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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:

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

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 $R=CH_3$.