents or the macromolecular solvents, as they are the segments in the polymer bulk), but also the intramolecular transference of activity at both sides of an active site, must be considered.

So, we have studied the evolution of the grafting level all along the time (from 5 min to 15 min) keeping constant the concentration of MAH (9%) and peroxide (2%). These values were chosen due

Table IV   Experiments in Solution at the Indicated Reaction Conditions and Solvents

| Weight Ratio					
a-PP/Solvent	a-PP/MAH	[POx] (%)	T (°C)	Solvent	Grafting (%)
1/5	1/1	0.75	140	Xylene	2.11
			180	Decalin	1.18

to the first concluded at this work about the values conducting the highest degree of modification.[22] Reaction time dependence has been studied both in solution and in the melt at the same working temperature, and besides the influence of temperature and stereospecificity have been tested by comparison to data obtained when modifying isotactic polypropylene at 190°C.[18,19]

In Figure 7 experimental values of grafting in order to check the validity of the experimental model obtained have been plotted. In fact, when graft versus reaction time for atactic polypropylene is plotted, a min−max evolution typical of quadratic responses evolutions can be observed. This kind of behavior has been reported in literature when studying the peroxide evolution in PVC[54] and a similar oscillation phenomenon has been reported in other cases of reactive modification of polypropylene in the molten state by grafting hindered amine light stabilizers into PP.[55−58] In those works authors proposed that reaction occurring was the following:

$$A^{\bullet} \underset{[H^{+}(e^{-}I]}{\overset{[H^{+}(e^{-}I]}{\rightleftharpoons}} AH$$
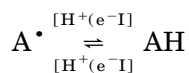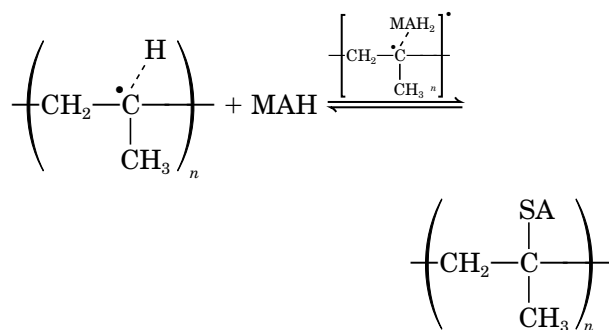
accepting then the existence of an equilibrium between the involved species.

At this point the dynamical situation for the PP/MAH system could be written as:
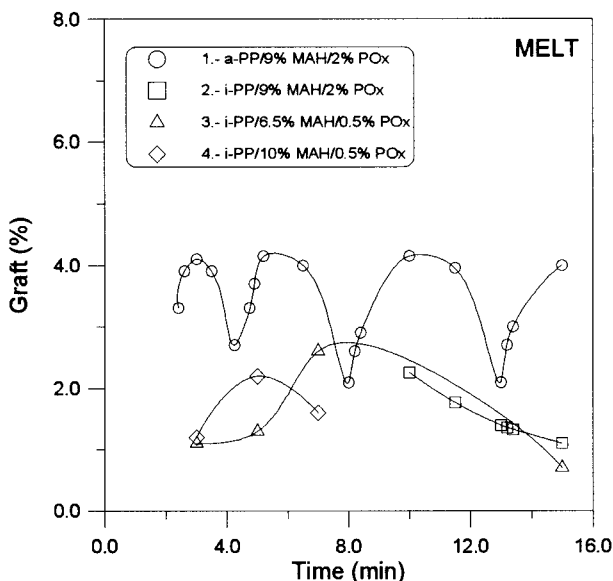
Figure 7 Evolution of grafting level reached for atactic and isotactic polypropylene all along the reaction time and in the molten state at the given reaction conditions.
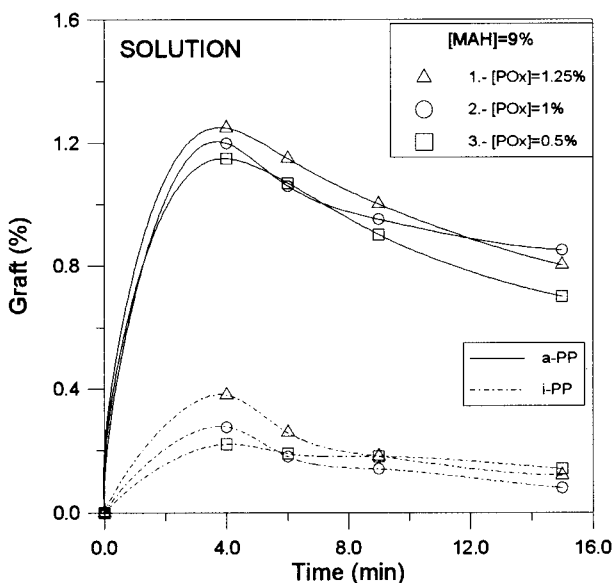

where SA would be the succinic anhydride groups.

If the reaction scheme written before for the case when "solvent" molecules are considered to be polymer chains, or better, segments of those chains, it is important to take in mind the existence of activity transfer inter or intrachain which possibilities cannot be easily distinguished. Nevertheless the latter would be dramatically affected by the conformational possibilities of the polymer backbone. In other words, sharp differences between grafting levels reached on polypropylenes must be expected in both stereospecific or nongrades. This is exactly what we found from data in Figure 7, that is, we find values almost twice higher for a-PP than for i-PP.

Furthermore, in the surroundings of the new active site created inside a certain chain segment, according to the previous one scheme, two situations may be taking place. On one hand it may happen that a new MAH molecule would be near enough to this active site and then a new succinic anhydride group would be grafted. This situation would be the most favored at the first stages of the process and more quickly when the level of free MAH in the reaction media is higher.

In the way the reaction is in progress a second situation would become more and more important, that is, the possibilities that interchain active sites don't find MAH molecules ready to be grafted. Then the process transfer would continue, both intra and intermolecular segments, conducting to degradation processes.[59] Obviously in the mechanistic point of view the basic units undergoing the process are always the same, but not in numerical terms because they are dynamically changing all along the reaction time.[22] These two kinds of contributions, intra and interchain activity transfer possibilities, could be checked with our suggestions about the role of the solvent if we compared, as it was done in Figure 7, both polypropylenes when reactions are performed by using classical solvents.

In fact, experimental data in Figure 8 have been plotted coming from the processes in xylene solution either for atactic or isotactic polymer and with no dependence of working temperature (140°C in both cases). In that plot it can be noticed the favorable effect the absence of stereospecificity again has over the reaction yielding besides the evolution of the process is similar in both polymers (i-PP and a-PP). Again in both cases a maximum level of grafting and then a decay with reaction time can be observed. Because here solvents are not segment chains of polypropylene, activity transfer means the end of the grafting possibilities, so very low values on the atactic polymer are obtained if we compare with those obtained in the molten state.

Nevertheless, the grafting on atactic polypropylene results to be significatively higher than that on isotactic polymer, near three times higher, confirming the importance of the free conformational intrachain possibilities in order to obtain a polymer containing grafted groups. It is by these reasons why a chemisorption phenomenon which kinetic constants would vary all along the time was proposed in Ref. 22 as a possible path to explain the phenomenon. Work in this sense is now in progress. From those results the heterogeneous distribution of the grafted groups all along the polymer backbone is immediately emerging, and obviously ought to affect the behavior of the modified polypropylenes. Work dealing with thermal behavior of those materials will be published soon.

CONCLUSION

We can conclude that it is possible to explain the process by modelization starting from the Box–Wilson experimental design results, as it was demonstrated by performing additional experiments confirming this affirmation. These models let us appreciate there are many competitive effects very difficult to isolate when researching classical random experimental methods. Besides, they have been proved to be very efficient when explaining the different effects the process variables have on the reaction yielding.

As mentioned before there are many competitive effects having influence in the reaction yielding. Then we conclude that with independence of the media the reaction takes place the absence of stereoregularity is proved to have a very positive effect in the amount of grafts obtained. Also, the influence of the kind of solvent, even higher than temperature contribution, has been demonstrated. However, at every case the existence of a certain critical value in reactive concentrations and reaction time conducting to the highest levels of grafting has been concluded.

Figure 8 Evolution of grafting level reached for atactic and isotactic polypropylene all along the reaction time and in solution at the given reaction conditions.

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