

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

II. A Comparison of the Batch Solution and Molten State Processes

J. M^a. García-Martínez, S. Areso, E. P. Collar

Departamento de Física e Ingeniería de Polímeros, Instituto de Ciencia y Tecnología de Polímeros, CSIC, C/Juan de la Cierva 3, 28006 Madrid, Spain

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ABSTRACT: This article compares the batch solution and molten state chemical modification of an atactic polypropylene to yield a grafted polypropylene. Short reaction times appear to be sufficient and indeed necessary for the highest graft yields to be obtained if degradative processes occurring in both reaction media are to be avoided. The consecutive reactions for the optimized grafting reaction pathway were proposed for the solution process in an earlier article. The present work attempts to correlate this pathway with that of the molten state process. Grafted succinic anhydride groups react with two resorcin molecules to yield grafted

succinyl-fluorescein groups. This work considers the resorcin units as true molecular probes, to be able to stabilize and activate the complexes formed between the succinic anhydride groups and the propylene sequence. This work shows the unsteady and later dynamic character of the process. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 345–351, 2007

Key words: modified polypropylenes; grafting; kinetic modeling; reaction pathway; unsteady processes

INTRODUCTION

More than 700 references in four reviews published in the last 5 years^{1–4} reveal the amount of research into the grafting of polar monomers onto polyolefins. However, despite recent publications^{5,6} on the chemical modification of polyolefins (especially polypropylene) via the grafting of polar groups (especially maleic anhydride (MAH)), the exact nature of the chemical pathways involved in the production-grafted polyolefins remains poorly understood.

A reaction pathway for obtaining grafted atactic polypropylenes (a-PP-Gs) in solution was recently proposed by the present authors.⁷ The main aim of this new article was to correlate this reaction pathway with the results obtained when performing the grafting reaction in a batch molten state reactor. Though very complex, this process could be of great economic importance.

EXPERIMENTAL

Materials

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

Procedures and characterization

Batch solution reactions were performed in a conventional glass flask equipped with a reflux column, a thermal probe, and an additional feed entrance. The reaction volume was 750 mL, and the temperature was 140°C (to that of the boiling solvent). The reactant and initiator concentrations and the reaction time were chosen as independent variables. Once the polymer was dissolved in boiling xylene (1/5 w/w polymer/

Correspondence to: E. P. Collar (ecollar@ictp.csic.es).

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TABLE I
Properties of the Atactic Polypropylene Used
in the Present Work

| | |
|------------------------------|--------|
| Molecular weight | |
| M_w | 54,000 |
| M_n | 2700 |
| HI (M_w/M_n) | 20 |
| DSC | |
| T_g (°C) | -22.4 |
| ΔH_m (J/g) | 10.6 |
| T_m (°C) | 113.0 |
| ΔH_c (J/g) | -20.1 |
| T_c (°C) | 75.9 |
| Density (g/cm ³) | 0.85 |

solvent ratio), to which 0.1% w/w of the thermal stabilizer had been added, the preheated xylene-dissolved MAH was incorporated. One minute later, this was followed by peroxide, which was also preheated and dissolved in xylene. This moment was taken as the reaction start point. Once the set reaction times had elapsed, the solution was rapidly precipitated in cool methanol, filtered, and the polymer was recovered and vacuum-dried for characterization. To ensure there was no free MAH trapped in the recovered grafted polymer bulk, a series of randomly chosen samples were dissolved, precipitated, and characterized, as described later. No differences in grafting values were appreciated.

Batch molten state reactions were performed in a Rheomix 600 mixer chamber attached to a Haake Rheocord 90 Series apparatus. The reaction temperature was 140°C. The dry blend of the reactants and thermal stabilizer were fed into the reactor. Once molten and once the torque and melt temperatures had stabilized, an initiator or catalyst (for radical or condensation reactions, respectively) was incorporated. This moment was taken as the reaction start point. Once the reaction was complete, the reactor was opened, and the reactant mass rapidly immersed in an ice bath.

The a-PP-G produced was dissolved for washing in xylene, recovered by precipitation in methanol, and vacuum-dried in preparation for characterization. A number of authors have previously attempted to qualitatively and/or quantitatively characterize these a-PP-Gs using FT-IR spectroscopy, NMR, and by determining their thermal and thermo-optical behavior.^{8–18} In the present work, however, the grafting levels of a-PP-G samples were determined using an improved hot-titration method.^{8,19} One gram of polymer was dissolved for 60 min in 150 mL of refluxed xylene-butyl alcohol–water mixture. The hot solution was then titrated, not allowing it to cool, with an excess of 0.05N ethanolic KOH, using thymol blue as an indicator. The deep blue solution obtained was back-titrated to a yellow end point by the addition of 0.05N isopro-

panolic HCl. Carboxylic acid groups attached to the a-PP-G were titrated in the absence of water. The results are expressed as moles of grafted group per gram of grafted polymer ($\text{mol g}^{-1}_{\text{a-PP-G}}$). In this way, negligible titration values ($<10^{-6}$) were obtained for the original polymer.

The a-PP-G samples were further characterized by *n*-heptane-selective extraction, using a conventional Soxhlet cartridge. Three different weight fractions were obtained from each sample: a nonsoluble fraction, retained by the Soxhlet cartridge; a soluble fraction, recovered by filtration after precipitation in methanol; and a third soluble fraction, recovered as a solid powder, after evaporation of the concentrated solvent/precipitant mixture to dryness.

RESULTS AND DISCUSSION

Background

The overall mass balance of the species involved in the modification of polypropylene in solution by MAH in the presence of a peroxide initiator has already been proposed.⁷ This was based on a series of grafting experiments performed in batch reactors (both in solution and in the molten state²⁰) as well as in continuous molten state reactors.²¹ The role of stereospecificity and the tertiary number of carbons as structural variables of the macromolecular reactants was examined in a more recent work.^{9,12}

The two-step modification process—a grafting step followed by a condensation reaction between the grafted succinic anhydride (SA) groups and resorcinol to yield grafted succinylfluorescein (SF) groups—involves only single SA groups grafting onto the a-PP-G backbone.⁹

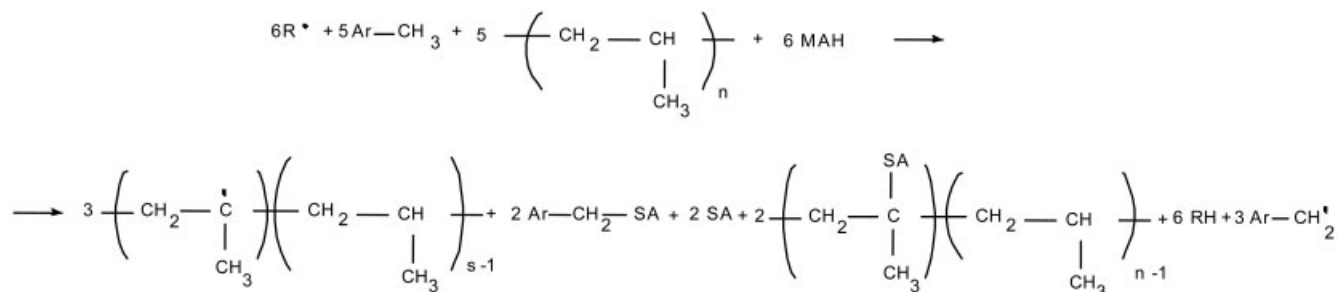
Starting with the mass balance of the species for the process performed in solution, the results of the present work allow the molten state reaction pathway to be correlated to the solution pathway.

Consecutive reaction model: Balance of species involved in the molten-state process

Scheme 1 shows the mass balance of the species involved in the batch solution process of polypropylene modification by MAH grafting in the presence of symmetric peroxide:⁷

where *s* sequences correspond to the macroradicals generated on polypropylene chains by activity transfer, each time one stable polypropylene/SA bond is obtained.

When performed in the molten state, i.e., when the polypropylene segments unable to yield grafted species act as “solvent” polypropylene—named as *s'* sequences—they can substitute those of the solvent in Scheme 1. This provides Scheme 2:



Scheme 1 Species mass balance for the batch solution process of MAH grafting in polypropylene in the presence of a symmetric peroxide.⁷

Here it can be seen that for each SA group grafted onto the PP backbone, a second is attached, but involving some other sequence of the “solvent” PP. Further, every two SA groups grafted onto a-PP-SA requires that three PP radicals remain active, i.e., transferring radical activity from the reactant mass, which will continue until full deactivation with increasing reaction time. These three active radicals are, by definition, unable to graft MAH. They therefore manifest their activity through, for example, degradation processes such as chain scissions (in the case of PP) or by reacting with other species in the reaction mass (with the exception of MAH) such as the thermal stabilizer molecules. This can slow down or even stop the degradation processes.

The two grafted SA units obtained in the species balance for the batch solution process (Scheme 1) may be considered grafted onto equivalent reactive sites (propylene sequences on the PP backbone). However, they must be essentially different to the two grafted SA groups obtained in the molten state, whose reaction surroundings are different because of the absence of solvent molecules.

Scheme 2 provides a coherent explanation for earlier findings^{20,21} regarding the higher grafting levels of i-PP-SA obtained with the molten state process than with the batch solution process (always with the same concentration of peroxide and MAH, with respect to polypropylene). These findings were confirmed when the macromolecular coreactant was a-PP, as discussed

elsewhere.^{8,9,13} As Scheme 2 shows, the presence of three active PP radicals for each two SA groups grafted at any given reaction time is coherent with the unsteady character of the reaction proposed.⁸

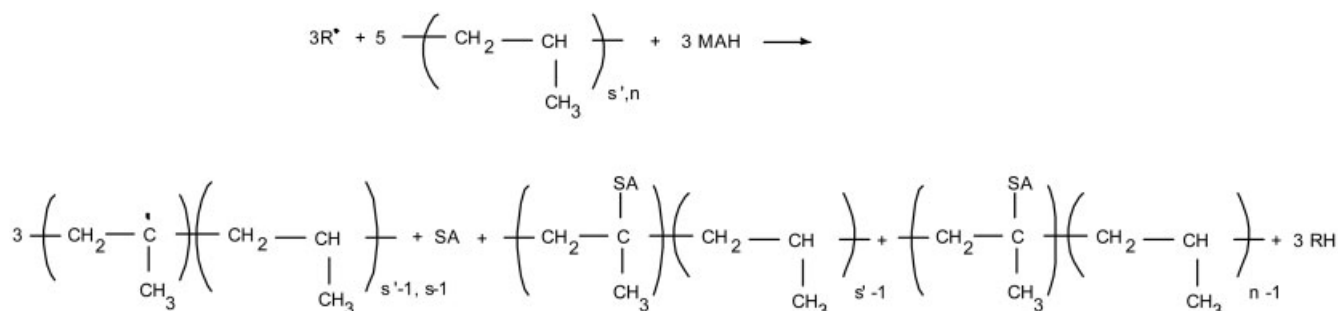
For the highest grafting levels to be obtained, cooling is required at the end of either process. This is achieved by opening the reactor to allow rapid cooling during precipitation in cool methanol in the batch solution process, or by immersion of the reactant mass in ice in the molten state process.

After washing the product to remove any non-grafted or unreacted species, the recovered polymer, now ready for characterization, should have a grafting level as close as possible to that obtained inside the reactor, just before it was opened.

The two-step (radical/condensation) process that yields polypropylene modified with SF groups¹¹ shows that the unsteady nature of the process, which provides the high number of polar groups grafted onto the polypropylene backbone, is a function of the reaction conditions. This validates the mechanistic approach first proposed,⁷ which was based on the classical consecutive reaction model^{22,23} shown in Figure 1.

Validation of the proposed model of consecutive reactions

This was undertaken with the a-PP/solvent/MAH system, taking the moment the peroxide was incorpo-



Scheme 2 Species mass balance for the molten state batch process of MAH grafting in polypropylene in the presence of a symmetric peroxide.⁷

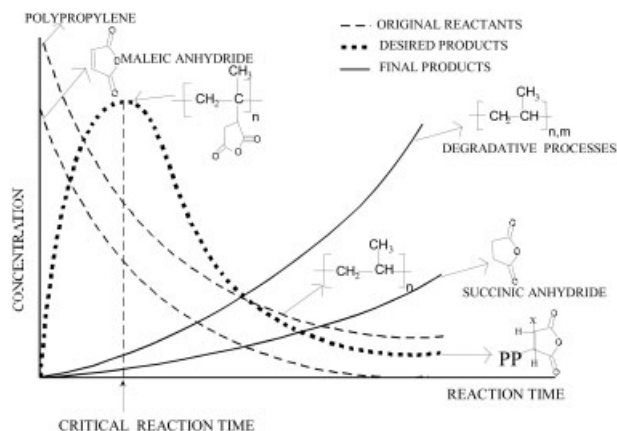


Figure 1 Changes in the concentration of reactants over the reaction time for a classical consecutive reaction model applied to the radical modification of PP by MAH.

rated as the start of the reaction. Five experiments were performed maintaining the initial w/w peroxide and MAH concentrations at 2.25% and 48.5%, respectively. The a-PP/solvent w/w ratio was 1/5.

The reactions were performed either as a single radical process or as a two-step radical/condensation process, in which the SA groups first grafted (in the presence of a zinc chloride catalyst) could become SF groups through a condensation reaction involving two resorcinol molecules. Table II shows the reaction times recorded and the grafting yields obtained for each process, expressed as the acid numbers obtained by the titration method (described earlier) in the presence or absence of water. This shows the number of carboxylic acid groups yielded by each a-PP-G sample.

According to the condensation reaction in Scheme 3, each SF produced has a carboxylic acid group at its end.⁹

This can be titrated with no water in the titration medium. Table II shows the “nonwater” results of the acid number, Acid Nr, (expressed as mg_{KOH} per gram of grafted polypropylene), which were calculated using eq. (1), where V_{KOH} is expressed in milliliters:

$$\text{Acid Nr.} = \frac{V_{\text{KOH}} N_{\text{KOH}} M_{\text{W}_{\text{KOH}}}}{g_{\text{aPP-G}}} \quad (1)$$

From this, it is easy to calculate the w/w concentration of grafted groups using the following eq. (2):

$$\text{Graft (\%)} = \frac{(\text{Acid Nr.}) M_{\text{W}_{\text{G}}}}{561 \chi} \quad (2)$$

where χ is the number of carboxylic acid groups in the titrated group—this takes a value of one for the SF-grafted groups, according to the reaction in Scheme 3.

When SA is the grafted group to be titrated, the anhydride which will be converted into the acid group must be hydrolyzed, and water must therefore be present in the titration medium. The χ parameter in eq. (2), therefore, takes the value of two.

Table II shows the acid number values to be very different when determined in the presence or absence of water. Spontaneously hydrolyzed anhydride groups (for example, those hydrolyzed by the two water molecules removed from the reaction medium when SA groups become SF groups) are potential contributors to the nonwater acid number titration values. However, the value of zero obtained for the nonwater titrated a-PP-SA sample in Table II allows this to be disregarded.

Assuming that all the nonwater titration values correspond to acid groups on the grafted SF groups, the number of grafted SA groups not converted into SF is obtained as the difference between the overall water and nonwater titration acid number values.

The almost constant ratio between the number of SF groups and the overall number of acid groups found by water titration analysis in the four experiments recorded in Table III (in which resorcinol was present in the condensation step) shows the number of unreacted SA-grafted groups obtained when the two-step reaction is complete (Table III).

Table III also shows the unsteady character of the grafting reaction. On comparing the total grafting

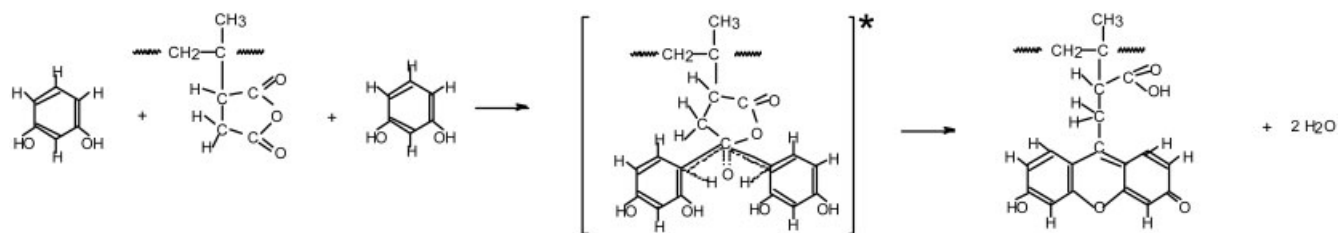
TABLE II
Experiments Where Resorcinol Plays a Role As Molecular Probe for the SA-Grafted Groups^a

| Sample | Reaction time (min) | | Acid number ($\text{mg}_{\text{KOH}}/g_{\text{aPP-G}}$) | | [RCOOH] ($10^4 \text{ mol}/g_{\text{aPP-G}}$) | | | |
|-------------|---------------------|-----------------------|---|----------------|---|------------|------|-----------|
| | Radical reaction | Condensation reaction | Without water (A) | With water (B) | Without water | With water | A/B | (B - A)/B |
| a-PP-SA | 10 | 0 | 0.0 | 34.6 | 0 | 6.1 | 0.00 | 1.00 |
| a-PP-SF (1) | 5 | 5 | 20.9 | 49.5 | 3.7 | 8.8 | 0.42 | 0.58 |
| a-PP-SF (2) | 10 | 5 | 13.6 | 29.8 | 2.4 | 5.3 | 0.45 | 0.54 |
| a-PP-SF (3) | 5 ^b | 5 | 11.2 | 23.9 | 2.0 | 4.2 | 0.47 | 0.53 |
| a-PP-SF (4) | 5 ^b | 5 ^c | 12.0 | 23.0 | 2.1 | 4.1 | 0.51 | 0.48 |

^a Titration results in the absence (A) or presence (B) of water.

^b a-PP-SA recovered from the batch solution reactor before performing the condensation step.

^c Condensation reaction step performed in the molten state.



Scheme 3 Reaction scheme for the obtention of chemically modified polypropylene by grafting of SF groups.⁹

level of the a-PP-SA and a-PP-SF (2) samples recovered from the reactor after 10 min of the radical step reaction, this was found to be 3.05×10^{-4} mol/g_{a-PP-G} for the a-PP-SA sample and it increased to 3.80×10^{-4} mol/g_{a-PP-G}; however, if the grafted polymer was kept inside the batch reactor for 5 more minutes, undergoing the second condensation reaction with resorcinol. If resorcinol was added to the reactor 5 min after the radical step had begun, [a-PP-SF (1)], polymers with the highest number of grafted polar groups were obtained -6.20×10^{-4} mol/g_{a-PP-G}. This is much greater than 3.10×10^{-4} mol/g_{a-PP-G}, obtained by stopping the radical step through opening the reactor and recovering the a-PP-SA produced up to that moment (samples [a-PP-SF (3) and a-PP-SF (4) in Table III).

Thus, if the a-PP-SA polymer (case of samples [a-PP-SF (3) and a-PP-SF (4)] is subjected to the condensation reaction, either in solution or in the molten state, the final numbers of SA- and SF-grafted groups are identical (Table III).

Termination processes and the distribution of grafted polar groups on the polypropylene backbone: Preliminary work

Why an almost constant SF/SA ratio (around 0.6 for samples in this work) should be obtained by the two-step grafting process in batch solution is an interesting question. This finding is in sharp contrast to that reported by the authors who have performed the reaction in the molten state. Under the present conditions,

all the SA groups grafted onto the a-PP-G appeared to yield SF groups during the condensation step with resorcinol.¹¹

Figure 2 shows the changes in grafting level over reaction time for the a-PP-G samples (circles and solid lines) (Table III), as well as the grafting values for the a-PP-G samples produced in the molten state (squares and dashed lines) at different reaction times, for both the radical and condensation steps (Table IV).

The ability of resorcinol to act as a molecular probe that stabilizes the SA groups on the polypropylene backbone throughout the reaction is clearly shown by the grafting value of the a-PP-SF (1) sample (6.20×10^{-4} mol/g_{a-PP-G}). In addition, there is a general trend for the molten state process to induce higher a-PP-G grafting values than does the solution process, even though their temperatures are identical (140°C), their initial w/w concentrations of peroxide are almost the same (2.1% for the molten state process and 2.25% for the solution process), and in spite of their initial concentrations of MAH (Table IV). The data plotted in Figure 2 (particularly those corresponding to the a-PP-SA sample as recorded in Table II) clearly show the very high risk of neglecting the early stages of the process—a problem of existing kinetic models for the grafting of polar monomers onto polyolefins.

Comparison of reactions in Schemes 1 and 2 shows that in the balances of the species involved in the solution and molten state processes, three polypropylene radicals remain active for every two SA groups

TABLE III
Titration Values for the Indicated Samples

| Sample | Reaction time (min) | | [RCOOH] belonging to anhydride groups (10^4 mol/g _{aPP-G}) | Grafting (10^4 mol/g _{aPP-G}) | | | | Grafting (% w/w) | |
|-------------|---------------------|-----------------------|---|--|-----|-------|-------|------------------|-----|
| | Radical reaction | Condensation reaction | | SA | SF | Total | SF/SA | SA | SF |
| a-PP-SA | 10 | 0 | 6.10 | 3.05 | 0.0 | 3.05 | 0.00 | 3.05 | 0.0 |
| a-PP-SF (1) | 5 | 5 | 5.12 | 2.50 | 3.7 | 6.20 | 0.59 | 2.50 | 3.7 |
| a-PP-SF (2) | 10 | 5 | 2.92 | 1.40 | 2.4 | 3.80 | 0.63 | 1.40 | 2.4 |
| a-PP-SF (3) | 5 ^a | 5 | 2.26 | 1.10 | 2.0 | 3.10 | 0.64 | 1.10 | 2.0 |
| a-PP-SF (4) | 5 ^a | 5 ^b | 2.00 | 1.00 | 2.1 | 3.10 | 0.68 | 1.00 | 2.1 |

^a a-PP-SA recovered from the batch solution reactor before performing the condensation step.

^b Condensation reaction step performed in the molten state.

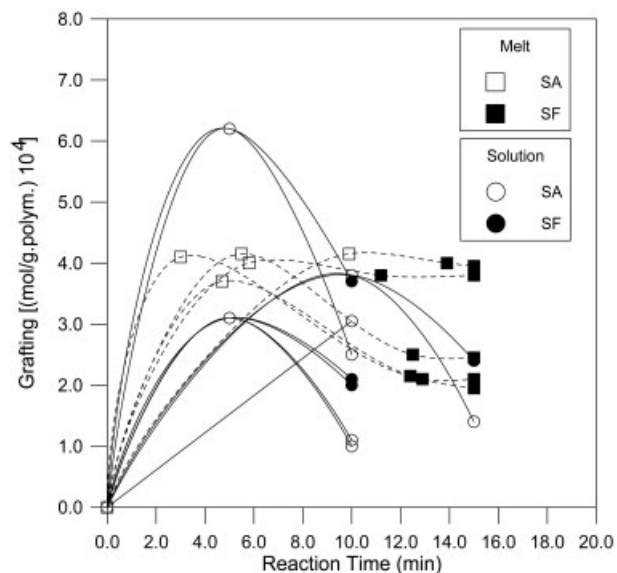


Figure 2 Grafting level versus reaction time for samples coming from solution (solid/circle line) or molten state processes (dashed/square line) (one- and two-step reactions).

grafted. These become involved in the termination of the radical step.

It is well accepted that disproportion and recombination are the two major processes involved in the termination step of the classical three-step radical processes. In the light of the present results, termination by disproportion would seem to be the dominant mechanism for the grafted species obtained in the molten state, while recombination between radical species yielding SA groups trapped between two polypropylene sequences may be responsible for some 40% of the SA units being unable to react with the resorcinol molecules. These could not undergo the structural rearrangement shown in Scheme 3. Such trapped SA groups would remain as SA-grafted units when the condensation step is complete.

For both the solution and the molten state reactions, the unsteady character of the process suggests a dynamic distribution of grafted groups along the polypropylene backbone. These would increase in

number until an optimum reaction time is reached. Once this has passed, an increasing number of grafted groups would form end chains. If the reaction is allowed to continue, a critical time would be reached, after which degradation processes would be the only means of deactivating the radical activity still remaining in the bulk of the reactant mass.

Table V shows three grafting population distributions for each of the a-PP-G samples produced by the batch solution and molten state processes. Three well-defined fractions were obtained by selective extraction in boiling *n*-heptane. The first was a nonsoluble fraction of a-PP-G unable to leave the Soxhlet cartridge. This was characterized by the highest grafting levels obtained for a single a-PP-G sample: in fact, its grafting value is close to the highest theoretically possible (according to sterical hindrance) for any given a-PP segment.

A second fraction from the “macroscopic” a-PP-G sample corresponded to soluble grafted chains that are able to leave the Soxhlet cartridge. These were recovered by classic precipitation in a nonsolvent, such as methanol. This fraction shows the lowest grafting levels—far below the average macroscopic graft value.

Finally, a third, soluble fraction—termed the soluble *ad infinitum* fraction—was recovered after solvent evaporation and vacuum-drying. This fraction was characterized by grafting values similar to those of the macroscopic average, and almost identical to those of the a-PP-G samples obtained by the batch solution process.

The last column in Table V shows good agreement between the macroscopic graft averages (i.e., that experimentally obtained and that obtained by mass balance between the three SA-grafted populations). For each of the batch solution a-PP-G samples, the three fractions show the decreasing weight sequence soluble > nonsoluble > soluble_∞, while those produced by the molten state process (with reaction conditions close to the optimum) follow the order soluble_∞ > soluble > nonsoluble. However, if the initial concentration of MAH is far from optimum, either by default or because of an excess of the optimum coating caused by the chemisorption process,⁸ an inversion occurs between the weight populations of the two soluble frac-

TABLE IV
Grafting Levels for the Two-Step Grafting Process of a-PP in the Molten State

| Sample | Radical step | | Condensation step | | | Overall process | | |
|--------|----------------------------|---|---------------------------------|---|---|------------------------|---|---|
| | t_{radical} (min) | Grafting SA (10^4 mol/g _{aPP-G}) | $t_{\text{condensation}}$ (min) | Grafting SF (10^4 mol/g _{aPP-G}) | Grafting SA (10^4 mol/g _{aPP-G}) | t_{end} (min) | Grafting SF (10^4 mol/g _{aPP-G}) | Grafting SA (10^4 mol/g _{aPP-G}) |
| BM-1 | 3.0 | 4.10 | 9.9 | 2.10 | 0.00 | 15.0 | 2.10 | 0.00 |
| BM-2 | 4.7 | 3.70 | 7.7 | 2.15 | 0.00 | 15.0 | 1.95 | 0.00 |
| BM-3 | 5.5 | 4.15 | 7.0 | 2.50 | 0.00 | 15.0 | 2.45 | 0.00 |
| BM-4 | 5.8 | 4.00 | 5.4 | 3.80 | 0.00 | 15.0 | 3.80 | 0.00 |
| BM-5 | 9.9 | 4.15 | 4.0 | 4.00 | 0.00 | 15.0 | 3.95 | 0.00 |

Process conditions: $T = 140^\circ\text{C}$; $[\text{MAH}]_0 = 9.0\%$ (w/w); $[\text{POx}]_0 = 2.1\%$ (w/w).

TABLE V
Boiling *n*-Heptane Selective Extraction Using a Conventional Soxhlet Cartridge: Results for Different Samples of a-PP-G

| Sample | Reaction medium | [POx] ₀ (%) | [MAH] ₀ (%) | t _r (min) | Grafting (10 ⁴ mol/g _{aPP-G}) | Soxhlet extraction [w/w (%)] vs. [Grafting (10 ⁴ mol/g _{aPP-G})] | | | Grafting mass Balance ^a (10 ⁴ mol/g _{aPP-G}) |
|---------|-----------------|------------------------|------------------------|----------------------|--|---|------------------|------------------------|--|
| | | | | | | Insoluble | Soluble | (Soluble) _∞ | |
| a-PP-SA | Solution | 2.25 | 48.5 | 10 | 3.05 | [25.0] vs.[11.45] | [68.0] vs.[0.42] | [7.0] vs.[3.53] | 3.38 |
| a-PP-SF | Solution | 2.25 | 48.5 | 10 | 6.20 | [35.6] vs.[19.87] | [59.0] vs.[0.14] | [5.34] vs.[6.24] | 7.46 |
| B1 | Melt | 2.10 | 0.51 | 15 | 0.50 | [0.4] vs.[14.70] | [64.3] vs.[0.10] | [35.3] vs.[1.10] | 0.51 |
| B2 | Melt | 2.10 | 17.50 | 15 | 0.50 | [0.8] vs.[23.70] | [64.7] vs.[0.04] | [34.5] vs.[0.53] | 0.40 |
| B3 | Melt | 2.10 | 9.00 | 9 | 3.00 | [4.8] vs.[19.90] | [33.3] vs.[0.25] | [62.9] vs.[2.72] | 2.75 |
| B§ | Melt | 2.10 | 9.00 | 15 | 2.10 | [5.7] vs.[17.20] | [54.3] vs.[1.40] | [40.0] vs.[0.40] | 1.90 |

^aΣ[(% w/w)_i × (grafting)_i]/100, for *i* = Ins, Sol, and (Sol)_∞ fractions.

tions. The sequence then becomes: soluble > soluble_∞ nonsoluble. The very low weight population of the nonsoluble fraction in all cases is in good agreement with a nonoptimum initial concentration of MAH.

In the light of present results, it may be assumed that the shortest chains, i.e., those coming from disproportion termination reactions plus others produced by chain scissions processes (if there are any) contribute to the [soluble]_∞ fraction. The inversion between the amounts of the different sequences, in fractions of samples produced by the solution process (the lowest weight population) and in those obtained by the molten state process when close to optimal conditions (the highest weight populations), agrees with the recombination termination processes proposed for the solution reactions. This contrasts with the disproportion reactions that seem to be dominant in the graft processes occurring in the molten state.

Further work on the molecular scale characterization of the different a-PP-G samples is in progress at our laboratories.

CONCLUSIONS

This work correlates a previously proposed kinetic pathway for the batch solution process to that obtained for the molten state process in which solvent molecules are substituted by "solvent polypropylene macromolecules." This agrees with a consecutive reaction mechanism where the desired product is that formed during the first stages of the reaction. The validity of this pathway, for either the solution or molten state processes, seems to be confirmed when resorcinol is used as a molecular probe to transform the SA-grafted groups into SF-grafted groups through a condensation reaction.

A number of aspects of the reaction terminating the radical kinetics, both in the solution and molten state processes, and the distribution of reactive sites on the polymer backbone, deserve further study.

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