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Coagent assisted polypropylene radical functionalization: monomer grafting modulation and molecular weight conservation

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Abstract

The occurrence of significant degradation by β-scission reaction is a severe drawback affecting the classical procedure of polypropylene (PP) functionalization in the melt with maleic anhydride (MAH) or derivatives and free radical initiators. The present work deals with the control of the PP blocks degradation by using a specially designed furan derivative, butyl 3-(2-furyl) propenoate (BFA), as coagent able to control the PP blocks scission during PP functionalization process. More specifically MAH or BFA were used as functionalizing reagents for a propylene/ethylene 77/23 mol% semi-block copolymer (PPC) either separately or as mixture (MAH/BFA) with different molar ratios. The PPC functionalized samples were then characterized by determining the number of grafted groups (functionalization degree FD) and the molecular weight (MW). Finally, the effect of the feed conditions on the process and on functionalized PPC properties are discussed by hypothesizing a reaction mechanism, which takes into account all the occurring parallel reactions.

Keywords: Polypropylene (PP); Functionalization; Molecular weight conservation

1. Introduction

Specialty polyolefins can be produced by grafting of functional vinyl monomers onto the macromolecule backbone in the presence of chemicals generating free radicals, like peroxides [1–4]. However, free radicals also initiate a host of reactions that may produce less desirable simultaneous modifications such as chain scission, branching and cross-linking [5,6]. Despite this, today polyolefin modification by free radical grafting of maleic anhydride derivatives, carried out in the melt under mechanical mixing, has gained a wide range of industrial applications. In the case of polyethylene (PE) and ethylene–propylene copolymers (EPM), the modulation of reaction conditions is sufficient to limit undesirable reactions [7,8]. On the contrary polypropylene (PP) undergoes chain β-scission [9–11], which causes difficulties in producing graft modified PP samples having good functionalization degrees without a substantial decrease of the molecular weight. As the control of the process to a significant extent appears fundamental in order to modulate the product characteristics, suitable reagents affecting the degradation reaction (by formation of a macroradical less liable to fragmentation) were object of several studies [12–18].

Radical coupling and β-scission reactions of EPM (with a high propylene amount) and peroxide vulcanization of amorphous PP were modulated by using monofunctional and polyfunctional monomers [19,20]. The polyfunctional unsaturated compounds added relatively fast to the rubber macroradicals (generated by the peroxide) by forming in the case of *p*-quinone dioxime resonance-stabilized intermediates giving coupling rather than transfer reactions. Among the monofunctional monomers tested, only vinyl pyridine and vinyl toluene were effective, even though with minor extent in comparison to the polyfunctional monomers. Diallyl maleate and pentaerythrityl tetramethacrylate were also used for the peroxide-curing of atactic and isotactic polypropylene [21].

Furan derivatives having the heterocyclic ring conjugated with a double bond bearing an electron attracting group substituent were also effective [22]. Actually, it was shown that these molecules called free-radical acceptors [23,24] react with

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macroradicals of homopolymers or copolymers of ethylene with α-olefins thereby forming more stable radicals, thus hindering the intra-chain transfer reaction responsible of PP degradation. Thus, the cross-linking of polypropylene was investigated under dynamic conditions using a peroxide and furan or bis-maleimide based coagents as cross-linking promoters [25,26]. Among the molecules used butyl 3-(2-furyl) propenoate (BFA) gave grafting on PP maintaining a low MFR value without cross-linking. BFA in combination with maleic anhydride (MAH) [22] also gave a moderate reduction of the polymer molecular weight and good functionalization degrees. Moreover, specially designed furan coagents bearing functional groups like –COOR and –CN were synthesized and used to prepare PP with high molecular weight and useful polar/reactive groups [22].

In the present study, three series of functionalization reactions of a propylene/ethylene semiblock copolymer (having 23 mol% of ethylene units) (PPC) were carried out according to: (A) the traditional approach with MAH and peroxide; (B) the use of BFA furan derivative as functionalizing agent, at variable peroxide/monomer ratio; (C) the use of BFA/MAH functionalization mixtures focusing the study on the effect of the peroxide/monomers ratio.

By comparing the FD and MW values of all the functionalized samples, it was possible to propose a mechanism of reaction relating macromolecular chain modifications to the process conditions.

2. Experimental section

2.1. Materials

Commercial polypropylene copolymer (PPC 5660) supplied by TOTAL PETROCHEMICALS, having a melt temperature of 167.4 °C and a melt flow rate (MFR) of 6–7 g/10′ (2.16 kg/230 °C) was used. The ^{1}H NMR spectrum of PPC 5660, carried out in $C_2D_2Cl_4$ at 90 °C, showed two main peaks: the former at 0.87 ppm corresponding to the $–CH_3$ protons of propylene units and the latter at 1.27 ppm related both to the $–CH_2$ protons of ethylene and propylene units as well as to the –CH proton of propylene units. By knowing the integral values of both peaks the amount of ethylene units was found to be 23 mol%, as calculated by the following equation:

$$\%\ \mathrm{PE_{mol}} = \frac{\left[I_1 - \left((I_2/3)\times 3\right)\right]\times(1/4)}{\left[I_1 - \left((I_2/3)\times(3/4)\right) + (I_2/3)\right]}$$

where I_1 is the integral value of the 1.27 ppm peak whereas I_2 is the integral value of the 0.87 ppm peak. The accurate characterization by ^{13}C NMR evidenced the presence of propylene and short ethylene sequences: signals corresponding to propylene pentad as well as signal due to secondary (methylene) carbons due to ethylene triad were observed thus highlighting the (semi)block structure of the copolymer. Moreover, the dynamic mechanical thermal analysis (DMTA) of PPC, carried out at 1 Hz in the range of temperatures between −100 and 140 °C, showed two well distinguished glass transitions: the first at −48 °C and the second at 13 °C.

2,5-Dimethyl-2,5-di-*tert*-butylperoxy hexane (Luperox 101, ARKEMA) and maleic anhydride (Sigma–Aldrich) were used as provided without further purification. Butyl 3-(2-furyl) propenoate (BFA) was synthesized as reported in literature [22,25,26].

2.2. BFA polymerization experiment

A BFA radical polymerization reaction was carried out without solvent in a small glass tube (10 ml) by adding under nitrogen atmosphere 1.5 g of BFA (7.7 mmol) and 63 mg of dicumyl peroxide (0.2 mmol) as initiator. The reaction mixture was opportunely degassed before to start the reaction, which was carried out at 180 °C for 1 h. The reaction product was characterized by mass spectroscopy (MS) by using an Applied BioSystems/MDS SCIEX API 4000 triple quadrupoles mass spectrometer and an ESI (electron spray ionization) source. The sample was diluted in methanol before being injected in the system (around 20 μl). Singly charged molecular-related ions were produced. Particularly protonated molecular ions $(M+H^+)$ and sodium adducts $(M+Na^+)$ were expected because the sample was analyzed under positive ionization conditions. Moreover, the *m*/*z* ions are singly charged and so the *m*/*z* value is consistent with the molecular weight as the value of *z* (number of charges) equals to 1. The *m*/*z* spectrum showed a dominant ion at *m*/*z* 195.4, which is consistent with the expected protonated BFA ion $(BFA+H^+)$ and an ion at *m*/*z* 216.9, which was identified as the sodium adduct $(BFA+Na)^+$. Moreover, an accurate analysis of the chromatogram evidenced peaks due to the BFA oligomers/ionic clusters formation (Table 1) such as: $ROBFABFAOR+Na^+$ at *m*/*z* 681.3, where RO is $PhC(CH_3)_2O$, and $ROBFABFA_{(-H)}+Na^+$ at *m*/*z* 545.3 due to termination by disproportionation reaction. Peaks due to the trimer and tetramer formation were also discernible.

Table 1
ESI-MS analysis of BFA polymerization products: sodium adducts of dimer, trimer and tetramer

Sodium adduct[a]	*m*/*z*
$RO(BFA)_2OR+Na^+$	681.3
$R(BFA)_2R+Na^+$	441.2
$RO(BFA)_2R+Na^+$	561.3
$RO(BFA)_{2(-H)}+Na^+$	545.3
$R(BFA)_{2(-H)}+Na^+$	425.1
$RO(BFA)_3OR+Na^+$	875.5
$R(BFA)_3R+Na^+$	635.3
$RO(BFA)_3R+Na^+$	755.5
$RO(BFA)_{3(-H)}+Na^+$	739.4
$R(BFA)_{3(-H)}+Na^+$	619.4
$RO(BFA)_4R+Na^+$	949.6
$R(BFA)_4R+Na^+$	829.5
$RO(BFA)_{4(-H)}+Na^+$	933.6
$R(BFA)_{4(-H)}+Na^+$	813.4

[a] $RO=PhC(CH_3)_2O$ and $R=CH_3$.

2.3. Functionalization experiments

PPC functionalization reactions were carried out in a Brabender Plastograph Mixer (mixer chamber 50 cm^3), torque and temperature data were acquired by Brabender Mixing software WinMix. All samples were prepared with the same procedure by melt-mixing the components at 200 °C and 50 rpm. Fourty g of PPC were introduced into the Brabender chamber and, after complete fusion of PPC, functionalizing molecule(s) and the peroxide were added to the molten bulk. The reactions were carried out for 20 min and then stopped. The recovered polymer was extracted with boiling acetone and the residue dried until constant weight.

2.4. Instruments

FT-infrared spectra were performed with a Fourier Transform Spectrometer 'Perkin–Elmer FT-IR 1760-X'. PPC samples spectra were acquired on films made by compression molding. UV spectra were acquired by using a 'Perkin–Elmer Lambda 650 UV–vis Spectrometer' on films made by compression molding starting from 500 to 200 nm (lamp change at 318 nm) with a 1 nm resolution. Proton and carbon-13 magnetic resonance spectra were performed with a spectrometer Varian Gemini 200 MHz; the spectrum of PPC was made in solution of $C_2D_2Cl_4$ at the temperature of 90 °C.

PPC sample molecular weights were obtained by gel permeation chromatography (SEC) by using a Waters Alliance GPCV 2000 Series System apparatus equipped with three Waters Styragel HT 6E columns (MW 5000–10,000,000) and one Waters Styragel HT 3 (MW 500–30,000) column, with an average particle size of 10 μm, a differential refractive index (DRI) and a differential viscometer as detectors. Polymer solutions were prepared with amounts of 2.5–3 mg of polymer in 4 ml of 1,2,4-trichlorobenzene (TCB) containing a little amount of antioxidant (BHT) to prevent any degradation and eluted at 145 °C, 1 ml/min flow rate. The calibration was made with narrow MWD polystyrene standards and calculations were carried out by Millennium software.

2.5. Extinction coefficients determination

For all PPC functionalized samples the FD determination was achieved by IR spectroscopy by using the signal at 1464 cm^{-1} (bending CH_2) as reference band for the PPC. The determination of the integral absorptivity (ε) for this band was carried out according to a method usually adopted in our laboratory [27]. Blends of PPC and polydiethylfumarate (PDF) at known composition were prepared by melt mixing and for each blend FT-IR spectra were acquired on films prepared by compression molding. From the IR spectra by using the correlation between blend compositions and the A_1/A_2 ratios ($[PDF]=(\varepsilon_{1464}/\varepsilon_{1736})(A_1/A_2)$), where A_1 is the peak area at 1736 cm^{-1} and A_2 is the peak area at 1464 cm^{-1}. By knowing the ε_{1736} value, the ε_{1464} was determined ($\varepsilon_{1464}=3.80\times 10^4$ L mol cm^{-2}) [28]. The integral absorptivity for the band at 1726 cm^{-1} (ε_{BFA}) due to the stretching of BFA carbonyl ester groups (unsaturated and saturated) was evaluated preparing both BFA and ethyl 3-(2-furyl) propanoate (EFP) chloroform/2,2,4-trimethylpentane (23/77 wt/wt) solutions at low concentration (ranging from 4×10^{-3} to 12×10^{-3} M) and calculating for each solution the area of the C=O stretching band. Therefore, from the Lambert–Beer law the extinction coefficients of the saturated molecule EFP and unsaturated molecule BFA were calculated and since they were found to be very close and equal to 1.10 L mol cm^{-2} this value was used, as approximation, for the C=O stretching band of the BFA grafted to the PPC chains and it was indicated in the text as ε_{BFA}.

2.6. Deconvolution procedure

The deconvolution procedure applied to the bands in the C=O stretching region of FT-IR spectra for MAH and MAH/BFA functionalized PPC samples was the same described in a previous work [22]. Five and six Lorentzian-shaped bands were considered, respectively, for MAH and MAH/BFA systems in the range between 1900 and 1650 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 (1737 cm^{-1}) and (6) $\nu_{C=O}$ of the carboxylic acid (1710 cm^{-1}), whose absorbances change by varying the functionalization degree. The deconvolution was performed by using a NLSF method (Non linear Least Squares Fitter) (Origin 6.0 software) by optimizing for each peak the value 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 pre-determined range.

3. Results and discussion

3.1. (A) Functionalization with peroxide and MAH

The free radical grafting of MAH onto polypropylene was widely studied in the past concerning the chemical mechanism and material properties. Therefore, the aim of this part of work was essentially the obtainment of a well characterized group of functionalized samples with PPC as reference for the successive steps. The first set of experiments was performed by varying the peroxide amount (2,5-dimethyl-2,5 di-*tert*-butylperoxy-hexane) from 0 to 0.072 mol% and the MAH concentration from 0 to 2.57 mol% with respect to the polymer (Table 2).

The mixing torque behavior (end-torque values, Table 2) of the used Brabender mixer was comparable for all the samples prepared independently of the amount of peroxide and MAH used in the feed. Torque values sharply decreased after the addition to the melt mass of the peroxide–monomer mixture and this drop was more marked when raising the amount of peroxide. The influence of MAH monomer on the mixing torque value was very low, nevertheless a slight growth was

Table 2
Modification of PPC with MAH and peroxide in the melt mixer at 200 °C

Sample	ROOR[a] (% mol)	MAH[a] (% mol)	R[b]	FD_{MAH}[c] ± SD[d]	MAH conv.[e]	Eff.[f]	End-torque values (N m)	$\bar{M}_n \times 10^{-3}$ (Dalton)	$\bar{M}_w \times 10^{-3}$ (Dalton)	$\bar{M}_n/\bar{M}_w$	[η] (dl/g)
PP	–	–	–	–	–	–	8.7	58	260	4.5	1.60
PPL1	0.015	–	–	–	–	–	2.3	35	124	3.5	0.97
PPL2	0.036	–	–	–	–	–	1.0	44	102	2.3	0.76
PPL3	0.072	–	–	–	–	–	0.4	31	74	2.4	0.60
PPMAH1	0.015	0.86	57.3	0.20±0.01	23.3	6.7	1.7	46	126	2.7	0.72
PPMAH2	0.015	1.71	114.0	0.24±0.04	14.6	8.0	1.7	47	130	2.8	0.74
PPMAH3	0.015	2.57	171.3	0.24±0.01	9.3	8.0	2.6	53	146	2.8	0.81
PPMAH4	0.036	0.86	23.9	0.43±0.13	50.8	6.0	0.8	31	81	2.7	0.63
PPMAH5	0.036	1.71	47.5	0.49±0.06	28.7	6.8	1.0	36	97	2.7	0.56
PPMAH6	0.036	2.57	71.4	0.60±0.05	23.1	8.3	1.3	29	87	3.0	0.59
PPMAH7	0.072	0.86	11.9	0.62±0.02	72.1	4.3	0.2	27	70	2.6	0.51
PPMAH8	0.072	1.71	23.7	0.87±0.06	50.7	6.0	0.4	30	73	2.4	0.49
PPMAH9	0.072	2.57	35.7	0.66±0.13	25.7	4.6	0.6	32	81	2.5	0.48

[a] Expressed with respect to 100 mol of monomeric units.

[b] MAH/ROOR molar ratio.

[c] FD = number of grafted succinic groups per 100 monomeric units.

[d] SD = standard deviation.

[e] Percentage of grafted MAH units with respect to the MAH concentration in the feed.

[f] Efficiency: molar ratio between the FD and the amount of primary radicals [Efficiency = $FD_{MAH}/2[ROOR]$].

observed by increasing the MAH concentration and keeping constant the amount of peroxide. All the samples were featured by FT-IR analysis after removing the un-reacted monomer and low molecular weight products by washing with boiling acetone. The FT-IR spectra (Fig. 1) showed the band centered at 1710 cm^{-1}, C=O stretching of the carboxylic acid group of grafted succinic acid (SA) obtained by hydrolysis, and the bands at 1770, 1790 cm^{-1} and 1840, 1860 cm^{-1} due to the symmetrical and asymmetrical C=O stretching of free and hydrogen bonded succinic anhydride groups (SAH), respectively, [29].

By a non-linear fitting of the experimental points a deconvolution of the spectra was performed in agreement with a validate procedure adopted in our laboratory [29]. After the obtainment of the diagnostic band areas (A_{SA} and A_{SAH}) and by knowing the integral absorptivity (ε) for all the bands used (see Section 2 for the determination of ε_{1464}) the functionalization degree (FD) was calculated (Table 2) as follows:

$$FD_{SAH,SA} = FD_{MAH} = \frac{\bar{\varepsilon}_{1464}}{\bar{\varepsilon}_{SA}} \frac{\bar{A}_{SA}}{\bar{A}_{1464}} + \frac{\bar{\varepsilon}_{1464}}{\bar{\varepsilon}_{SAH}} \frac{\sum_i \bar{A}_{SAH,i}}{\bar{A}_{1464}}$$

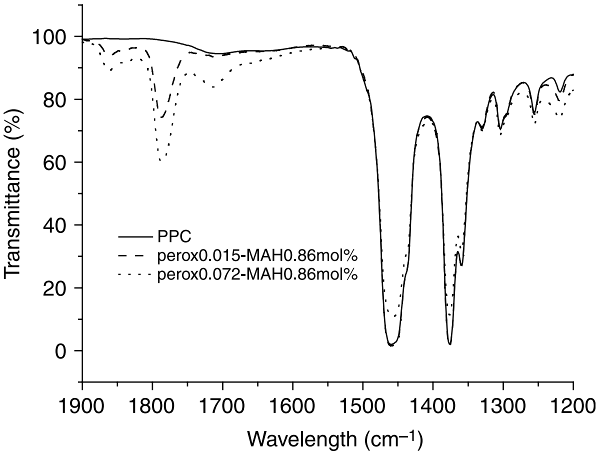


Fig. 1. FT-IR spectra in the range 1900–1200 cm^{-1} of PPC samples functionalized with MAH in different amounts: (—) reference PPC treated in the mixer (run PP); (- - -) ROOR 0.015% by mol, MAH 0.86% by mol (run PPMAH1); (…) ROOR 0.072% by mol, MAH 0.86% by mol (run PPMAH7).

The FD values increased when both peroxide and MAH concentration in the feed grew, except for the highest amount of MAH (2.57 mol%) used (Fig. 2). Phase separation between PPC and MAH was probably responsible for this last result.

The efficiency values [7,8] (where the efficiency is defined as the ratio between the FD and the moles of Luperox 101 per 2) were always >1 confirming the occurrence of the H-transfer reaction from the PP–MAH macroradicals to PPC chains. The MAH conversion depended on the [MAH]/[peroxide] ratio (R) and the corresponding yield grafting was over 50 mol% for R value lower than 20.

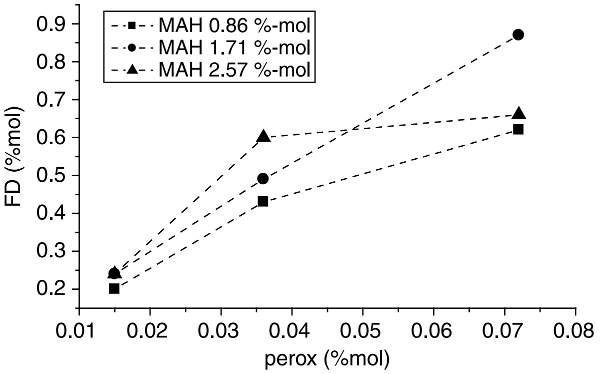


Fig. 2. FD_{MAH} of PPC as a function of the peroxide concentration at three different MAH concentration.

Table 3
Modification of PPC with BFA and peroxide in the melt mixer at 200 °C

Sample	ROOR (% mol)	BFA (% mol)	R[a]	FD_{BFA}[b] ± SD[c]	BFA conv.[d]	Eff.[e]	End-torque values (N m)	$\bar{M}_n \times 10^{-3}$ (Dalton)	$\bar{M}_w \times 10^{-3}$ (Dalton)	$\bar{M}_n/\bar{M}_w$	[η] (dl/g)
PP	–	–	–	–	–	–	8.7	58	260	4.5	1.60
PPL2	0.036	–	–	–	–	–	1.0	44	102	2.3	0.76
PPBFA1	–	0.20	–	–	–	–	6.7	58	199	3.4	1.20
PPBFA2	0.036	0.20	5.5	0.09±0.02	45.0	1.2	5.2	59	223	3.8	1.06
PPBFA3	0.036	0.86	23.9	0.10±0.01	11.6	1.4	5.8	50	244	4.9	1.12
PPBFA4	0.036	1.71	47.5	0.14±0.01	8.0	1.9	4.9	56	202	3.6	1.09
PPBFA5	0.036	2.57	71.4	0.19±0.02	7.4	2.6	4.6	56	226	3.8	1.19
PPBFA6	0.200	0.40	2.0	0.25±0.02	63.3	0.6	4.0	51	396	7.7	0.71

[a] BFA/ROOR molar ratio.

[b] FD= number of grafted BFA groups per 100 monomeric units.

[c] SD=standard deviation.

[d] Percentage of grafted BFA units with respect to the BFA concentration in the feed.

[e] Efficiency: molar ratio between the FD and the amount of primary radicals [Efficiency=FD_{BFA}/2[ROOR]].

Molecular weight and viscosity showed a decrease when the peroxide concentration in the feed was raised, which was limited by increasing the amount of MAH in the feed and keeping constant the peroxide concentration.

3.2. (B) Functionalization with peroxide and BFA

BFA was here used as functionalizing agent for its capacity to limit the polymer degradation. The initiator and monomer concentrations were chosen very similar to those adopted in the previous set (A) with MAH. The sample PPBFA6 was obtained under stoichiometric 1:1 conditions between BFA and primary radicals (assuming two free radicals per peroxide molecule) (Table 3).

The end torque values (Fig. 3) measured for samples prepared with the same amount of peroxide (0.036 mol%) and with BFA concentration varying from 0.86 to 2.57 mol% (runs PPBFA3–PPBFA5, Table 3) were higher than in the case of MAH (runs PPMAH4–PPMAH6 Table 2).

Again all the samples were washed with boiling acetone and dried until constant weight before being characterized, but unlike the FD_{MAH} determination no mathematical deconvolution was necessary to calculate the FD_{BFA} since here only one peak was detectable in the carbonyl absorption region. The value of the extinction coefficient of the carbonyl at 1726 cm^{-1}, ε_{BFA}, necessary to calculate the $FD_{BFA}=[(\varepsilon_{1464}/\varepsilon_{BFA})(A_{BFA}/A_{1464})]$, was evaluated as reported in the Section 2.

FD_{BFA} values grew with the monomer amount in the feed, but reached lower values than with MAH. The efficiency values ranged between 1 and 2.6 and were significantly lower than those obtained by using MAH (in this last case efficiency values over 8 were reached). The lack of transfer reactions in the case of BFA grafting was probably the main important parameter affecting the low efficiency values. Moreover, it was demonstrated (Section 2.2) the BFA tendency to generate oligomers (2, 3 and 4 monomeric units) terminated by disproportionation and coupling reaction, reactions that can contribute to lower the radical concentration. Besides MAH can homopropagate to grafted oligomers [5,29].

The UV characterization in the solid state of BFA functionalized films was compared with that of reference films prepared by melt mixing PPC with BFA and PPC with a commercially available ethyl 3-(2-furyl) propanoate (EFP), model compound of the saturated BFA grafted groups (Fig. 4).

PPC mixed with the BFA molecule showed a single broad band at 296 nm due to the absorption of the carbonyl group

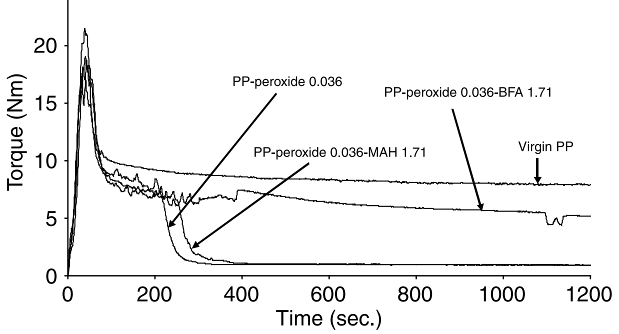


Fig. 3. Mixing torque during Brabender treatment of PPC, PPL2, PPMAH5, PPBFA4 (Tables 1 and 2) samples.

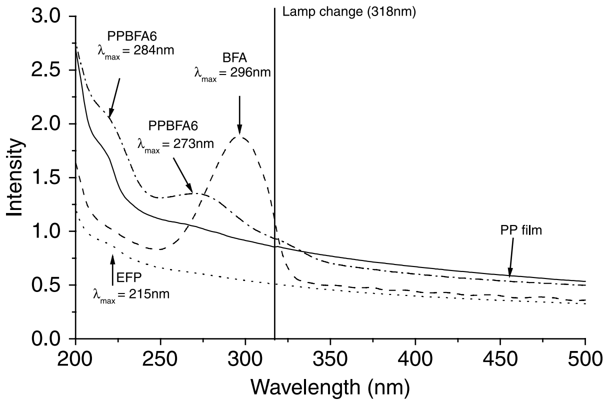
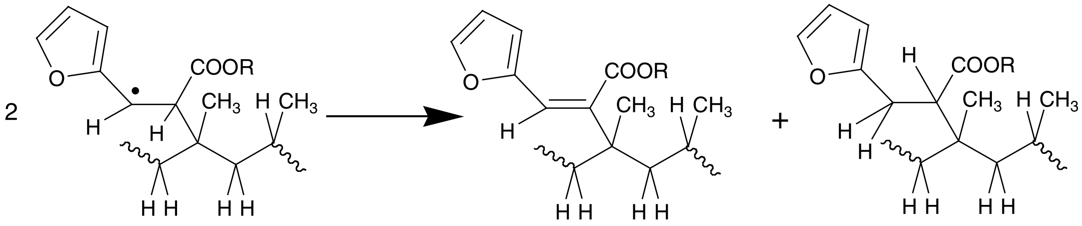


Fig. 4. UV spectra of (—) PPC, (–·–·–). PPC functionalized with BFA (spectrum PPBFA6), (- - -) PPC melt mixed with BFA (0.6%-mol, spectrum BFA) and (…) PPC melt mixed with the EFP molecule (0.6%-mol, spectrum EFP).



Scheme 1. Disproportionation reaction of PPBFA$^\bullet$ macroradicals.

conjugated with the double bond and the furan ring (sample BFA, Fig. 4). The PPC melt mixed with the saturated molecule EFP did not show detectable absorptions between 230 and 500 nm (the signal at 215 nm is likely caused by the furan ring). The band attributable to the carbonyl group was not detectable here because it has a smaller ε than furan (sample EFP, Fig. 4). The UV spectrum of the BFA functionalized PPC (sample PPBFA6), previously washed in boiling acetone and accurately dried, showed a band at 273 nm not observed in the EFP spectrum and attributable to the presence of unsaturated grafted groups. The shift of 23 nm between the BFA and the PPBFA6 absorption band could be ascribed to the influence of the bonded bulky PPC chain. The presence of both unsaturated and saturated BFA grafted groups (Fig. 4) can be ascribed to disproportionation reactions of PPBFA$^\cdot$ macroradicals (Scheme 1).

In addition to the low transfer tendency of PPBFA$^\cdot$ macroradicals, this 'termination' reaction (disproportionation) is responsible for the low efficiency (low FD) observed by using BFA. Indeed a good FD_{BFA} (0.25 mol%) and monomer conversion (62.5%) were obtained only under stoichiometric conditions between expected primary radicals and BFA (run PPBFA6).

SEC results for this second set of experiments (Table 3) showed a substantial conservation of $\bar{M}_w$, $[\eta]$ and MWD with only a moderate decrease of $\bar{M}_w$ (10–25%) with molar ratio monomeric units/peroxide >2500 and BFA/peroxide >5.5. As soon as monomeric units/peroxide and BFA/peroxide ratios were lowered to 500 and 2, respectively (sample PPBFA6), $\bar{M}_n$ decreased of about 10% while $\bar{M}_w$ increased of about 50% giving a broader MWD, thus suggesting the occurrence of chain branching according also to the lower viscosity. At such very high peroxide concentration, the stoichiometric amount of BFA was not sufficient to quench all macroradicals on the PP chains and to prevent their combination. As reported in literature [30,31] under these conditions (high macroradicals concentration), the rate of macroradicals combination is much faster than the rate of chain scission and some branching or chain extension can be favored.

3.3. (C) Functionalization with peroxide, BFA and MAH

MAH and BFA were used jointly in order to simultaneously improve the functionalization degree and limit the degradation. 3 samples (PPMAHBFA1–PPMAHBFA3) were obtained by using an excess of BFA and MAH with respect to the primary radicals (with constant BFA and varying MAH content); 5 more samples were prepared under stoichiometric conditions with [BFA]:[MAH]:[primary radicals] $=1:1:1$ (PPMAHBFA4–PPMAHBFA8). Moreover other 4 samples (PPMAHBFA9–PPMAHBFA12) were prepared by arranging a 1/1 molar ratio between BFA and primary radicals while varying the MAH amount and the peroxide with respect to the polymer (Table 4).

The functionalization degree of all the samples was here calculated by FT-IR analysis (Fig. 5) after the mathematical deconvolution of the spectra in analogy to the procedure adopted in the set (A), but considering also the band due to the ester group of grafted BFA molecules (Section 2).

The comparison of the three sets of functionalization experiments showed (Fig. 6) that in all cases FD increased by increasing the functionalizing monomer (either MAH or BFA) concentration while MAH gave the higher FD. The effect of monomer concentration on molecular weight was for each set very limited but BFA showed a better conservation of chain length than MAH.

MAH conversion was rather low when BFA was added to the system, whereas the BFA conversion resulted quite high and increased with the increase of MAH concentration.

Looking at samples obtained under stoichiometric conditions a remarkable increase of FD and $\bar{M}_w$ (Fig. 7) occurred by raising all the reagent concentration with [BFA]:[MAH]:[primary radicals] $=1:1:1$ molar ratio (runs PPMAHBFA4–PPMAHBFA8, Table 4 and Fig. 7). Monomer conversion increased as well and maximum values were reached by using higher reagent concentrations.

Samples PPMAHBFA6 and PPMAHBFA7 showed very high $\bar{M}_w$ and large polydispersity indicating the possible formation of a chain branched structure. Also the sample PPMAHBFA8 resulted 38% by weight not extractable with boiling xylene suggesting the partial formation of cross-linked or highly-branched polymer. Besides, for the two groups of samples (PPMAHBFA5, PPMAHBFA9, PPMAHBFA10 and PPMAHBFA7, PPMAHBFA11, PPMAHBFA12), prepared by keeping 1:1 the ratio between primary radicals and BFA, the FD values increased whereas $\bar{M}_w$ decreased by raising the MAH in the feed (Fig. 8).

For the lowest peroxide concentration the $\bar{M}_w$ decrease was very limited and the BFA conversion raised up to 100% by increasing the MAH concentration (series A, Fig. 8).

By taking into account all the experimental results collected from set (A), (B) and (C) several reactions appeared to take

Table 4
Modification of PPC with MAH, BFA and peroxide in the melt mixer at 200 °C

Sample	ROOR (% mol)	MAH (% mol)	BFA (% mol)	FD_{MAH}[a] ± SD[b]	FD_{BFA}[a] ± SD[b]	MAH conv.[c]	BFA conv.[c]	$\bar{M}_n \times 10^{-3}$ (Dalton)	$\bar{M}_w \times 10^{-3}$ (Dalton)	$\bar{M}_n/\bar{M}_w$	[η] (dl/g)
PP	–	–	–	–	–	–	–	58	260	4.5	1.60
PPMAHBFA1	0.036	0.86	0.20	0.12±0.02	0.08±0.01	14.0	40.0	55	172	3.1	0.97
PPMAHBFA2	0.036	1.71	0.20	0.14±0.02	0.10±0.02	8.2	50.0	54	185	3.4	0.99
PPMAHBFA3	0.036	2.57	0.20	0.18±0.01	0.13±0.01	7.1	66.7	49	192	3.9	1.03
PPMAHBFA4	0.050	0.10	0.10	0.04±0.02	0.02±0.01	53.3	16.7	48	156	3.3	0.91
PPMAHBFA5	0.100	0.20	0.20	0.13±0.01	0.07±0.01	65.0	33.3	55	168	3.0	0.67
PPMAHBFA6	0.200	0.40	0.40	0.26±0.01	0.18±0.02	65.0	45.8	47	257	5.4	0.73
PPMAHBFA7	0.300	0.60	0.60	0.39±0.02	0.20±0.01	64.4	33.9	53	298	5.6	0.66
PPMAHBFA8	0.400	0.80	0.80	0.47±0.06	0.34±0.01	58.3	42.5	nd[d)]	nd[d)]	nd[d)]	nd[d)]
PPMAHBFA9	0.100	0.86	0.20	0.39±0.05	0.18±0.02	45.3	90.0	58	167	2.9	0.59
PPMAHBFA10	0.100	1.71	0.20	0.58±0.07	0.20±0.01	34.1	100.0	49	151	3.1	0.60
PPMAHBFA11	0.300	0.86	0.60	0.58±0.07	0.35±0.06	67.8	58.9	45	233	5.3	0.59
PPMAHBFA12	0.300	1.71	0.60	1.18±0.12	0.55±0.05	68.7	91.7	32	126	4.0	0.48

[a] Number of grafted groups per 100 monomeric units.
[b] SD = standard deviation.
[c] Percentage of grafted MAH or BFA units with respect to their concentration in the feed.
[d] The functionalized sample PPMAHBFA8 is not totally soluble in TCB at 145 °C.

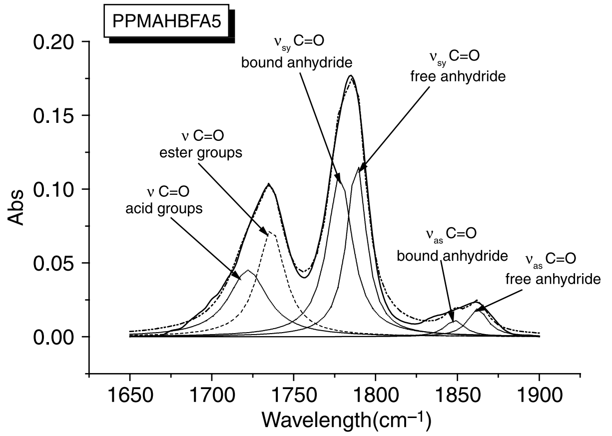


Fig. 5. Deconvolution of PPMAHBFA5 FT-IR spectrum in the range 1900–1650 cm^{-1}.

place simultaneously after the initial formation of macroradicals (PP$^{\bullet}$) (1) as tentatively illustrated in Scheme 2.

With MAH as functionalizing monomer reaction 2 occurred significantly (set (A)) [the SEC analysis showed that the PPC $\bar{M}_w$ decreased from 260,000 (PPC) to 70,000 (PPMAH7)]. Reaction 3 was rather efficient and the FD_{MAH} quite elevated. Indeed, it is known that grafted MAH (onto PP$^{\bullet}$ or PP$'^{\bullet}$) has a strong tendency to give H-abstraction (reaction 4) and then transfer to increase FD. Clearly the macroradicals on polypropylene chains can also give degradation.

When BFA was used as functionalizing monomer (set (B)) reaction 2 was drastically inhibited. Since, the IR analysis showed the successful functionalization of PPC macromolecules, it can be supposed that the control of the polymer degradation is strongly connected with the BFA grafting. The PP–BFA$^{\bullet}$ radical was probably promptly formed by reaction 6 as suggested by literature [23,24]. This macroradical is stabilized by resonance and has a lower tendency compared to PP–MAH$^{\bullet}$ to give H-abstraction and therefore it is more likely involved in coupling (reaction 7) or in disproportionation (reaction 8). Actually, in stoichiometric conditions, the SEC analysis showed that PPC $\bar{M}_w$ increased from 260,000 to 396,000 (PPBFA6) by increasing the reagent concentrations and the UV analyses performed on PPBFA sample films showed that the BFA was grafted on the polymer backbone both as saturated and unsaturated group. Moreover, the efficiency values were very low (between 1 and 2). Reaction 5 cannot be excluded even if the homopolymerization experiment of BFA showed the low tendency of the monomer to oligomerize. Consequently reaction 9 has to be taken into account on the basis of radicals balance and efficiency values. In order to increase the FD by keeping unchanged or controlled the PPC molecular weight a growing amount of peroxide can be used, by maintaining the ratio between primary radicals and BFA equal to 1. In the case of PPBFA6 (2ROOR = BFA = 0.4 mol%) a higher FD value was obtained with respect to the PPBFA5 (ROOR = 0.036 mol%, BFA = 2.57 mol%) prepared by using an excess of BFA compared to primary radicals.

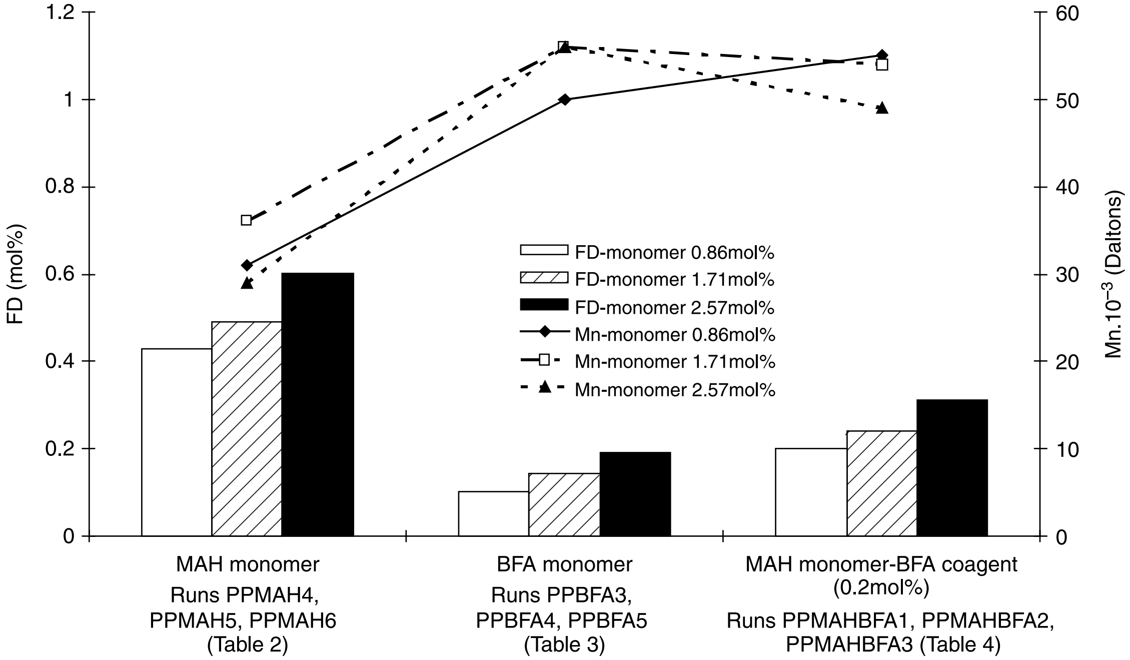


Fig. 6. FD and $\bar{M}_n$ as function of monomer nature (MAH, BFA and MAH with BFA) and concentration for a fixed concentration of peroxide in the feed (0.036 mol%).

When BFA and MAH were used jointly the competition between coupling, disproportionation and transfer reactions was function of the different macroradicals (PP$^{\bullet}$, PPBFA$^{\bullet}$ and PPMAH$^{\bullet}$) reactivity and concentration. Moreover, the coupling reaction between PP–MAH$^{\bullet}$ and PP–BFA$^{\bullet}$ (reaction 10) as well as the addition of these macroradicals to the double bond of free functionalizing molecules can occur (reactions 11 and 12). Even if at the moment it is not possible to totally exclude one or more of the proposed group of reactions, the results evidenced again that the best data in terms of FD and MW conservation can be reached by using a stoichiometric ratio between all the reagents ([BFA]:[MAH]:[primary radicals] = 1:1:1).

The use of a coagent able to assist the PP radical functionalization avoiding the material degradation and improving the FD is a method already attempted in the past [16–18] as demonstrated by exhaustive and detailed papers

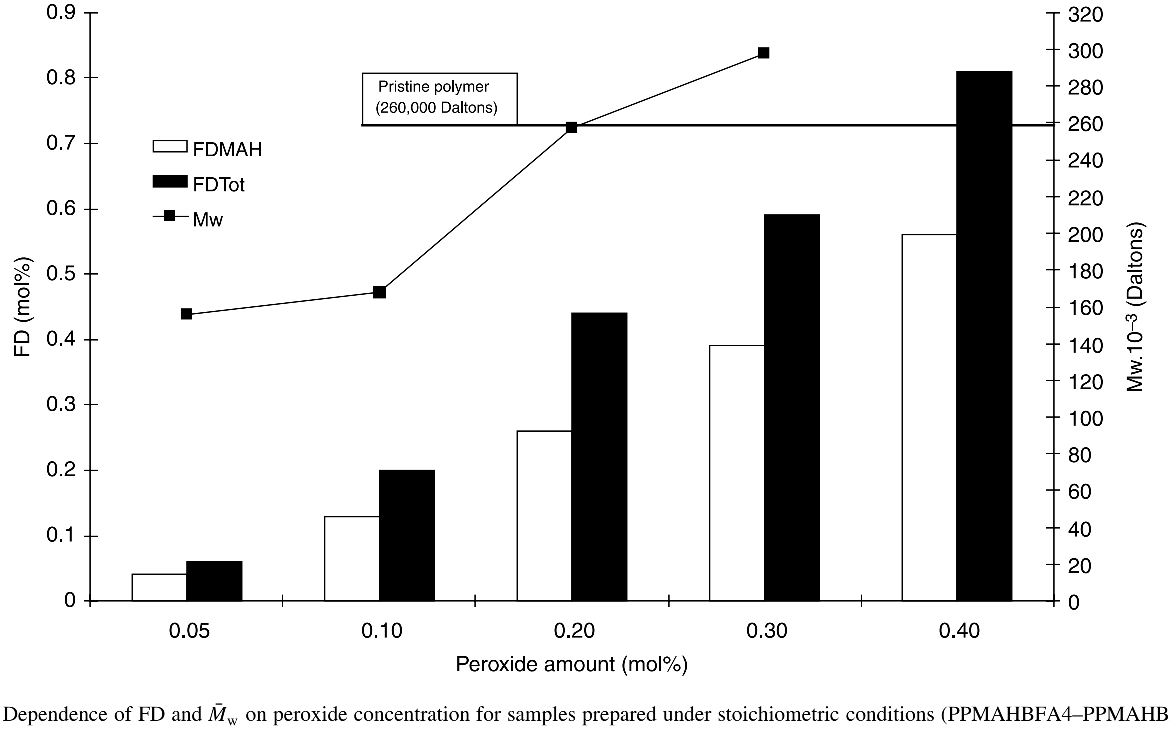


Fig. 7. Dependence of FD and $\bar{M}_w$ on peroxide concentration for samples prepared under stoichiometric conditions (PPMAHBFA4–PPMAHBFA8).

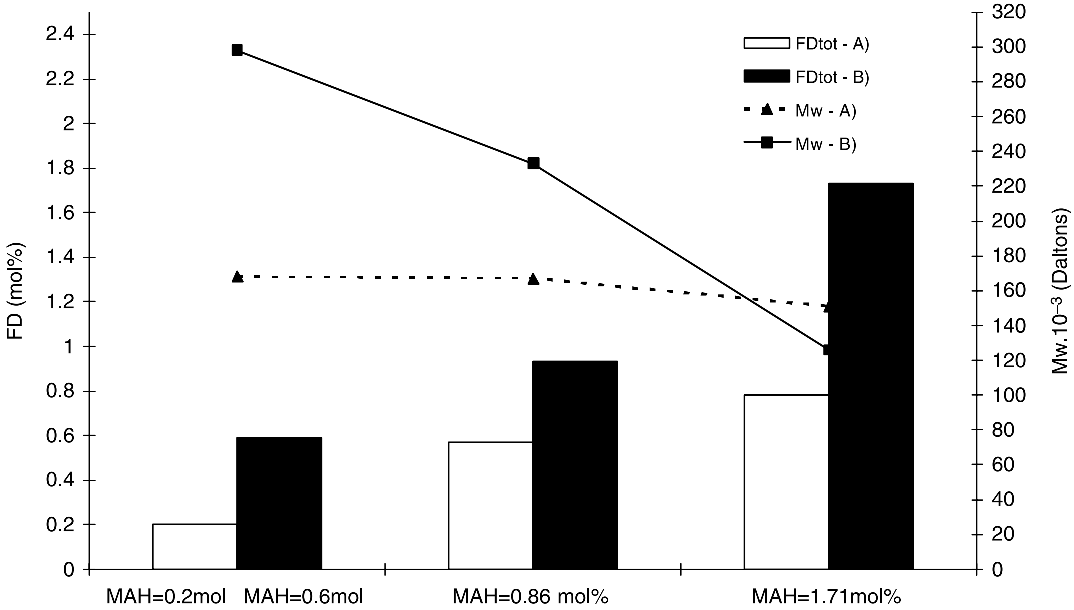


Fig. 8. Total FD ($FD_{MAH}+FD_{BFA}$) dependence on MAH concentration in the feed for PPC samples functionalized under stoichiometric primary radicals and BFA conditions: (A) [ROOR] = 0.1 mol% and [BFA] = 0.2 mol%; (B) [ROOR] = 0.3 mol% and [BFA] = 0.6 mol%.

concerning the use of the styrene as co-monomer during the PP functionalization with MAH, glycidyl methacrylate, etc. Both styrene and BFA are able to limit the PP degradation and this results can be correlated to a sort of quenching of PP tertiary macroradicals reactivity in term of β-scission reaction.

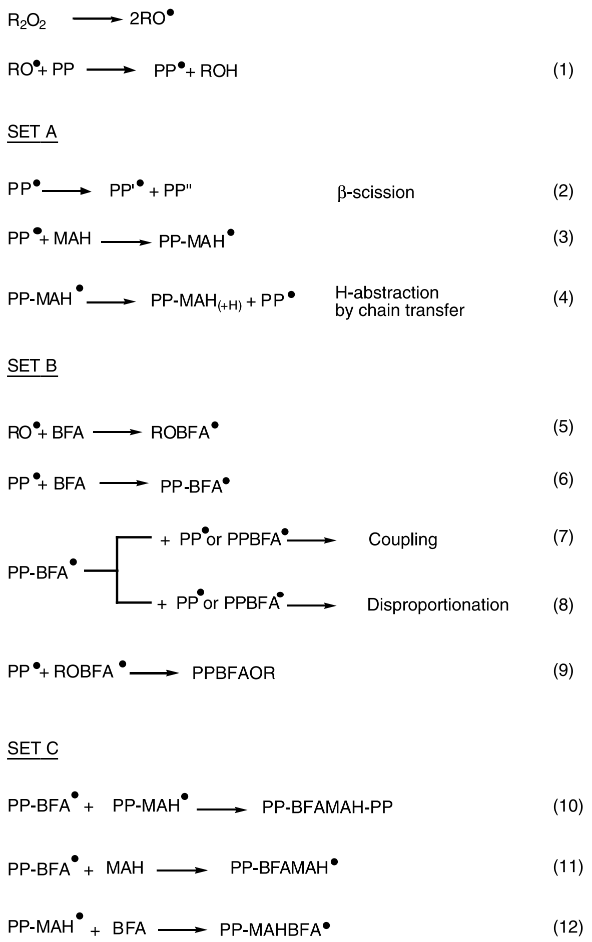
4. Conclusions

By using BFA, which stabilizes macroradicals during the PPC functionalization with MAH it was possible to obtain PPC with good FD values and molecular weight conservation depending on the different molar ratio between chemical reagents.

BFA molecule showed a higher reactivity towards macroradicals generated onto PPC with respect to MAH but a lower tendency to do transfer reactions: it was able to preserve fairly unchanged the MW of the pure polymer even if the efficiency values for functionalization were generally low due to the occurrence of termination reactions through disproportionation or coupling. The grafting level was increased by raising the amount of primary radicals and by keeping them in stoichiometric ratio with BFA.

By using MAH as functionalizing agent assisted by the BFA coagent, the best results in terms of FD and MW conservation were achieved by working again under stoichiometric conditions among all the reagents. This approach ensured to preserve the PPC MW and to reach at the same time good conversion level of both the monomers up to FD of 1.6% by mol.

The optimal ratio BFA/primary radicals equal to 1 acts in the degradation/branching competition favoring the latter one and limiting considerably or totally the effect of the β-scission.



Scheme 2. Predominant reactions of the PP macroradicals under three different feed conditions used: (A) PPC functionalization with peroxide and MAH; (B) PPC functionalization with peroxide and BFA; (C) PPC functionalization with peroxide, BFA and MAH.

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