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Control of Degradation Reactions during Radical Functionalization of Polypropylene in the Melt

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ABSTRACT: Isotactic polypropylene (iPP) gives very extensive degradation when treated with peroxides above its melting temperature in mechanical mixers or extruders. This undesired reaction is very modestly affected by maleate molecules which on the contrary actively compete with side reactions of macroradicals in the case of ethylene polymers. In this work iPP was treated in a Brabender mixer at 180 °C with peroxide and different selected molecules capable of promptly reacting with the macroradical formed on iPP chain and converting it into a more stable free radical. Furan derivatives, successfully used for iPP cross-linking without any remarkable increase of MFR, were used as free radical removers and maleic anhydride as functionalizing monomer. The results indicate a detectable improvement with respect to the use of maleic monomers and peroxide only, allowing to us get a significant grafting of functional groups and only partial degradation. Moreover, furan derivatives bearing various reactive substituents were used as functionalizing molecules. The results are discussed in the frame of the general mechanism proposed for the free radical functionalization of polyolefin in the melt.

Introduction

The chemical modification of already existing polymers is widely used for the conversion of low cost commodity polymers, such as the polyolefins (PO), into useful reactive polymers. The functionalization reaction of POs has been studied intensively by grafting of polar groups onto the polymer backbone.[1−5] Indeed these products act as in situ compatibilizer[6] of polymer blends and composites.[7] Free radical initiators give rise, in the bulk and at the high-temperature necessary for good rheology, to scission, grafting, branching, and cross-linking reactions.[8] The polymer degradation through β-scission reactions[4,9] predominates over the other reactions in the case of isotactic polypropylene (iPP). Probably hydrogen abstraction from PP backbone proceeds preferably at the level of the tertiary carbon atom, even though the abstraction from secondary carbon atoms or from methyl groups is possible as well.[10,11] Primary and secondary radicals are reported to give more easily the coupling reaction than the tertiary ones which instead undergo β-scission reactions or disproportionation reactions. Moreover, the reactive radical formed by the addition of the macroradical to the double bond of the functionalizing monomers gives transfer reaction to the polymer backbone, thus producing again tertiary macroradicals which lead again to β-scission.[12−14] In many works, different reactive monomers and organic peroxides have been employed for PP radical functionalization in the melt. The most studied monomers are maleic anhydride (MAH)[15−17] or glycidyl methacrylate (GMA).[18−20] A careful analysis of the products shows, in any reaction conditions, the decreasing of the average molecular weight of the polymer correlating to an increase of the melt flow rate (MFR). The grafting reaction occurs by the addition of the terminal macroradical, formed through β-scission, to the monomer double bond. As for polyethylene,[21] diethyl maleate (DEM) or a mixture of DEM/MAH 2:1 mol:mol with dicumyl peroxide (DCP) gave PP with good functionalization degrees (FDs), ranging from 0.2 to 1.0 mol %, but with a remarkable decrement of PP molecular weight (MW).[22] The competition of the projected grafting reaction against chain scission can be improved through the formation of stabilized macroradicals. The recent researches on this topic concern the control of the degradation reactions. With this aim molecules or molecular systems (X) have been proposed, able to create a new stabilized macroradical not involved in β-scission, which gives place to transfer and/or coupling reactions.[23] Cartier et al.[24] studied the radical functionalization of PP with MAH or GMA and a suitable comonomer such as the styrene (STY). The styrene reacts with macroradicals creating more stabilized radicals which subsequently react with the polar monomer. The reactivity of GMA toward the styryl radical is believed to be greater than its reactivity toward the PP macroradical; hence, the use of this comonomer produces a synergistic effect on the grafting. In this way, it is possible to limit the degradation and simultaneously to obtain functionalized products.

Recently the chemical cross-linking of polypropylene[25] has been studied and performed under dynamic conditions using a peroxide and a furan or bis(maleimide) based coagent, such as bis(2-furanyl)aldazine (VP3) or *N*,*N*-*p*-phenylenebis(maleimide) (BMI), as the cross-linking promoter.[26−32] These coagents are able to react properly with the macroradicals, produced by the primary radicals, thus spacing the free radical from the backbone and promoting chain extension and/or preventing the β-scission (Scheme 1).

The furan derivatives, having the heterocyclic ring conjugated with a double bond bearing an electron attracting group substituent, display a high addition rate to the macroradical with the formation of resonance

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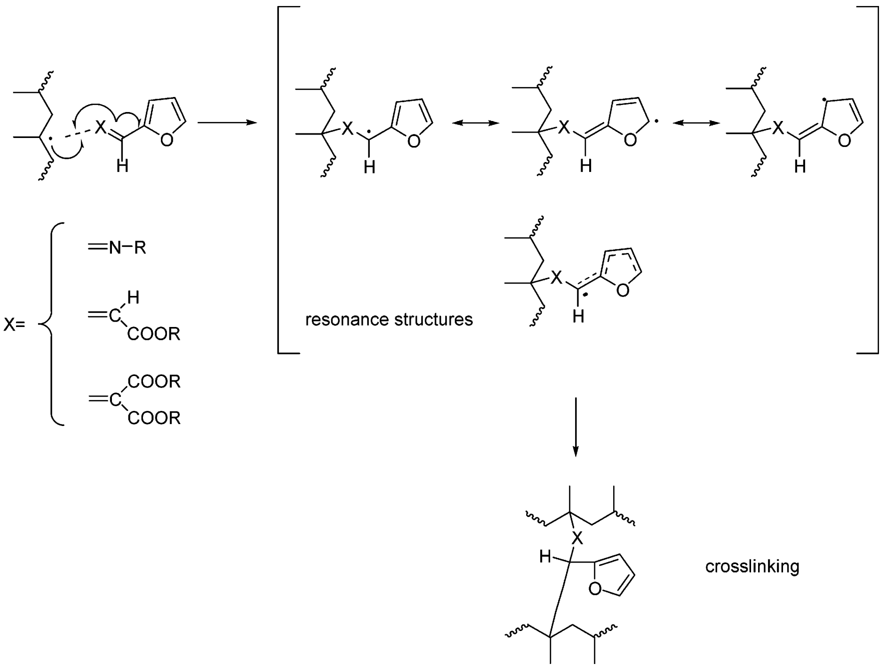
Scheme 1. PP Macroradicals Reactions with Furan Coagents



stabilized radicals. These molecules are now (Scheme 1) proposed as functionalization coagents able to control the intrachain transfer reaction, responsible of PP extensive degradation, and able to introduce onto the polymer backbone suitable polar groups.

On this basis, the iPP radical functionalization reactions in the melt by peroxide, maleate derivatives, and furan coagents have been studied as a function of the feed composition, aiming at obtaining of high grafting values (FDs), keeping unaltered the MW of PP and trying to rationalize the complex mechanism of the process in order to check the capability of furan coagents to control the PP degradation. Two series of experiments have been carried out: in the former case maleic anhydride (MAH) and a furan derivative, butyl 3-(2-furanyl)propenoate (BFA), have been employed; in the latter case, furan coagents bearing suitable functional groups and able to control the PP β-scission reaction have been used in the absence of any maleic derivatives.

Experimental Section

Materials and Reagents. Isotactic polypropylene (iPP) homopolymer having a melt flow rate (MFR) of 0.24 g/10 min supplied by Borealis BE 50/E1271, and propylene homopolymer Moplen Q30P, MFR of 1.0 g/10 min, have been used. 2,5-Dimethyl-2,5-di-*tert*-butylperoxi hexane (Akzo-Nobel) and dicumyl peroxide (Sigma-Aldrich) have been used as provided without further purification. Maleic anhydride (Sigma-Aldrich) has been recrystallized from benzene. 2-Furaldehyde (Sigma-Aldrich), diethyl malonate (Sigma-Aldrich), and ethyl cyanoacetate (Sigma-Aldrich) have been purified by distillation under reduced pressure. Pyridine and piperidine (Carlo Erba) have been purified by distillation on KOH pellets. Solvents have been purified by standard procedures.

Synthesis of Furanyl Derivatives. Butyl 3-(2-furanyl) propenoate (BFA) and ethyl 2-carboxyethyl 3-(2-furanyl) propenoate (CEFA) were prepared as reported in the literature.[25,32] The structural characteristics of these two composites are summarized in Appendix 1.

Synthesis of Cyano 3-(2-Furanyl)propenoate (CFA). Into a three-neck 500 mL flask, equipped with a charge funnel, refrigerant, and mechanical agitator, were introduced, in a nitrogen atmosphere, reactants in the following order: dioxane (440 mL), furfuraldehyde (15 g, 0.156 mol), and ethyl cyanoacetate (21.4 g, 0.189 mol). Afterward, 2.4 mL of a solution piperidine−acetic acid (1:3 vol) was added. The solution was maintained at reflux of the solvent for 24 h. The solvent was distilled off at reduced pressure. Then the remainder was dissolved in dichloromethane and washed with water. The organic phase was dried on anhydrous Na_2SO_4 and then evaporated. The resulting oil was separated in its components through chromatography using silica as stationary phase and chloroform as eluent. The cyano 3-(2-furanyl) propenoate (a yellow solid) was recovered through crystallization from a solution in ethyl acetate−hexane (1:1 vol). A 19.3 g (64.8%) yield was obtained. IR main peaks (cm^{-1}): 3130−3040 $\nu_{H-C=}$, 2997−2970 ν_{H-C-}, 2223 ν_{CN}, 1716 $\nu_{C=O}$, 1621 $\nu_{C=C}$, 1464 δ_{CH_2-O-CO}, 932 $\gamma_{CH\ furan\ ring}$, 877 $\gamma_{CH\ furan\ ring}$. ^1H NMR assignments: 1.2 ppm, 3 protons, triplet (CH_3 ethyl groups); 4.2 ppm, 4 protons, quartet, ($O-CH_2$ ethyl); 6.5 ppm, double doublet, 1 proton (furane ring position 4); 7.2 ppm, doublet, 1 proton, (furane ring position 3); 7.6 ppm, doublet,1 proton (olefin position 3); 7.9 ppm, doublet 1 proton (furane ring position 5).

Instruments. PP samples have been prepared using a Brabender Plastograph PL2100 mixer, torque and temperature data have been acquired by Brabender Mixing software WinMix ver.1.0. FT-Infrared spectra were performed with a Fourier Transform spectrometer "Perkin-Elmer FT-IR 1760-X". Spectra of chemicals have been made on films produced by evaporation of $CHCl_3$ solutions on KBr windows. PP sample spectra have been acquired on films made by compression molding. Proton magnetic resonance spectra were performed with a spectrometer "Varian Gemini 200 MHz"; the spectra of chemicals were obtained on solutions of the compounds in deuterochloroform, and chemical shifts were assigned in ppm using tetramethylsilane (TMS) as internal standard.

Melt Functionalization of PP Samples. All samples were prepared, with the same procedure, in the Brabender mixer by melt-mixing the components at the temperature of 180 °C and rotor speed of 50 rpm. Then, 20 g of iPP were introduced into the Brabender chamber. After complete fusion of PP, functionalizing molecules and peroxide were added to the molten bulk. The reaction was carried out for 25 min and then stopped. The recovered polymer was sequentially extracted with boiling acetone and toluene. In each case, the residues were dried until constant weight.

Theoretical Calculation for Extinction Coefficient Determination. Quantum mechanical calculations of the extinction coefficients were performed by using density functional theory (DFT)[33] with the B3LYP[34] hybrid functional and

Table 1. Modification of PP Samples with MAH, Peroxide and Variable Amounts of BFA

sample[a]	peroxide (% mol)	BFA (% mol)	MAH (% mol)	R^b	end-torque values (N·m)	$FD_{SAH, SA}$[c] (% mol)	FD_{BFA}[d] (% mol)	FY[e] (%)
PPAMC1.0	0.06		4.28		2.9	0.46		10.7
PPAMC1.1	0.06	0.09	4.28	47.5	4.2	0.48	0.08	11.8
PPAMC1.2	0.06	0.13	4.28	33	4.8	0.51	0.06	12.4
PPAMC1.3	0.06	0.17	4.28	25	5.1	0.54	0.07	13.2
PPAMC1.4	0.06	0.22	4.28	19	5.4	0.85	0.20	21.6

[a] The PP used is Moplen Q30P; MFR = 1 g/10 min. [b] R is the MAH/BFA molar ratio in the feed. [c] Number of succinic anhydride (SAH) and succinic acid (SA) inserted groups per 100 monomeric units of the polymer. [d] Number of BFA inserted groups per 100 monomeric units of the polymer. [e] FY = functionalization yield, percent of PP attached carbonyl groups with respect to their total initial number. [$FY = 2FD_{SAH,SA} + FD_{BFA}/BFA + 2MAH \times 100$].

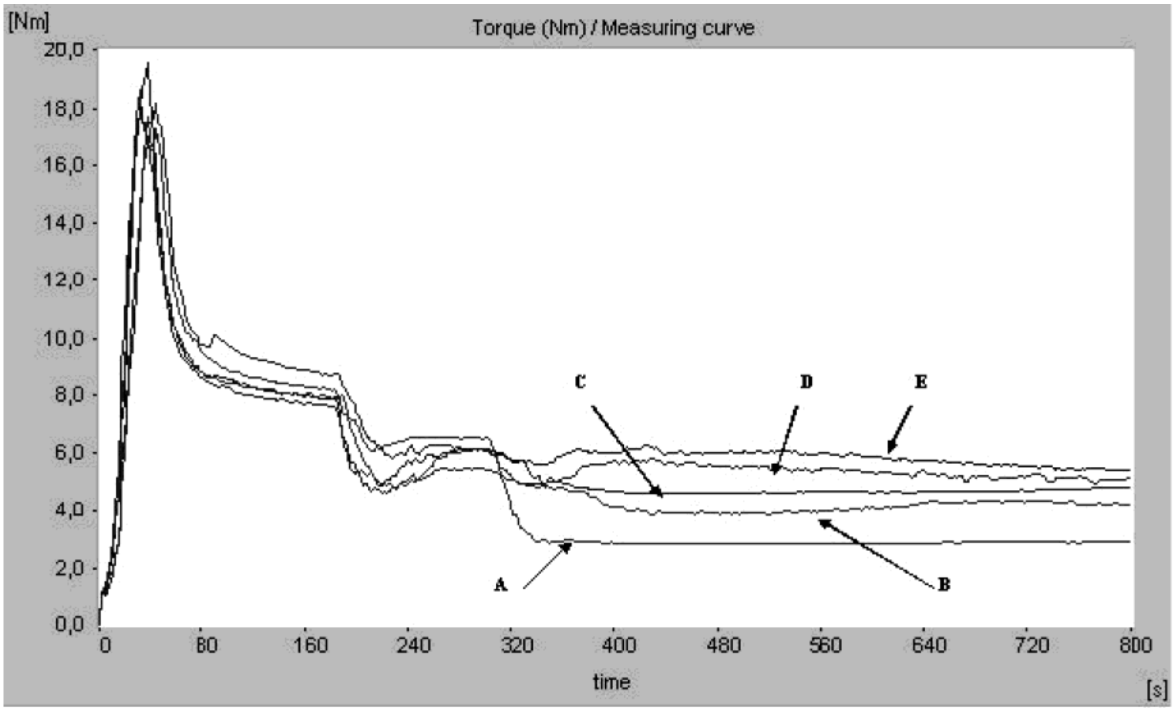


Figure 1. Behavior of the mixing torque for the samples modified with BFA, peroxide and a constant amount of MAH: (A) PPAMC1.0; (B) PPAMC1.1; (C) PPAMC1.2; (D) PPAMC1.3; (E) PPAMC1.4.

the 6-31G* basis set.[35] The Gaussian program[36] was exploited. The frequencies and extinction coefficients were calculated for the geometries of all the species optimized at the same quantum mechanical level. The quantum mechanical model which was exploited here has been proven to give reliable results for both frequencies and extinction coefficients of carbonyl stretching modes: see, for example, ref 37.

Deconvolution Methods. The deconvolution procedure applied to the bands in the C═O stretching region of FT-IR spectra of MAH/BFA functionalized PP samples was the same described for PE samples functionalized by using a MAH/diethyl maleate (DEM) mixture.[38] Six Lorentzian-shaped bands were considered in the range between 2000 and 1600 cm^{-1}: (1) symmetric $\nu_{C=O}$ of free anhydride (1790 cm^{-1}); (2) symmetric $\nu_{C=O}$ of hydrogen bonded anhydride (1770 cm^{-1}); (3) asymmetric $\nu_{C=O}$ of free anhydride (1860 cm^{-1}); (4) asymmetric $\nu_{C=O}$ of hydrogen bonded anhydride (1840 cm^{-1}); (5) $\nu_{C=O}$ of the ester (1736 cm^{-1}); (6) $\nu_{C=O}$ of the carboxylic acid (1710 cm^{-1}), whose absorbances vary by increasing the functionalization degree. As an example, in Figure 6 (Appendix 2), we show the results of the deconvolution procedure for PPAMC1.1 functionalized with the BFA/MAH system. The deconvolution was performed by using a NLSF method (nonlinear least squares fitter) (Origin 6.0 software) by optimizing for each peak the values of the area, the half-width of the band, and the maximum of the peak starting from determined values and by varying them between a predetermined range.

Viscosity Measurements. A capillary Ubbehlode viscometer has been used. Viscosity measurements have been achieved at 135 °C on decahydronaphthalene solution of samples previously washed with warm acetone. For each analyzed samples three solutions at different concentrations have been prepared adding a polymer amount ranging from 5 to 35 mg to 10 mL of solvent. Through the evaluation of the flow time for the solvent and for the three solutions, for each sample, the intrinsic viscosity [η] values have been determined by linear fitting of experimental points. The average viscometric molecular weight (PM_η) was determined by the Mark−Houwink equation ($a = 0.8$ and $K_\eta = 11.0 \times 10^{-3}$ mL/g[39]).

Gel Permeation Chromatography. A Waters Alliance GPCV-2000 Series System apparatus equipped with three Waters Styragel HT 6E columns (MW 5000−1000000) and one Waters Styragel HT 3 (MW 500−30000) column, with an average particle size of 10 μm, a differential refractive index (DRI) detector, and a differential viscometer was used. Polymer solutions were prepared with amounts of 4−5 mg of polymer in 8 mL of 1,2,4-trichlorobenzene (TCB) containing a little amount of antioxidant (BHT) to prevent any degradation and eluted at 160 °C and 1 mL/min flow rate. The calibration was made with narrow MWD standards polystyrene, and calculations were carried out by Millennium software.

Results and Discussion

A. Functionalizing System Based on Peroxide, Maleic Anhydride, and Coagent.

As already mentioned, the previously described selected furan derivatives favor polypropylene cross-linking and chain ex-

Table 2. Modification of PP Samples with BFA, Peroxide and Variable Amounts of MAH

sample[a]	peroxide (% mol)	BFA (% mol)	MAH (% mol)	R[b]	end-torque values (N·m)	$FD_{SAH,\ SA}$[c] (% mol)	FD_{BFA}[d] (% mol)	FY[e] (%)
PPAMC2.0	0.06	0.17			2.6		0.15	
PPAMC2.1	0.06	0.17	0.86	5	3.5	0.20	0.16	29.6
PPAMC2.2	0.06	0.17	2.57	15	4.7	0.36	0.14	16.2
PPAMC2.3	0.06	0.17	3.43	20	4.5	0.47	0.16	15.6

[a] The PP used is Moplen Q30P; MFR = 1 g/10 min. [b] R is the MAH/BFA molar ratio in the feed. [c] Number of succinic anhydride (SAH) and succinic acid (SA) inserted groups per 100 monomeric units of the polymer. [d] Number of BFA inserted groups per 100 monomeric units of the polymer. [e] FY = functionalization yield, percent of PP attached carbonyl groups with respect to their total initial number [FY $= 2FD_{SAH,SA} + FD_{BFA}/BFA + 2MAH \times 100$].

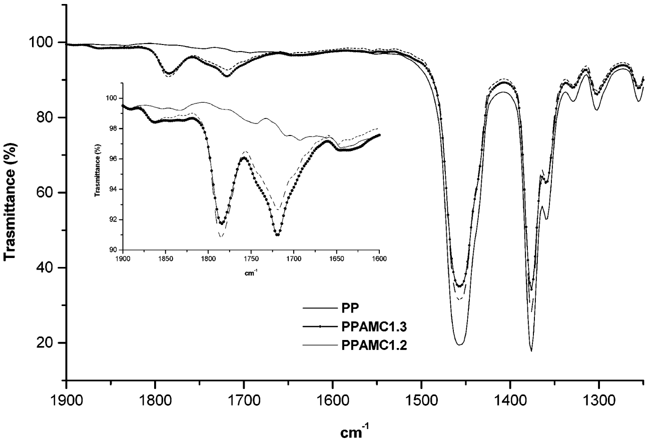


Figure 2. FT-IR spectra in the range 1950−1250 cm^{-1} of PP samples modified with peroxide, MAH and variable amounts of BFA.

Table 3. Molecular Weight of Functionalized IPP Samples

sample[a]	peroxide (% mol)	BFA (% mol)	MAH (% mol)	FD_{TOT}[b] (% mol)	[η] (dL/g)	MW_η (g/mol)
PP				0	1.6	161 000
PPAMC1.0	0.06		4.28	0.46	0.9	78 000
PPAMC1.3	0.06	0.17	4.28	0.61	2.1	224 000
PPAMC2.0	0.06	0.17		0.15	1.1	100 000

[a] The PP used is Moplen Q30P; MFR = 1 g/10 min. [b] Number of total functional inserted groups per 100 monomeric units of the polymer.

tension (or branching) toward chain scission. The formation of cross-linking points is shown by the mixing torque growth after addition of the reagents and also by the high gel content and low values of the melt flow rate (MFR).[25] Among the above furan derivatives, the butyl 3-(2-furanyl)propenoate (BFA) was used in the present work during PP functionalization reactions together with MAH and peroxide. Indeed BFA grafts on PP, maintaining a low MFR value without cross-linking.[25]

A first set of experiments was performed starting with constant amounts of 2,5-dimethyl-2,5-di-*tert*-butylperoxihexane and maleic anhydride (MAH) while varying the amount of BFA (Table 1).

The mixing torque (Figure 1) shows in the last experiments a decrease after the addition (180 s) of the reagents to the molten polymer, but with increasing amounts of BFA in the feed (runs PPAMC1.1−PPAMC1.4), the effect is reduced thus suggesting a lower degradation (Table 1).

The final samples were analyzed by FT-IR after washing with boiling acetone in order to remove the unreacted monomers and low MW products. FT-IR spectra present superposition of diagnostic bands (ester, anhydride, and acid obtained by hydrolysis of anhydride groups) (Figure 2) with peaks at 1710 cm^{-1} stretching C=O (ν_{CO}) for the carboxylic group, at 1780 and 1865 cm^{-1} ν_{CO} symmetrical and ν_{CO} asymmetrical, respectively, for the anhydride groups, and at 1736 cm^{-1} ν_{CO} for BFA ester group. This indicates that different types of groups are grafted onto PP chains.

By a nonlinear fitting of experimental points, a deconvolution of the spectra has been performed. In this way it is possible to obtain separately the diagnostic band areas, thus allowing the determination of the type and content of the various functional groups derived from MAH and BFA grafting, respectively (Appendix 2). The calculated FDs show (Table 1) that the increase of BFA concentration in the feed, while MAH and peroxide are kept constant, gives an increase not only of FD_{BFA} but also of $FD_{SAH,SA.}$ It appears therefore that the presence of BFA coagent during the PP radical functionalization with peroxide and MAH, beyond limiting the polymer degradation, favors the grafting reaction of MAH, with larger monomer conversion (functionalization yield) by increasing the amount of BFA (thanks to the increase of efficiency observed in the experiments with MAH/BFA = 19) (Table 1).

A second set of experiments was performed by keeping constant the BFA feed content and peroxide amount while varying the MAH amount (Table 2). The MAH/BFA ratio was kept below 20, as this value had given the best FY in the former set of experiments.

The mixing torque shows a similar trend as in the previous case, however the end-torque values increase with increasing the amount of starting MAH. The FDs indicate that in the selected conditions the grafting of BFA is almost complete and the amount of grafted MAH increases with its presence in the feed, while the functionalization yield (FY) goes in the opposite direction.

After the functionalization reactions all the first and second set samples were completely soluble in toluene, as the starting iPP; therefore, it is possible to assume that no cross-linking has taken place, but degradation reactions cannot be excluded. To estimate the possible PP degradation, the viscometric molecular weight (MW_η) was evaluated for a few selected samples. In the case of the functionalization of PP with MAH and peroxide (run PPAMC1.0) a remarkable decrease of MW_η was observed (Table 3).

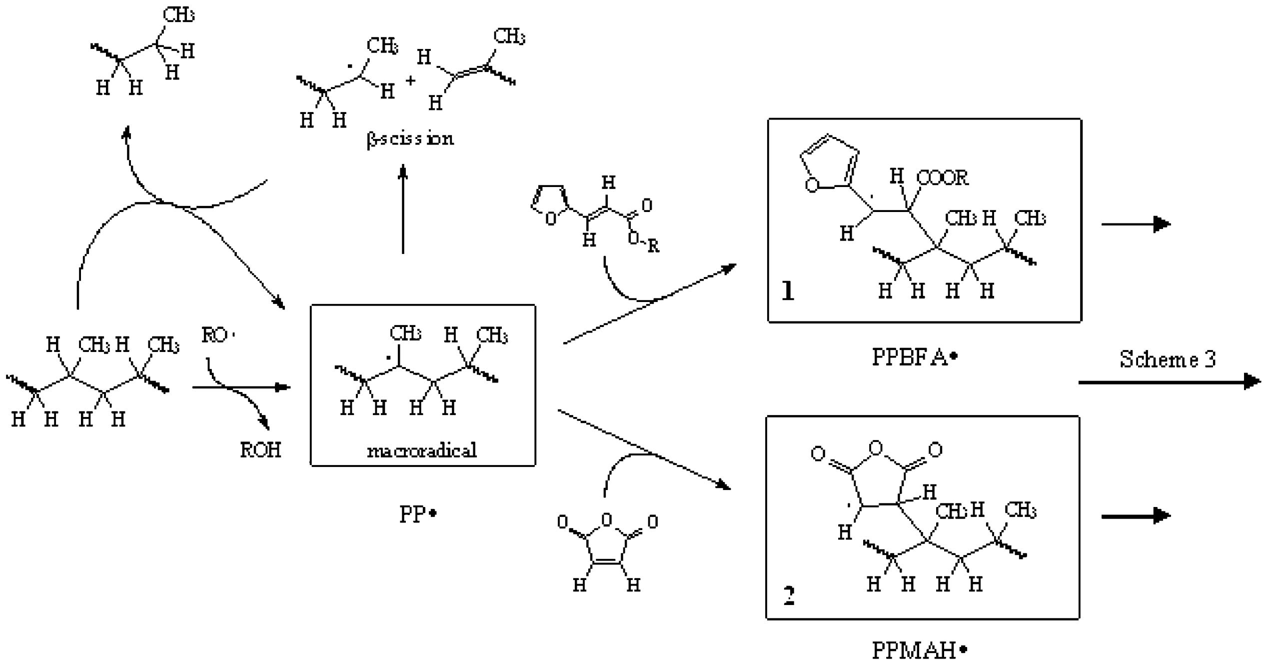
The replacement of MAH with BFA (run PPAMC2.0) gives still a decrease of MW_η but to a lower extent, in spite the BFA/peroxide ratio is only 2.5. In the presence of both BFA and MAH (run PPAMC1.3) the MW_η becomes even higher than that of not-treated PP. The values as such are not directly comparable as the viscosity is certainly increased by the presence of ester groups. A very rough correction can be introduced by

Table 4. Molecular Weight Averages and Polydispersity Index of Functionalized iPP Samples

sample[a]	peroxide (% mol)	BFA (% mol)	MAH (% mol)	SEC measurements (g/mol) $\overline{M}_n$	$\overline{M}_w$	D_n	FD_{TOT}[b] (% mol)
PPtq				121 000	525 000	4.3	
PPAMC1.0	0.06		4.28	45 400	124 000	2.7	0.46
PPAMC1.2	0.06	0.13	4.28	113 000	319 000	2.8	0.57
PPAMC1.3	0.06	0.17	4.28	128 000	386 000	3.0	0.61
PPAMC1.4	0.06	0.22	4.28	97 400	282 000	2.9	1.05
PPAMC2.0	0.06	0.17		102 000	396 000	3.9	0.15
PPAMC2.2	0.06	0.17	2.57	131 000	340 000	2.6	0.50
PPAMC2.3	0.06	0.17	3.43	102 000	299 000	2.9	0.63

[a] The PP used is Moplen Q30P; MFR = 1 g/10 min. [b] Number of total functional inserted groups per 100 monomeric units of the polymer.

Scheme 2. Probable Reactions of the PP Macroradical Using the BFA/MAH Peroxide System



dividing MW_η by the FD; the values of $MW_\eta/FD \times 10^{-3}$ are respectively 170, 367, and 667 for the runs PPAMC1.0, PPAMC1.3, and PPAMC2.0, thus indicating a remarkable effect of BFA to hinder the chain scission. These data indicate that the BFA/MAH combination allows one to improve the functionalization degree and control the degradation.

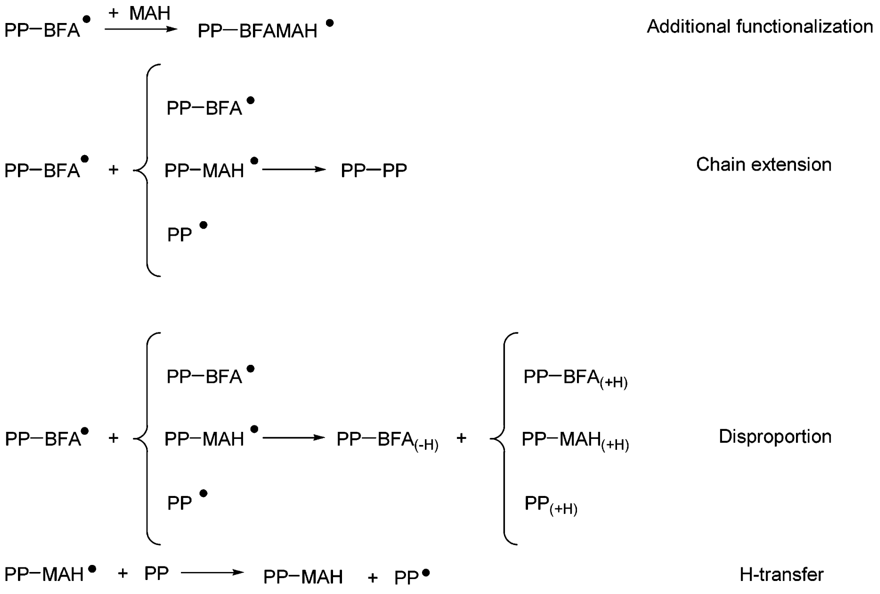
The molecular weight distributions were also analyzed by size exclusion chromatography (SEC). The calculated values of the major molecular weight averages, $\overline{M}_n$ and $\overline{M}_w$, and the polydispersity index, $D_n = \overline{M}_w/\overline{M}_n$, are given in Table 4.

By using MAH and peroxide alone (PPAMC1.0 sample) the molecular weight distribution is narrowed with respect to the neat PP, and the percentage of high molecular weight species is also decreased. Besides, the degradation of the polymer is less significant for all the sample treated with BFA, as evinced by the higher $\overline{M}_w$ and D_n values. Moreover this effect seems major by increasing the BFA concentration in the feed. In fact, with the MAH kept constant and by the BFA concentration increased (samples PPAMC1.0, PPAMC1.2, PPAMC1.3, and PPAMC1.4), the $\overline{M}_w$ grows until reaching a maximum value equal to 386 000 g/mol. Further, for the same amount of BFA with rising the MAH (samples PPAMC2.0, PPAMC2.2, PPAMC2.3, PPAMC1.3) the $\overline{M}_w$ goes from a maximum value of 396 000 (sample PPAMC2.0) to lower values, except for the sample PPAMC1.3 prepared by using the higher amount of MAH, for which the $\overline{M}_w$ was higher than for the samples PPAMC2.2 and PPAMC2.3.

On the basis of these results, the related mechanism can be tentatively described as follows. The primary radicals formed by decomposition of the peroxide can produce PP macroradicals ($PP^\bullet$) by hydrogen abstraction. These $PP^\bullet$ macroradicals can now either undergo β-scission or react with BFA or MAH. In the latter case, the free radical is removed from the chain backbone (as shown in the Scheme 2) to give **1** and **2**, respectively.

1 is stabilized by resonance and has low tendency to give H-abstraction; it should react predominantly with itself or other macroradicals to give chain extension and to a minor extent the disproportionation reactions. Actually Romani et al.[25] in their experiments about PP radical cross-linking by using BFA showed through FT-IR evidences, supported by rheological experiments, that this coagent is able to prevent the β-scission process not promoting the cross-linking by coupling of macroradicals. In particular, the FT-IR analysis of the PP samples treated with BFA pointed out the presence of a peak at 1646 cm^{-1}, visible also in few our BFA/MAH modified samples, which is assignable to a C=C stretching as

Scheme 3. Prevalent Reactions of the Various Macroradicals in the PP/Peroxide/BFA/MAH System



described in the paper. They concluded admitting that there is a new organic group chemically grafted to the PP bearing a C=C double bond and suggesting the occurrence of the disproportionation reaction reported in Scheme 2.

On the other side **2** gives, as in the case of PE,[40] the transfer reaction with hydrogen abstraction from the PP backbone recreating the corresponding macroradicals (PP$^•$). In this way, the instantaneous PP$^•$ concentration is lower with BFA than with MAH (Scheme 3). The relative probability of these reactions clearly depends on the MAH/BFA ratio, which should be optimized considering also that BFA reacts more promptly than MAH with PP$^•$.

This hypothesis provides a possible explanation for the role of BFA in reducing the chain degradation. However as shown by the MW decrease even in the conditions of BFA/peroxide = 2.5, the presence of BFA in a molecular amount larger than the number of primary radicals does not cancel degradation and the grafting of BFA is practically complete. Therefore, it appears that PPBFA$^•$ undergoes also some H-transfer even if to a modest extent. Finally the chain termination by free radical coupling in the presence of BFA occurs between longer (not degradated) macroradicals, thus maintaining a high molecular weight.

B. Functionalization with Furan Derivatives. Taking into account the above observations and the in someway competitive action of BFA and MAH, we have attempted PP functionalization without MAH but using furan derivatives with two functional groups, thus increasing their functionalization capacity. The known ethyl 2-carboxyethyl 3-(2 furanyl)propenoate (CEFA) and the newly synthesized cyano 3-(2-furanyl)propenoate (CFA) (Figure 3) were used as degradation stabilizers and functionalizing molecules at the same time.

(CEFA) (CFA)

Figure 3. CEFA and CFA coagents.

Starting from a commercially available PP (Borealis BE 50/E1271), two series of experiments were performed using CEFA or CFA and DCP as peroxide (Table 4). The mixing torque graph for the two series of samples (Figure 4) shows a different behavior if compared with that obtained for PP treated in the melt with maleate molecules, peroxide and the coagent BFA (e.g., Figure 1).

Indeed the mixing torque increases after the addition of the peroxide, probably because of a significant extent of chain extension reactions, and successively decreases. This result can be correlated to the successive formation of a PP cross-linked fraction which is dispersed in the non-cross-linked matrix during the reaction course.[25] A considerable amount of boiling toluene insoluble polymer was observed (Table 5) for samples prepared with coagent/initiator ratio larger than 6–7, but it can be markedly reduced with lower values of the above ratio.

The FT-IR spectra of the modified polypropylene samples, after washing with acetone, show the presence of the absorption peak at 1737 cm^{-1} in the case of CEFA (Figure 5) and at 1743 cm^{-1} in the case of CFA correlated with the carboxyethyl groups C=O stretching of the grafted molecules.

To achieve a suitable comparison for the different functionalized samples prepared, the functionalization degree (FD) was determined for each sample evaluating, like in the previously discussed case, the ratio between the band area of the C=O functional groups stretching and the PP area band at 1166 cm^{-1} (A1/A2) (Appendix 3) and by knowing the integral absorptivity (ϵ) for the two bands. In the case of PP functionalized with CEFA as well as with CFA, the FD values increase, both increasing the coagent/PP ratio and the DCP/PP ratio. The FD depends clearly also on the coagent/initiator ratio according to the fact that the grafting of CEFA or CFA requires first the formation of the PP$^•$. Thus, the maximum number of grafted CEFA or CFA units should be equal to the double of the peroxide molecules (initiator efficiency = 1). In general the FD for CEFA, CFA, and BFA is larger than this number, and some H-transfer by PP-coagent macroradicals (**3**) (Scheme 4) must occur.

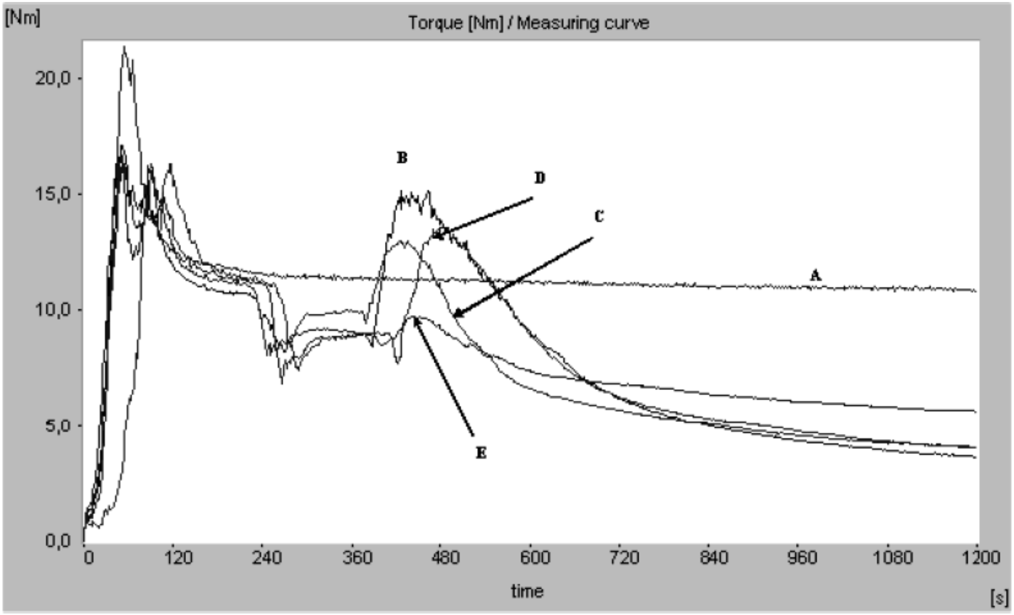


Figure 4. Behavior of the mixing torque for a few samples modified with CEFA: (A) PP01; (B) PP32; (C) PP34; (D) PP33; (E) PP35.

Table 5. Polypropylene Modified with Peroxide and CEFA or CFA

sample[a]	DCP (% mol)	CEFA (% mol)	CFA (% mol)	coagent/ initiator	end-torque values (N·m)	FD[c] (% mol)	FY[d] (%)	residue toluene extraction[e] (wt %)
PP01[b]					10.9			82.9
PP02	0.08				1.4			1.1
PP16	0.08	1.76		22.0	4.4	0.41	23	26.1
PP23	0.15	4.41		29.4	5.3	0.52	12	45.9
PP27	0.30	4.41		14.7	3.8	0.93	21	58.0
PP32	0.30	0.88		2.9	3.2	0.75	85	6.0
PP33	0.30	1.76		5.9	3.7	0.74	42	1.4
PP34	0.15	0.88		5.9	3.8	0.30	34	5.0
PP35	0.15	1.76		11.7	5.3	0.41	23	5.1
PP15	0.08		2.20	27.5	5.0	0.37	17	22.7
PP19	0.15		2.20	14.7	4.8	0.51	23	46.2
PP20	0.15		3.30	22.0	3.7	0.86	25	49.6
PP22	0.15		4.40	29.3	3.3	0.49	11	30.6
PP28	0.30		4.40	14.7	3.6	1.10	25	2.3
PP29	0.15		1.10	7.3	4.4	0.56	51	16.5
PP30	0.30		1.10	3.7	4.9	0.86	78	4.3
PP31	0.30		2.20	7.3	4.1	0.86	39	1.7

[a] The PP used is isotactic polypropylene (iPP) homopolymer by Borealis BE 50/E1271; MFR = 0.24 g/10 min. [b] Polypropylene treated in Brabender at 180 °C without peroxide and functionalizing monomers. [c] Number of functional inserted groups per 100 monomeric units of the polymer. [d] FY = funtionalization yield, percent of PP attached carbonyl groups with respect to their total initial number. [e] Weight percent of polymer insoluble in boiling toluene.

If an excess of coagent is present all $PP^{\bullet}$ numerically formed are converted into the macroradical (**3**) and the higher concentration of this last favors cross-linking. Also under these conditions (**3**) may react with larger probability with the coagent with formation of very short coagent blocks. Consequently the grafting remains of the same extent but the measured FD increases, and the highest FDs are obtained with the maximum amount of coagent in the feed (Table 5). As far as the functionalization yield FY is concerned, the highest values are observed with the lowest coagent/peroxide ratio according to the fact that the grafting needs, as with MAH, the formation of $PP^{\bullet}$. In any case the values of FY are certainly larger than expected for a stoichiometric (1:1) reaction of $PP^{\bullet}$ with CEFA or CFA, and this implies a certain occurrence of the transfer reactions. The lower FY appears to be flanked by a higher fraction of insoluble (cross-linked) PP, but a univocal interpretation is at present not easy due to the evident contemporary occurrence of several competitive reactions.

Conclusions

Furan derivatives, having a ring conjugated with a double bond substituted with electron attracting groups, promote, thanks to high addition rate to the macroradical, the formation of a stabilized radical due to the presence of the heteroaromatic ring. For this reason these molecules act as good functionalization coagents able to control intrachain hydrogen transfer reaction responsible of PP degradation. Moreover, the coagents molecular structure can be opportunely modulated to improve their capability to prevent the β-scission reaction and at the same time to limit the cross-linking reaction. In this work we demonstrated that with the use of the above furan derivatives the polypropylene radical functionalization can be achieved with limited

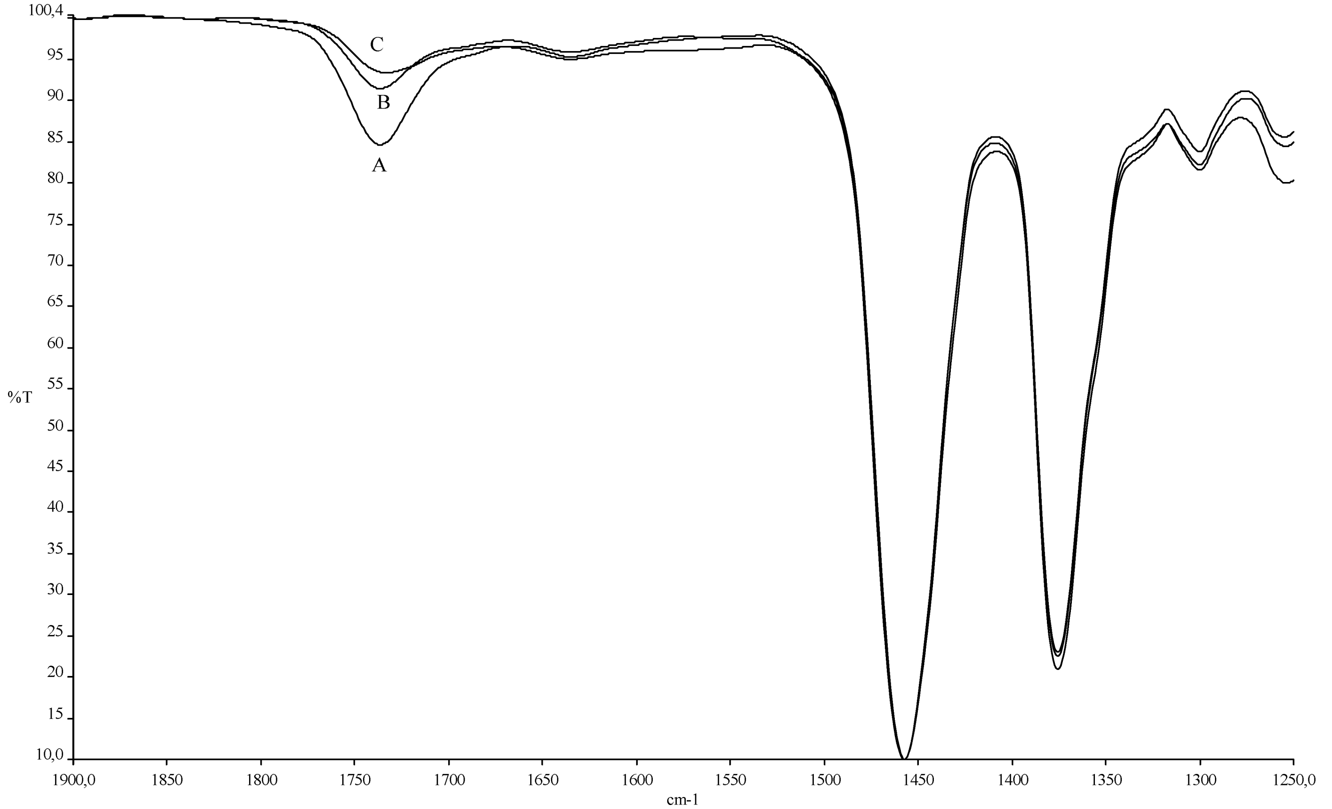
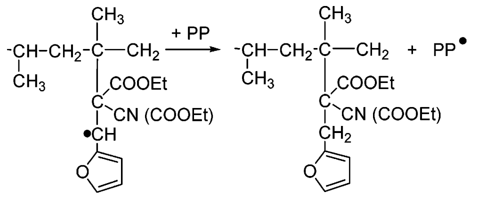


Figure 5. FT-IR spectra of a few samples modified with CEFA: (A) PP27; (B) PP23; (C) PP16.

Scheme 4. H-Transfer Reactions by PP-Coagent Macroradical



(3)

reduction of the MW: by combining the above coagents with maleic derivatives or by using specially designed coagents with suitable functional groups.

In the former case, the furan coagent prompt reaction with the tertiary polypropylene macroradicals prevents the β-scission while MAH gives grafting. By using the BFA coagent together with maleic anhydride, good functionalization degrees have been obtained and a good control of the degradation reaction has been realized. Low amounts of BFA suffice to limit the PP degradation and are responsible for increasing MAH functionalization degrees. The use of BFA favors the functionalization (FD) values and also the functional monomer conversion. The monofunctional ethyl 2-carboxyethyl 3-(2-furanyl)propenoate (CEFA) and the bifunctional cyano 3-(2-furanyl)propenoate (CFA) coagents have been used for PP radical functionalization reactions without MAH. The role of the different species can be rationalized with a modified mechanism of the grafting process (Scheme 4), where the role of the relative stability of the various free radicals present in the system has been taken into account. Further studies in due course are devoted to the described structural analysis of the products for a better quantitative evaluation of the various factors including a mathematical modeling of the process.

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Appendix

Appendix 1: Structural Characteristics of the Butyl 3-(2-Furanyl)propenoate (BFA) and Ethyl 2-Carboxyethyl-3-(2-furanyl)propenoate (CEFA). The BFA coagent was synthesized as reported in the literature[25,32] and a colorless viscous oil with a bp = 138 °C at 10^{-1} mmHg was obtained with a yield of 75 wt %. IR main peaks (cm^{-1}): 3015−3005 $\nu_{\mathrm{H-C=}}$, 2997−2970 $\nu_{\mathrm{H-C-}}$, 1715 $\nu_{\mathrm{C=O}}$, 1640 $\nu_{\mathrm{C=C}}$, 1158 $\nu_{\mathrm{C-C(=O-O)}}$. ^{1}H NMR assignments: 0.9 ppm, 3 protons, triplet (CH_3 butyl); 1.3 ppm, 2 protons, multiplet; 1.6 ppm 2 protons, multiplet, (CH_2-CH_2 butyl); 4.2 ppm triplet 2 protons ($O-CH_2$ butyl); 6,2−6,3 ppm doublet 1 proton, (olefin position 2); 6.4 ppm double doublet, 1 proton, (furan ring position 4); 6.6 ppm doublet 1 proton, (furan ring position 3); 7.4−7.5 doublet,1 proton, (olefin position 3); 7.5 doublet 1 proton, (furan ring position 5). The CEFA coagent was synthesized as reported in the literature,[25,32] and a colorless solid having a melting point of 49,1 °C was prepared with a yield of 43.3 wt %. IR main peaks: 3015−3005 $\nu_{\mathrm{H-C=}}$, 2997−2970 $\nu_{\mathrm{H-C-}}$, 1720 $\nu_{\mathrm{C=O}}$, 1643 $\nu_{\mathrm{C=C}}$, 1479 $\delta_{\mathrm{CH_2-O-CO}}$, 934 $\gamma_{\mathrm{CH\ furan\ ring}}$, 881 $\gamma_{\mathrm{CH\ furan\ ring}}$. ^{1}H NMR assignments: 1.1−1.2 ppm, 6 protons, 2 near triplets (CH_3 ethyl groups); 4.1−4.2 ppm, 4 protons, 2 near quartets, ($O-CH_2$ ethyl); 6.3 ppm, double doublet, 1 proton (furan ring position 4); 6.6 ppm doublet, 1 proton, (furan ring position 3); 7.2 doublet,1 proton (olefin position 3); 7.3 doublet 1 proton (furan ring position 5).

Appendix 2: Evaluation of Grafted Groups by FT-IR Spectra Deconvolution. By a nonlinear fitting of experimental points, a deconvolution of the spectra

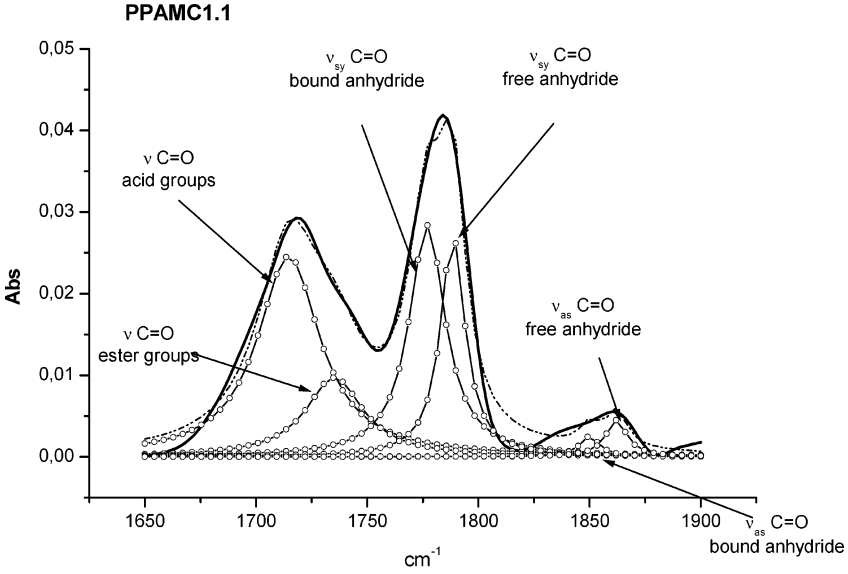

Figure 6. Deconvolution PPAMC1.1 spectrum in the range 1900−1650 cm^{-1}.

Table 6. Extinction Coefficients for the C=O Stretching of the Functionalizing Molecules and the PP Band at 1166 cm^{-1}

grafted molecules	extinction coeff (km/mol)[a]
diethyl succinate	392
succinic acid	491
succinic anhydride	691
BFA grafted	209
CEFA grafted	377
CFA grafted	197
PP band at 1166 cm^{-1}	348

[a] Calculated at the B3LYP/6-31G* level.

has been performed obtaining the diagnostic band (Figure 6).

Comparing the above absorption bands with the typical absorption band of PP at 1166 cm^{-1} (stretching of C−CH_3 groups on PP chains) and using the integral absorptivity (ϵ) for all the bands used allowed the FD values related to BFA and MAH to be calculated according to the following equations:

$$\mathrm{FD}_{\mathrm{BFA}} = \frac{\overline{\epsilon_{1166}}}{\overline{\epsilon_{\mathrm{BFA}}}} \cdot \frac{\overline{A_{\mathrm{BFA}}}}{\overline{A_{1166}}}$$

$$\mathrm{FD}_{\mathrm{SAH,SA}} = \frac{\overline{\epsilon_{1166}}}{\overline{\epsilon_{\mathrm{SA}}}} \cdot \frac{\overline{A_{\mathrm{SA}}}}{\overline{A_{1166}}} + \frac{\overline{\epsilon_{1166}}}{\overline{\epsilon_{\mathrm{SAH}}}} \cdot \frac{\sum_i \overline{A_{\mathrm{SAH},i}}}{\overline{A_{1166}}}$$

The extinction coefficient for all the bands used has been calculated by following the computational procedure reported in the experimental part and described in a recent work of our group.[41] In Table 6, the values obtained are reported.

The extinction coefficient for the PP band at 1166 cm^{-1} was calculated by considering a linear correlation, found in a previous work,[22] between the FD, calculated by ^1H NMR, for PP samples functionalized with diethyl maleate and the peak areas ratio (A1/A2), where A1 is the band at 1736 cm^{-1} (ν_{CO} dithyl succinate groups grafted onto the PP chains) and A2 at 1166 cm^{-1}. By knowing the theoretical value of the ϵ_{DES}, obtained by the computational procedure, ϵ_{1166} cm^{-1} was evaluated.

Appendix 3: Evaluation of Functionalization Degrees by FT-IR for Samples Functionaled with CEFA or CFA. The functionalization degrees were calculated in accordance with the following reactions:

$$\mathrm{FD}_{\mathrm{CEFA}} = \frac{\overline{\epsilon_{1166}}}{\overline{\epsilon_{\mathrm{CEFA}}}} \cdot \frac{\overline{A_{\mathrm{CEFA}}}}{\overline{A_{1166}}}$$

$$\mathrm{FD}_{\mathrm{CFA}} = \frac{\overline{\epsilon_{1166}}}{\overline{\epsilon_{\mathrm{CFA}}}} \cdot \frac{\overline{A_{\mathrm{CFA}}}}{\overline{A_{1166}}}$$

The extinction coefficient for all the bands used has been calculated in accord to the computational procedure reported in the experimental part. In Table 5, the values obtained are showed.

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