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Functionalization of Polyolefins by Reactive Processing: Influence of Starting Reagents on Content and Type of Grafted Groups

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Summary: Previous studies carried out in our laboratory on the functionalization of ethylene polymers (homo and copolymers) through free radical processes, using mechanical mixers and/or extruders with diethylmaleate (DEM) and dicumyl peroxide (DCP), have shown that the presence of branched α-olefin blocks favours degradation versus functionalization and crosslinking whereas these last are more effective with linear ethylene blocks.
In this contest the present paper reports about attempts to extend the same processes to propylene polymers by benefitting of the indications of previous results. In particular the one step functionalization of EPM with two or more different groups was carried through the use of different monomers. Moreover the procedure was extended to polypropylene thus obtaining a significant functionalization degree flanked by a remarkable decrease of molecular weight.

Keywords: ethylene-propylene rubber (EPM), functionalization, FT-IR, melt processing, Poly(propylene) (PP)

Introduction

The free radical initiated functionalization of polyolefins (PO) is a method largely used from an industrial point of view to prepare modified materials used as chemical coupling agents to increase the polymer interfacial interactions with inorganic fillers and the miscibility with polar polymers as well as to produce polyolefins with improved adhesion and dyeability.

In the last two decades, thanks to the studies concerning the PO radical grafting,[1,2,3] mainly of maleic derivatives, a large number of results were reported and the commercial use of functionalized PO in polymer blends was substantially increased.

Modifying reactions promoted by free radicals, derived from thermal decomposition of initiator, and carried out on the molten material in extruders or mechanical mixers, are

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versatile and easy to apply. They allow to obtain functionalized PO macromolecules by grafting to the PO backbone a limited amount (generally around 1% mol) of functional groups used for a growing number of industrial applications. On the other side the formation of extremely reactive not very selective free radical species brings to the contemporary occurrence of side reactions like degradation, chain extension and crosslinking. The modulation of the feed composition (monomer/radical initiator ratio)[4] was used in order to promote the desired reaction while suppressing the side reactions.

Also the functionalization degree (FD) depends both on the structure of the polyolefin and on the feed composition. The presence of isolated α-olefin units favours higher FD values due to the easier formation of macromolecular free radicals by hydrogen abstraction from tertiary C-atoms (LLDPE, VLDPE, EPR). Also the presence of double bonds increases FD due to a contribution of the "ene" reaction between these double bonds and the monomer. The polyolefins, which are degraded by chain scission, such as PP or SEBS, show the lowest FD.[4,5]

In previous papers[6] starting from the above mentioned results it was possible to find a proper feed composition range within which the FD was linearly dependent on functionalizing monomer concentration according to the equation:

$$FD = k_g \left(\frac{2fk_D [DCP]_0}{k_t} \right)^{1/2} \cdot [DEM] \qquad (1)$$

where k_g = rate constant of the grafting reaction, k_D and k_t are the rate constant of initiator decomposition and termination reactions; [DCP] is the molar concentration dicumyl peroxide, the radical initiator, and [DEM] is the molar concentration of diethyl maleate, the functionalizing monomer. In proper composition range both degradation and crosslinking were negligible in respect to the grafting (functionalization) reaction. Thus the evolution of the process could be very well simulated by a mathematical kinetic model validated by DSC measurement of the heat evolution *vs* time.[7]

In order to further develop this very convenient process in the direction of producing functionalized propylene polymers, we have investigated in this paper the effect of monomer structure and feed composition on the reaction behaviour in the attempt to identify the best conditions for introducing different functional groups in one step and to extend the process also to propylene homopolymers.

Experimental Part

Isotactic Polypropylene (iPP) homopolymer having a melt flow rate (MFR) of 0.24 g/10 min was supplied by Borealis BE 50/E1271; poly(diethyl fumarate) (PDEF) was prepared by radical initiator (AIBN) as reported in the literature.[8]

Dicumyl peroxyde DCP (Sigma-Aldrich) was used as provided without further purification. Azobisisobutyronitrile AIBN (Sigma-Aldrich) and maleic anhydride MAH were recrystallized from acetone and benzene respectively. Diethylmaleate (DEM), Sigma-Aldrich product, was used after distillation under reduced pressure (0.33 mmHg, 53°C). The cetyl maleate monomer was a commercial product about 98% pure as checked by gas-chromatography.

Modified EPM samples were prepared using a Brabender Plastograph PL2100 mixer, torque and temperature data have been acquired by Brabender Mixing software WinMix ver.1.0. Two different temperatures: 180°C in the case of EPM1 run and 230°C in the case of EPM2 run were used and the reaction time was 10 minutes and rpm=30. The polymers recovered were extracted with boiling acetone (see Table 1).

The modified PP samples were prepared with the same procedure by melt-mixing the components at a temperature of 180°C and rotor speed of 50 rpm. 20 g of iPP were introduced into the Brabender chamber. After complete fusion, 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 (see Table 2).

FT-Infrared spectra were performed with a Fourier Transform Spectrometer “Perkin Elmer FT-IR 1760-X” on films made by compression moulding. Proton magnetic resonance spectra were performed with a spectrometer “Varian Gemini 200 MHz”; the spectra of functionalized polymers were made in solution of 1,2,4-trichlorobenzene, using 1,1,2,2-tetrafluorodideuteroethane as internal standard, at the temperature of 90°C.

Results and Discussion

One Step Multifunctionalization of EPM

The contemporary use of DEM and MAH as monomers allowed to produce EPM macromolecules containing different functional groups;[9] however some interference were observed between the two monomers leading to a different composition in respect to the feed and low monomer conversion at least for DEM.[8] In order to attempt the preparation of a similar multifunctionalized EPM and avoid the problem of using a mixture of comonomers with different compatibility in the EPM melt, a monoester of maleic acid was used. The compatibility problem with the hydrophobic PO was solved by the use of a long alkyl chain (cetyl) which provided a substantial homogeneity of the reaction mixture.

Reaction samples were prepared starting from an ethylene-propylene copolymer (EPM) characterized by 22.7% propylene units with DCP as radical initiator (Table 1).

Table 1. Functionalization runs of EPM with cetyl maleate.

Runs	cetyl maleate monomer content %by mol	DCP peroxide content % by mol
EPM1[a)]	0.88	0.06
EPM2[b)]	0.88	0.06

[a)] the run has been carried out in the Brabender mixer at 180°C, rpm=30, t=10min
[b)] the run has been carried out in the Brabender mixer at 230°C, rpm=30, t=10min

The IR spectra have been acquired on the samples after the reaction and washed with boiling acetone. The presence (Figure 1) of four absorption peaks, partially overlapped, between 1700÷1900 cm^{-1}, related to carbonyl stretching, suggests that different groups are grafted to the polyolefin chain.

According to literature data the vibrations in the C=O stretching region can be assigned as follows: peak at 1735 cm^{-1}: ν_{co} ester group, peak at 1710 cm^{-1}: ν_{co} acid group, peaks at 1780 cm^{-1} and 1865 cm^{-1}: ν_{co} symmetrical and ν_{co} asymmetrical of the anhydride group.

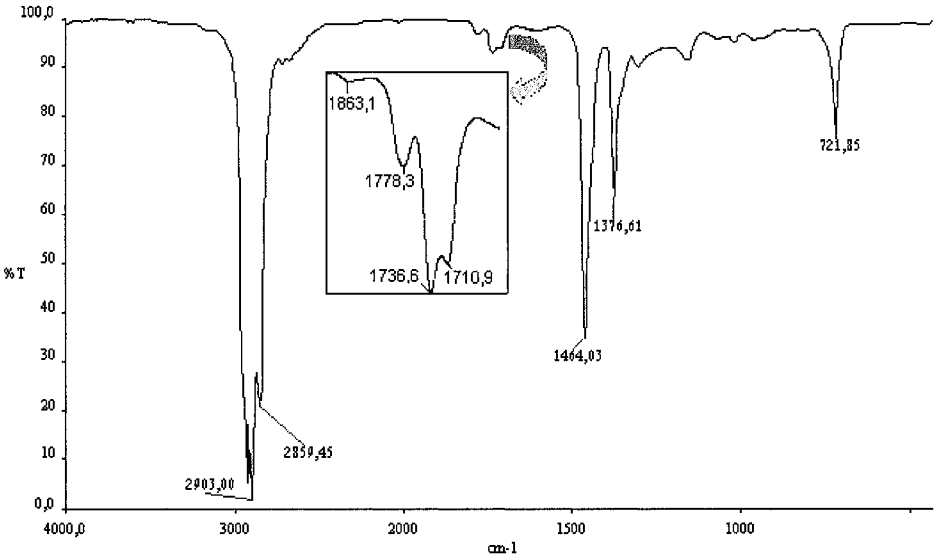

Fig. 1. IR spectrum of EPM2 run.

One can suppose that the three different types of groups reported in Figure 2 are grafted to the EPM chains. The presence of the anhydride group (B) suggests the possible intermediate formation of succinic acid groups (C) after the insertion which can undergo cyclization at high temperature. It is however not possible to exclude that maleic acid and maleic anhydride are formed from the maleic acid cetyl monoester before the grafting.

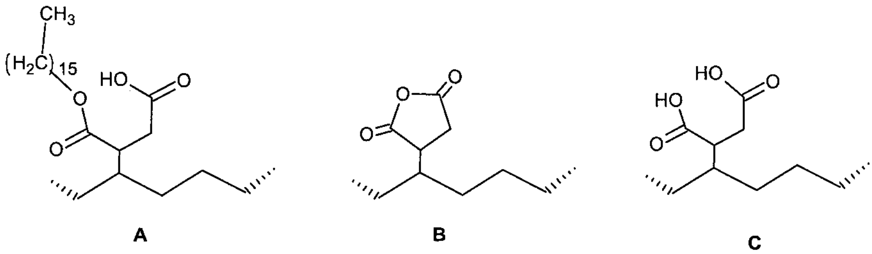

Fig. 2. Functional groups inserted onto polyolefin chain (EPM).

Indeed the thermogravimetric analysis (TGA) of the mono cetyl maleate carried out under an atmosphere of nitrogen consists of two steps. Starting from 100°C we observed a weight loss of 63% wt connected probably with the development of cetyl alcohol at T_{max} at 237°C. As this last temperature is close to that of reaction, the presence of the anhydride groups onto the polymer backbone can be associated with a similar mechanism.

The deconvolution of the EPM2 spectrum (Figure 3) has been performed to detect the functionalization degree and type of grafted groups.

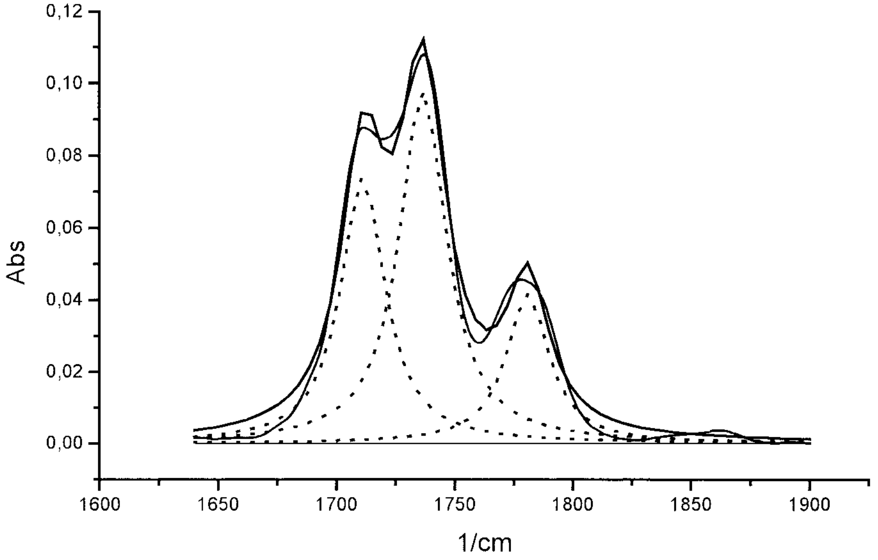

Fig. 3. Deconvolution of the carbonyl stretching region of the EPM2 IR spectrum.

The FD value referred to diethysuccinate groups were found to be $FD_{(SAH)} \cong 0.05\%$ mol. For the same sample ^{1}H-NMR signal at 4.15 ppm (-O-CH_2-) of the ester groups grafted onto the polymer chain, gives FD $\cong$ 0.2% mol. By considering the total amount of the primary radicals (0.12 to respect 100 monomeric units of the polymer) it is possible to calculate the value of the efficiency that is slightly larger than 2. Moreover, on the basis of the amount of the monomer in the feed, conversion of about 30% was calculated.

These results are quite in agreement with those obtained in the case of the functionalization reaction with diethylmaleate thus confirming preliminarily the same mechanism for both the functionalizing monomers.

One Step Multifunctionalization of PP

The functionalization reactions of iPP was carried out, above its melting temperature, with maleic acid derivatives and radical initiator under conditions granting low extent of side reactions for ethylene polymers.[6]

Two series of experiments have been performed. In the former (runs PP03-09, Table 2) diethyl maleate (DEM) and dicumyl peroxide (DCP), and in the latter, a mixture of DEM/maleic anhydride (MAH) 2:1 mol and DCP (runs PP10-11 Table 2) were used.

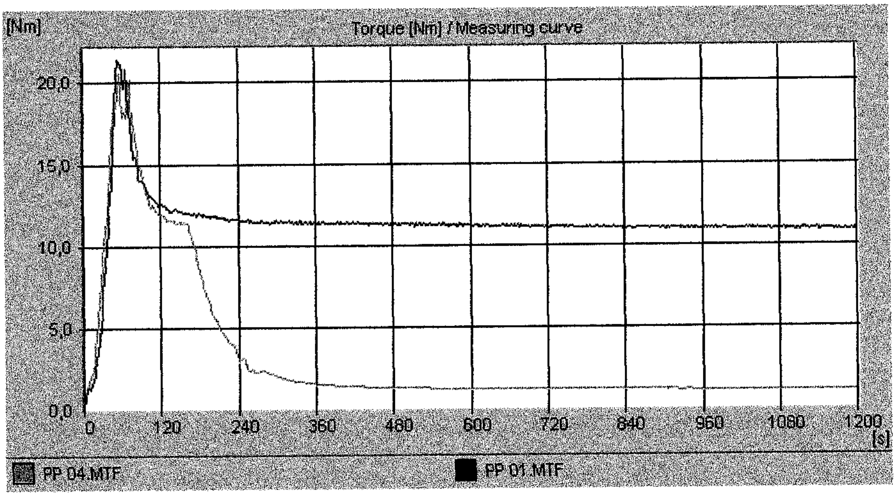

Fig. 4. Torque *vs* time for the runs PP01 (Polypropylene treated in Brabender at 180°C without peroxide and functionalizing monomers) and PP04 (PP with DCP and DEM).

The mixing torque graph (Figure 4) is similar for all the samples independently of the monomers/DCP fed ratio in the Brabender chamber with a sharp decrease of the torque values after addition of the monomer-DCP solution to the molten polymer. The described behaviour can be correlated to the viscosity decrease of the molten polymer caused by degradation reactions. In fact, in the case of isotactic polypropylene (iPP) the treatment with peroxide initiators in the melt gives to the polymer degradation through β-scission reactions.[10]

The samples were analysed by FT-IR after washing with boiling acetone before the functionalization degree (FD) determination. The standardization curve was obtained by preparing mixtures of known composition of iPP with poly(diethyl fumarate) (PDEF), according to the method usually adopted in our laboratory.[11]

Bands at 1736 cm^{-1} (A1) and at 1166 cm^{-1} (A2) have been taken into consideration. By plotting the peak areas ratio (A1/A2) versus the composition of the mixtures iPP/PDEF, ranging from 0.15% mol to 0.85% mol of PDEF, a good linear correlation has been obtained. This suggests that the A1/A2 band areas ratio can be safely used also for detecting FD of iPP samples functionalized by DEM grafting (PP-g-DES). The FD values range from 0.2% to 1% mol (Table 2) with DEM conversion values from 7 to 30%; these values are lower than those obtained in the case of polyethylenes (PE) functionalization probably due to the occurrence of secondary reactions with particular reference to the degradation process.

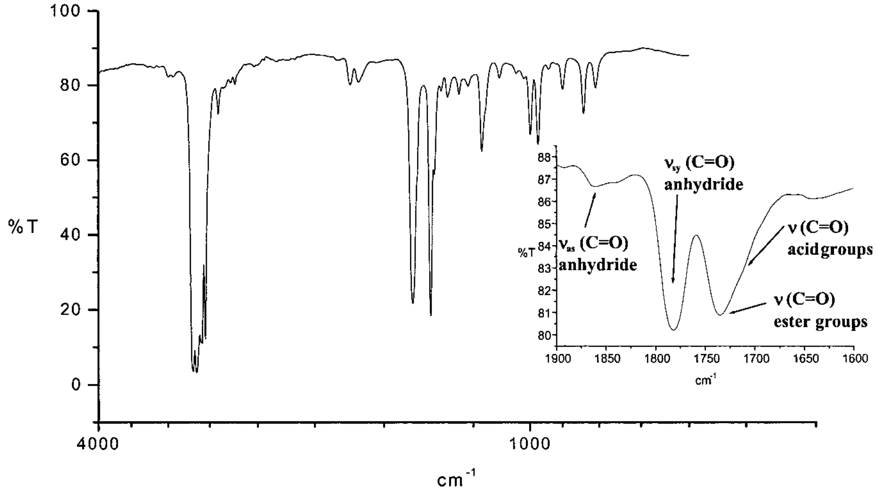

Fig. 5. FT-IR spectrum for PP10 sample.

With a DEM/MAH mixture FD determination is more complex as different types of groups are grafted on iPP chains. FT-IR spectra present superposition of diagnostic bands (ester, anhydride, acid obtained by hydrolysis of anhydride groups) (Figure 5).

The deconvolution of the spectra carried out by a non-linear fitting of experimental points allows to obtain separately the diagnostic band areas (Figure 6).

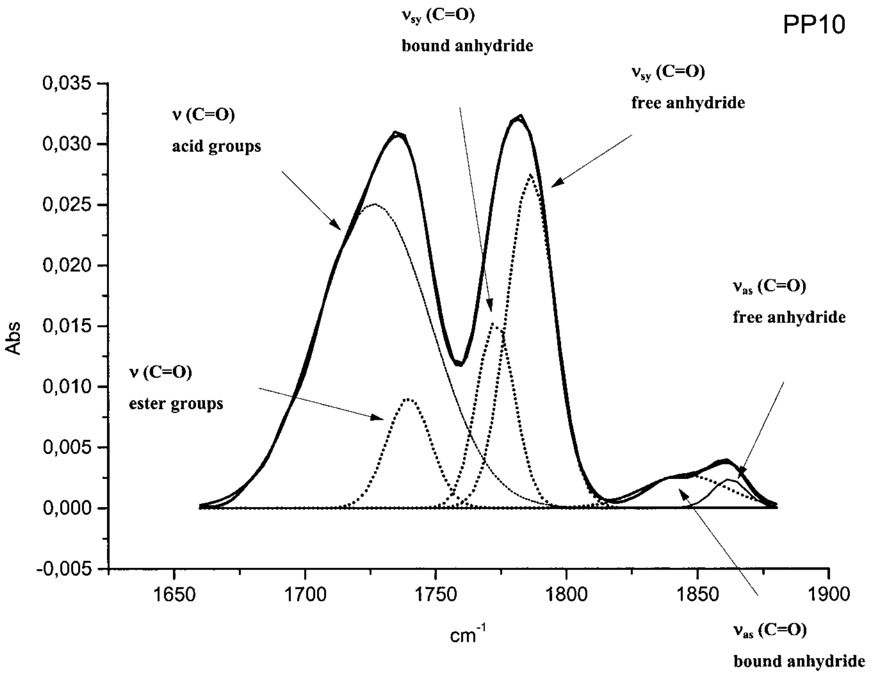

Fig. 6. Deconvolution of PP10 IR spectrum ranging from 1660 cm^{-1} to 1880 cm^{-1}.

The knowledge of the integral absorptivity (ε) for all the bands used, allows the evaluation of the FD values (Table 2) relative to DES, SAH and SA groups have been calculated:

$$FD_{(DES)} = \frac{\overline{\varepsilon_{1166}}}{\overline{\varepsilon_{DES}}} \cdot \frac{\overline{A_{DES}}}{\overline{A_{1166}}} \qquad (2)$$

$$FD_{(SAH,SA)} = \frac{\overline{\varepsilon_{1166}}}{\overline{\varepsilon_{SA}}} \cdot \frac{\overline{A_{SA}}}{\overline{A_{1166}}} + \frac{\overline{\varepsilon_{1166}}}{\overline{\varepsilon_{SAH}}} \cdot \frac{\sum_i \overline{A_{SAH,i}}}{\overline{A_{1166}}} \qquad (3)$$

SAH = succinic anhydride grafted groups

SA = succinic acid grafted groups

Table 2. FD values of functionalized iPP samples.

Runs	DEM % mol	MAH % mol	DCP % mol	M/DCP[a)] mol/mol	FD_{DEM}[b)]	FD_{MAH}[b)]	DEM conv.[c)]	MAH conv.[c)]
PP03	2.44	-	0.08	30.5	0.17	-	7.0	-
PP04	4.88	-	0.08	61.0	0.34	-	7.0	-
PP05	4.88	-	0.16	30.5	0.86	-	17.6	-
PP06	4.88	-	0.23	21.2	1.04	-	21.3	-
PP07	1.22	-	0.08	15.2	0.20	-	16.4	-
PP08	2.44	-	0.16	15.2	0.58	-	23.8	-
PP09	2.44	-	0.23	10.6	0.73	-	29.9	-
PP10	1.90	0.95	0.08	35.6	0.10	0.65	5.3	65.3
PP11	1.90	0.95	0.16	17.8	0.09	0.86	4.7	90.5

a) monomer/DCP molar ratio
b) number of inserted groups to respect 100 of monomeric units of the polymer
c) conversion (% by mol)

MAH seems more reactive than DEM; probably for its capability to give oligomer chains grafted onto iPP macromolecules.[9] Moreover, the mixing solid monomer MAH with liquid monomer DEM could favour its penetration into the molten polymer and promote the MAH grafting reactions. After the functionalizing reactions all samples are completely soluble in toluene (insoluble fractions <1% wt) and therefore it is possible to assume that changes of MW and structure of PP have taken place (Table 3). Indeed about 80% wt of starting iPP and also of iPP treated in Brabender mixer without additives is insoluble under the employed conditions.

These data show that the treatment of iPP in the melt with peroxide and maleate molecules yields good functionalization degrees, but at the same time the chains β-scission process, due to the presence of many tertiary carbon atoms, is responsible for extensive degradation and decrease of MW. The efficiency values of the peroxide for iPP is lower than in the case of polyethylene and EPM copolymer (Table 4) thus confirming the occurrence of secondary reactions reducing the macroradicals amount which reacts with the functionalizing monomers.

Table 3. Solubility and molecular weight of functionalized iPP samples.

Sample	DEM % mol	MAH % mol	DCP % mol	Residue toluene extraction % wt	[η] (dL/g)	MW_η
PP01[a)]	–	–	–	82.9	3.12	370000
PP02	–	–	0.08	1.1	1.12	100000
PP03	2.44	–	0.08	1.5	–	–
PP04	4.88	–	0.08	<1	1.20	110000
PP05	4.88	–	0.16	<1	–	–
PP06	4.88	–	0.23	<1	–	–
PP07	1.22	–	0.08	<1	–	–
PP08	2.44	–	0.16	<1	–	–
PP09	2.44	–	0.23	<1	–	–
PP10	1.90	0.95	0.08	2.5	1.25	120000
PP11	1.90	0.95	0.16	<1	–	–

[a)] Polypropylene treated in Brabender at 180°C without peroxide and functionalizing monomers

Table 4. Initiator efficiency in iPP, LLDPE and EPM polymer treatment with DEM and DCP as functionalizing agents.

Runs	DCP % mol	M/DCP[a)] mol/mol	Efficiency[b)]
PP04	0.08	61	2.1
PP05	0.16	30.5	2.7
PP06	0.23	21.2	2.3
E12[c)]	0.11	32.7	5.7
E16[c)]	0.22	16.4	3.9
EPR2-01[c)]	0.11	16.4	5.7
EPR2-08[c)]	0.05	36	9.7

[a)] monomer/DCP molar ratio
[b)] defined as the molar ratio between the functionalization degree and the amount of primary radicals[4]
[c)] data reported in the reference 4

Beside the grafting reaction, free radicals derived from the peroxide decomposition produces a remarkable degradation of PP chains under mixing conditions. Indeed the run PP02 shows that by treatment with the sole peroxide $MW\eta$ goes from 370000 of the original polymer to 100000 of the processed PP.[6] The same effect occurs even in the presence of MAH or DEM (see runs PP04 and PP10) and is largely responsible of the increased solubility in toluene of the produced PP (Table 3). The average viscosimetric molecular weight (MWη) has been determinated by the Mark-Houwink equation.[12]

By successive self-nucleation and annealing DSC (SSA-DSC)[13,14] a distribution of melting points induced by SSA treatment has also been observed. PP01 sample has a melting peak centred at about 170°C. The PP02 sample and the functionalized samples showed lower values of Tm, around 165°C, and many peaks appear at lower temperatures probably related to the degradation by β-scission of PP macromolecules into shorter chains some of which having probably lower stereoregularity.

Final Remarks

The functionalization of different polyolefins in the melt in the presence of a free radical initiator and unsaturated monomers can be carried out with a significant control of the process by proper selection of the feed composition in relation to the starting PO structure.

In case of EPM the previously selected conditions to optimize the functionalization reactions against degradation and crosslinking can be successfully used to insert different functional groups either by starting with a mixture of monomers (DEM+MAH) or with a monoester of maleic acid. Under analogous feed composition polypropylene gives a significant functionalization but degradation cannot be avoided according to the fact that β-scission is not extensively hindered by the presence of maleate.

On the basis of these indications further study of the functionalization of PP is in due course with different reactive monomers.

Acknowledgement

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[1] G. Moad, *Prog. Polym. Sci.* **1999**, *24*, 81-142
[2] S. Al-Malaika, *"Reactive modifiers for polymers"*, Academic & Professional, London, UK, **1997**
[3] A.V. Machado, J.A. Covas, M. Van Duin, *Polymer* **2001**, *42*, 3649-3655
[4] E. Passaglia, M. Marrucci, G. Ruggeri, M. Aglietto, *Gazzetta Chimica Italiana* **1997**, *127*, 91-95
[5] E. Passaglia, S. Ghetti, F. Picchioni, G. Ruggeri, *Polymer* **2000**, *41*, 4389-4400
[6] F. Ciardelli, M. Aglietto, E. Passaglia, G. Ruggeri, *Macromol. Symp.* **1998**, *129*, 79-88
[7] E. Passaglia, P. Siciliano, F. Ciardelli, G. Maschio, *Polym Int.* **2000**, *49*, 949-952
[8] T. Otsu, O. Ito, N. Toyoda, S. Mori, *Makromol. Chem. Rapid Commun.* **1981**, *2*, 725-728
[9] E. Passaglia, L. Corsi, M. Aglietto, F. Ciardelli, M. Michelotti, G. Suffredini, *J.Appl.Polym.Sci.* **2002**, in press

[10] E: Borsig, M. Lazar, A. Fiedlerova, L. Hrčková, M. Rätzsch, A. Marcinčin, *Macromol Symp.* **2001**, *176*, 289-298

[11] M. Aglietto, R. Bertani, G. Ruggeri, F. Ciardelli, *Makromol Chem.* **1992**, *193*, 179-186

[12] J. Brandrup, E.H. Immergut, Editors "Polymer Handbook" Second Edition, IV-9, John Wiley & Sons New York, 1975

[13] M. L. Arnal, M. E. Matos, R. A. Morales, O. O. Santana, A. J. Muller, *Macromol. Chem. Phys.*, **199**, 2275 (1998)

[14] M. L. Arnal, V. Balsamo, G. Ronca, A. Sanchez, A. J. Muller, E. Canizales, C. Urbino de Navarro, *J. Therm. Anal. Cal.*, **59**, 451 (2000)