

Modification of Isotactic Polypropylene by the Free-Radical Grafting of 1,1,1-Trimethylolpropane Trimethacrylate

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ABSTRACT: The chemical modification of isotactic polypropylene was performed by the free-radical-promoted grafting of 1,1,1-trimethylolpropane trimethacrylate (TMPTMA) in the presence of dicumyl peroxide (DCP) as the initiator. The reaction was carried out both in a batch internal mixer and in a corotating twin-screw extruder; the effects of the peroxide and monomer concentrations on the extent of modification in terms of the grafting efficiency and polymer chain structure variations were investigated. The modified samples were characterized with Fourier transform infrared to determine the structure of the grafted groups and the degree of functionalization, with gel permeation chromatography and the melt flow index to evaluate changes in the molecular weight, and with differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical thermal analysis to measure the final thermal properties. In addition, solvent extrac-

tion with xylene was performed to highlight the presence of gel and its extent. The structure of the grafted groups was determined, and the number of grafted groups was quantitatively evaluated. The degree of functionalization increased with an increasing TMPTMA/DCP molar ratio. Thermal analysis results hinted at the presence of grafted chains with an increased percentage of TMPTMA. Although degradation reactions predominated at high amounts of peroxide, grafting and branching processes became competitive at high levels of TMPTMA. The balance between competing β -scission and grafting/branching reactions could be adjusted on the basis of feed conditions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 950–958, 2007

Key words: functionalization of polymers; poly(propylene) (PP); reactive processing

INTRODUCTION

Polypropylene (PP) is used in different applications such as automobiles, packaging, and fiber spinning because of its good mechanical properties, but for particular uses, some characteristics are not totally suitable and have to be improved.¹ For example, its melt strength is low, and it does not show strain hardening.² In recent years, the chemical modification of the PP structure has been approached to change the mechanical and rheological properties of PP-based materials. Tzoganakis et al.³ prepared PPs with narrow molecular weights through radical-induced chain scission and studied the rheological properties of samples

as a function of the amount of peroxide used in the reaction. Branched PPs were prepared by Wang et al.⁴ and Graebing,⁵ who employed peroxide and a polyfunctional monomer during a reactive-extrusion process. Wong and Baker⁶ examined the rheological behavior of a family of glycidyl methacrylate and styrene grafted PPs obtained by a free-radical-mediated process. Lu and Chung⁷ used amine-terminated PP and maleic anhydride grafted PP to prepare branched PP by a condensation reaction between the functional groups.

Romani et al.⁸ synthesized crosslinked/branched PP samples with furan or bismaleimide-based coagents as crosslinking promoters together with peroxide. Four different reagents were used, and their effect on the crosslinking degree was estimated by gel fraction determination and rheological measurements. Recently, Augier et al.⁹ used butyl 3-(2-furanyl)propanoate as a coagent during maleic anhydride grafting on PP to keep chain-scission degradation reactions under control, which generally affect the radical functionalization reaction of PP.

In addition, some researchers have used high-energy beam irradiation such as electron beams and

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γ -rays for PP modification.^{10–12} The irradiated products generally were crosslinked and branched PP.

In this study, the chemical modification of PP in the presence of 1,1,1-trimethylolpropane trimethacrylate (TMPTMA) was investigated. The feed composition and processing conditions were changed to optimize the functionalization extent and minimize side reactions of degradation and crosslinking. Accurate characterizations highlighting changes in the chain structure of the polymer were performed by gel permeation chromatography (GPC) and melt flow index (MFI) analysis.

EXPERIMENTAL

Materials

PP (Poliran PI0800, Bandar Imam Pharmaceutical Co. (BIPC), Bandar Imam, Iran), supplied by Iran Petrochemical, had an MFI of 7 g/10 min (at 230°C/2.16 kg). Poly(diethyl fumarate) (PDF) was synthesized according to ref. 13. Dicumyl peroxide (DCP) as an initiator and TMPTMA (Merck, Darmstadt, Germany) as a monomer were used without further purification. Acetone and xylene and 2,2,4-trimethyl pentane (TMP) were provided by Carlo Erba (Milan, Italy) and Aldrich (Milan, Italy), respectively, and used as received.

Sample preparation

Polymer functionalization reactions were performed with a Brabender plastograph mixer (50 cc) (Belotti, Milan, Italy) and an intermeshing, corotating twin-screw extruder with a 32 : 1 length-to-diameter ratio. For the sample preparation in the Brabender mixer, 35 g of PP was introduced into the mixing room at the temperature of 190°C and rotor speed of 40 rpm. After 5 min, the monomer was added to the molten polymer.

After 2 min from the addition of the monomer, the initiator was also added. Then, the reaction was carried out for 8 min. The sample codes and compositions are listed in Table I.

The modification process in a twin-screw extruder was performed at feed rate of 0.65 kg/h and a screw speed of 150 rpm. The temperatures at different zones, from feeding to the die, were set at 160, 190, 210, and 210°C. The polymer, monomer, and initiator were physically mixed in a 1000-mL beaker and then fed into extruder. The feed composition is reported in Table I. The product was cooled in water and then pelletized.

All recovered polymers were washed with boiling acetone to remove unreacted reagents and low-molecular-weight fractions for 8 h and then dried *in vacuo* for 2 days until a constant weight was reached.

Sample characterization

The degree of functionalization (FD), defined as the number of grafted groups per 100 monomeric units, was determined with the following equation:¹⁴

$$FD = \frac{\epsilon_{PP}}{\epsilon_{TMPTMA}} \cdot \frac{A_{TMPTMA}}{A_{PP}} \quad (1)$$

where A_{TMPTMA} and A_{PP} are the area bands of the carbonyl stretching of TMPTMA in the range of 1725–1745 cm^{-1} and the bending of CH_2 of PP at 1464 cm^{-1} , respectively. ϵ_{TMPTMA} and ϵ_{PP} are the extinction coefficients (integral absorptivity) of the chosen bands.

The determination of the integral absorptivity (ϵ) for the band at 1464 cm^{-1} was carried out according to a method usually adopted in our laboratory.¹⁵ Blends of PP and PDF of known compositions were prepared by melt mixing, and for each blend, Fourier transform infrared (FTIR) spectra were obtained on films pre-

TABLE I
Solvent-Extraction Results and FD Determination for Functionalized PP

Sample	TMPTMA (mol %)	DCP (mol %)	R^a	Acetone-soluble fraction (wt %)	Xylene-insoluble fraction (wt %)	FD (mol %) ^b	Grafting yield (%) ^c	Efficiency of grafting ^d
1	0.074	0.012	6.17	0.37	0	0.055	74	4.6
2	0.074	0.023	3.22	0.44	0	0.056	76	2.4
3	0.074	0.079	0.94	0.64	0	0.073	98	1.0
4	0.124	0.023	5.39	0.81	0	0.077	63	3.3
5	0.186	0.023	8.09	1.22	0	0.080	43	3.5
6	0.372	0.023	16.17	1.30	0	0.148	40	6.4
7	0.372	0.140	2.66	0.52	4.47	0.248	67	1.8
8 ^e	0.084	0.012	7.00	0.36	0	0.047	56	3.9

^a Molar ratio of TMPTMA to DCP.

^b The data were obtained with the procedure reported in the Experimental section by IR spectroscopy after washing with acetone.

^c Refers to the molar concentration of the monomer TMPTMA, that is, $(FD/[TMPTMA]) \times 100$.

^d Efficiency of grafting = $FD/[DCP]$ (defined as the number of functional groups inserted per mole of DCP).

^e The sample was prepared in the extruder.

pared by compression molding. From the IR spectra, the correlation between the molar composition of the blend ([PDF]) and the A_1/A_2 ratio was determined:

$$[\text{PDF}] = \frac{\varepsilon_{1464}}{\varepsilon_{1736}} \cdot \frac{A_1}{A_2} \quad (2)$$

where A_1 is the peak area at 1736 cm^{-1} and A_2 is the peak area at 1464 cm^{-1} . Thus given the value of ε_{1736} , we determined the value of ε_{1464} . The latter was calculated as $\varepsilon_{\text{PP}} = 4.42 \times 10^4 \text{ L mol cm}^{-2}$ in this work. The integral absorptivity for the bands related to the C=O stretching ($\varepsilon_{\text{TMPTMA}}$) of the carbonyl ester groups was evaluated by the preparation of TMPTMA/TMP solutions at low concentrations (ranging from 4×10^{-3} to $12 \times 10^{-3} \text{ M}$) and the calculation for each solution of the area of the C=O stretching band. Therefore, according to the Lambert–Beer law, $\varepsilon_{\text{TMPTMA}}$ was calculated as $\varepsilon_{\text{TMPTMA}} = \varepsilon_{\text{PP}} = 3.1 \times 10^4 \text{ L mol cm}^{-2}$. This value was used, as an approximation, for the C=O stretching band of TMPTMA grafted to PP and used in eq. (1) to calculate the FD values of the processed samples.

MFI of the PP samples was measured with an MFI instrument (Ceast, Milan, Italy) at 190°C under a loading of 2.16 kg.

The gel fraction was measured by Kumagawa extraction with xylene for 16 h and calculated with the following equation:

$$\text{Gel fraction} = \frac{W_2}{W_1} \times 100 \quad (3)$$

where W_1 and W_2 are the initial weight and insoluble portion weight of the sample, respectively.

The molecular weights of modified and unmodified samples were determined by GPC with a Waters Alliance GPCV 2000 (Vimodrone, Milan, Italy) series system apparatus equipped with three Waters Styragel HT 6E columns (molecular weight = 5000–10,000,000) and one Waters Styragel HT 3 column (molecular weight = 500–30,000), with an average particle size of $10 \mu\text{m}$, and with a differential refractive-index and differential viscometer as detectors. The polymer solutions were prepared with 2.5–3 mg of the polymer in 4 mL of 1,2,4-trichlorobenzene containing a small amount of an antioxidant (BHT (2,6 di-ter-butyl 4-methyl phenol)) and eluted at 145°C and at 1 mL/min flow rate. The calibration was performed with narrow molecular weight distribution polystyrene standards, and the calculations were carried out with Millennium software. Differential scanning calorimetry (DSC) was carried out on a PerkinElmer DSC7 (Monza, Milan, Italy) thermal analyzer under a nitrogen atmosphere at a heating/cooling rate of $10^\circ\text{C}/\text{min}$ between 40 and 200°C . After the first heating, each sample was held at 200°C for 1 min. Then, the cooling step started, and finally, the second heating

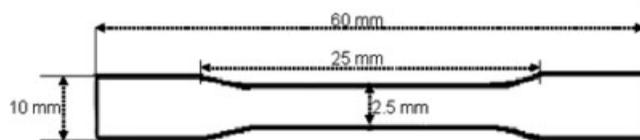


Figure 1 Type III tensile specimen (ASTM D 638).

step was performed. All the calculations reported in Table III (shown later) refer to the second heating.

The dynamic mechanical thermal analysis (DMTA; DMA7^e, PerkinElmer) was performed in the three-point-bending rectangular mode. The experiments were carried out at a frequency of 1 Hz from -100 to 120°C at a heating rate of $5^\circ\text{C}/\text{min}$. The loss modulus and loss tangent ($\tan \delta$) were measured for all the samples under these conditions.

A Tinius Olsen (H10KT, Horsham, PA) tensometer was used to study the mechanical properties of the samples. The tensile specimens were punched out from the molded sheets according to ASTM D 638 Type III (see Fig. 1). The tests were carried out at a crosshead speed of 10 mm/min at 25°C .

Thermogravimetric analysis (TGA) was performed (TGA/SDTA851^e, Mettler, Novato, Milanese, Italy) through the heating of the samples from 25 to 700°C under a nitrogen atmosphere at a flow rate of 60 mL/min. The heating rate was $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The functionalization runs (Table I) were performed through changes in the feed conditions and in particular the ratio of the monomer to peroxide, which ranged from 0.94 to 16.17. For runs 1–3 and 6–7, the TMPTMA concentration was kept constant (a low concentration of 0.074 mol % for runs 1–3 and a high concentration of 0.372 mol % for runs 6–7) by increasing the amount of DCP; for runs 4–6, the DCP concentration was kept constant (0.023 mol %) by increasing the TMPTMA content. Run 8 was performed in the extruder with feed conditions very similar to those of run 1.

Characterization of the grafted monomer structure

The FTIR spectra of PP, a physical mixture of PP and the TMPTMA monomer, and chemically modified PPs after washing with acetone are shown in Figure 2. The IR spectra of the physical mixture of the polymer and monomer show two absorption peaks at 1727 and 1639 cm^{-1} , which are assigned to the carbonyl stretching of ester groups and double bonds of the monomer, respectively. For the chemically modified samples, the absorption peaks due to these groups are shifted to different values, and the carbonyl stretching is split into two signals at 1727 and 1742 cm^{-1} . The first is assigned to car-

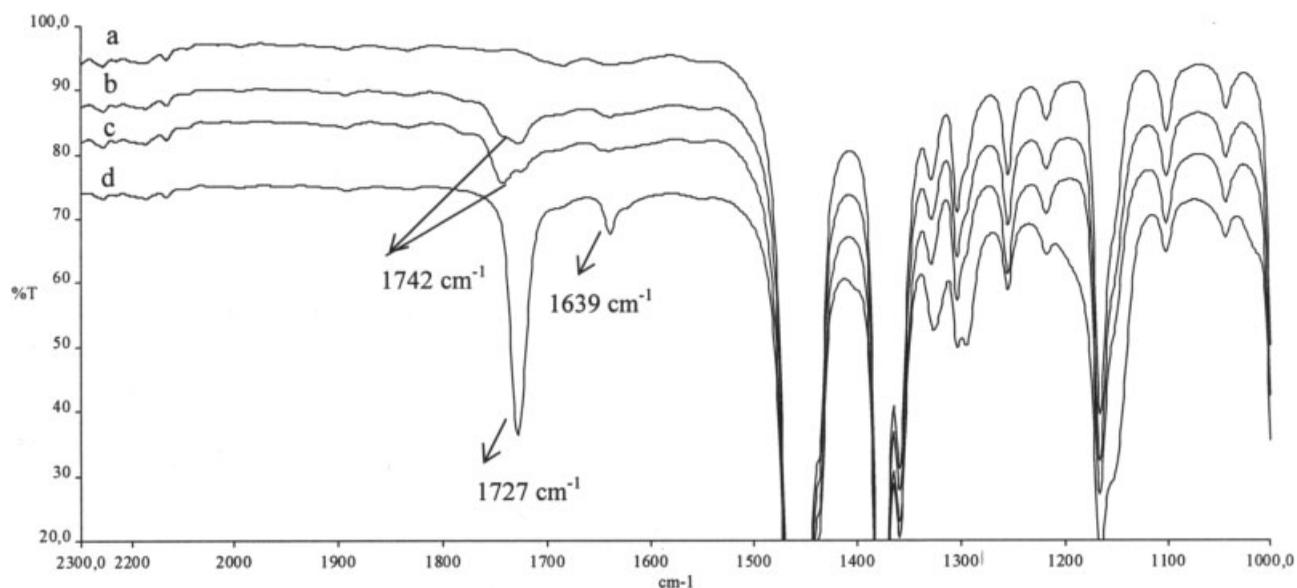


Figure 2 FTIR spectra of the carbonyl stretching regions of (a) untreated PP, (b) sample 4, (c) sample 3, and (d) a mixture of the polymer and TMPTMA monomer (3 wt %).

bonyl groups bearing double bonds in the α position, and the second is assigned to carbonyl groups grafted in the α position; both belong to the grafted monomer. In addition, the intensity of the absorption made by the monomer double bonds strongly decreases.

The grafted groups can contain one or two free acrylic groups, depending on the extent of the grafting, branching, and crosslinking reactions, as depicted in Scheme 1.^{16,17}

The increase in the frequency absorption of the carbonyl peak in the range of 1736–1742 cm^{-1} , observed for samples 1–3 with an increasing amount of peroxide but a constant initial concentration of TMPTMA, can be related to the conversion of double-bond groups by grafting and branching/crosslinking reactions,^{18,19} which generate higher amounts of saturated grafted groups (Fig. 3).

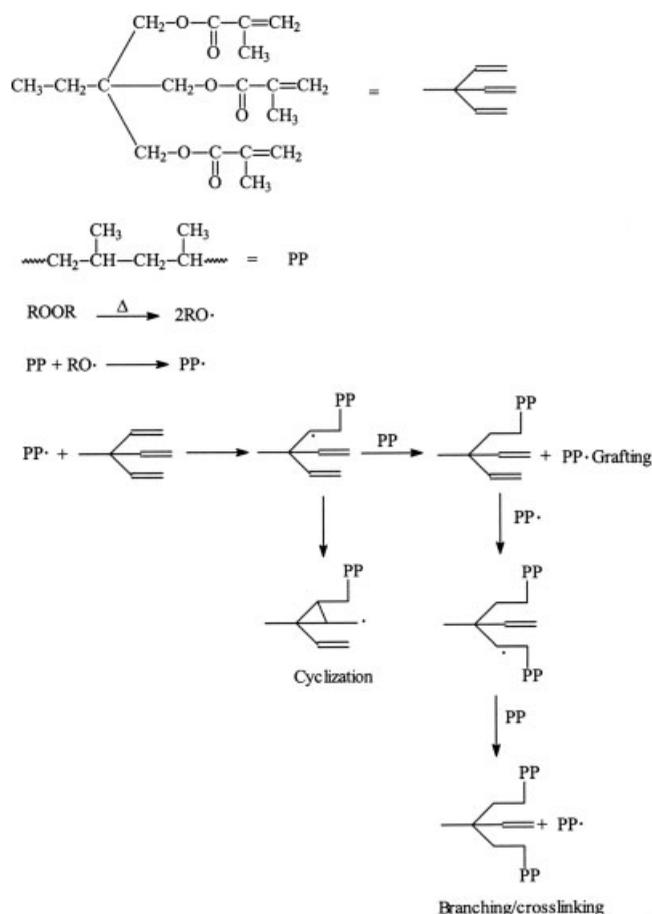
At the same time, the same effect could also be due to the presence of a cyclic structure for TMPTMA grafted onto the polymer chain, as suggested by many authors^{18,20,21} (Scheme 1).

The increase in the TMPTMA concentration in the feed gives a higher grafting content; the C=O stretching bands evolve into a single peak band centered at about 1735 cm^{-1} by a concomitant increase in the intensity (Fig. 4). This has also been observed for polymethacrylates.¹⁹

Solvent-extraction results: FD and its dependence on the feed composition

All samples were extracted with boiling acetone to remove the unreacted TMPTMA monomer, its homopolymer fraction, products derived from peroxide decomposition, and very low-molecular-weight PP formed through degradation (Table I). The acetone-

soluble fraction was quite low for all the samples, ranging from 0.36 to 1.3 wt % and slightly increasing with increasing amounts of the monomers at low



Scheme 1 Probable mechanism of the radical-initiated reactions of TMPTMA with PP.

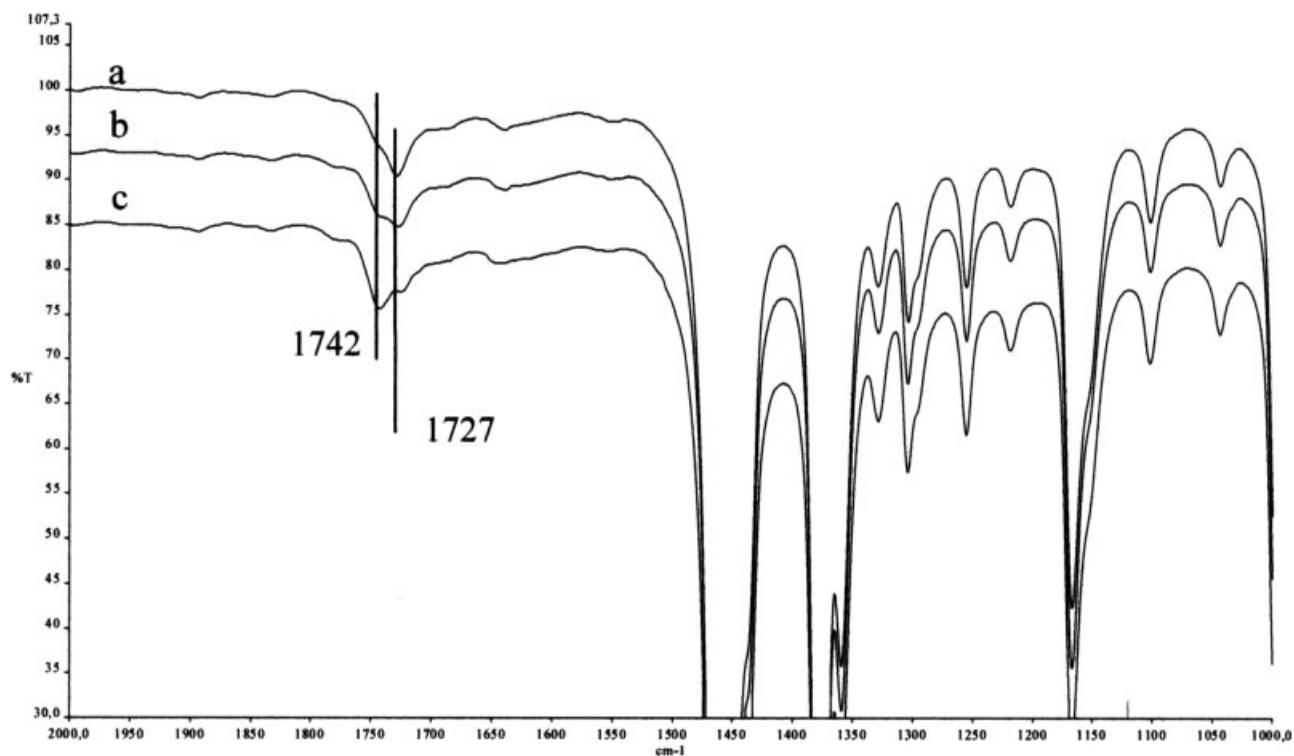


Figure 3 FTIR spectra of the carbonyl stretching regions of (a) sample 1, (b) sample 2, and (c) sample 3 obtained with a constant amount of the monomer but an increasing peroxide concentration.

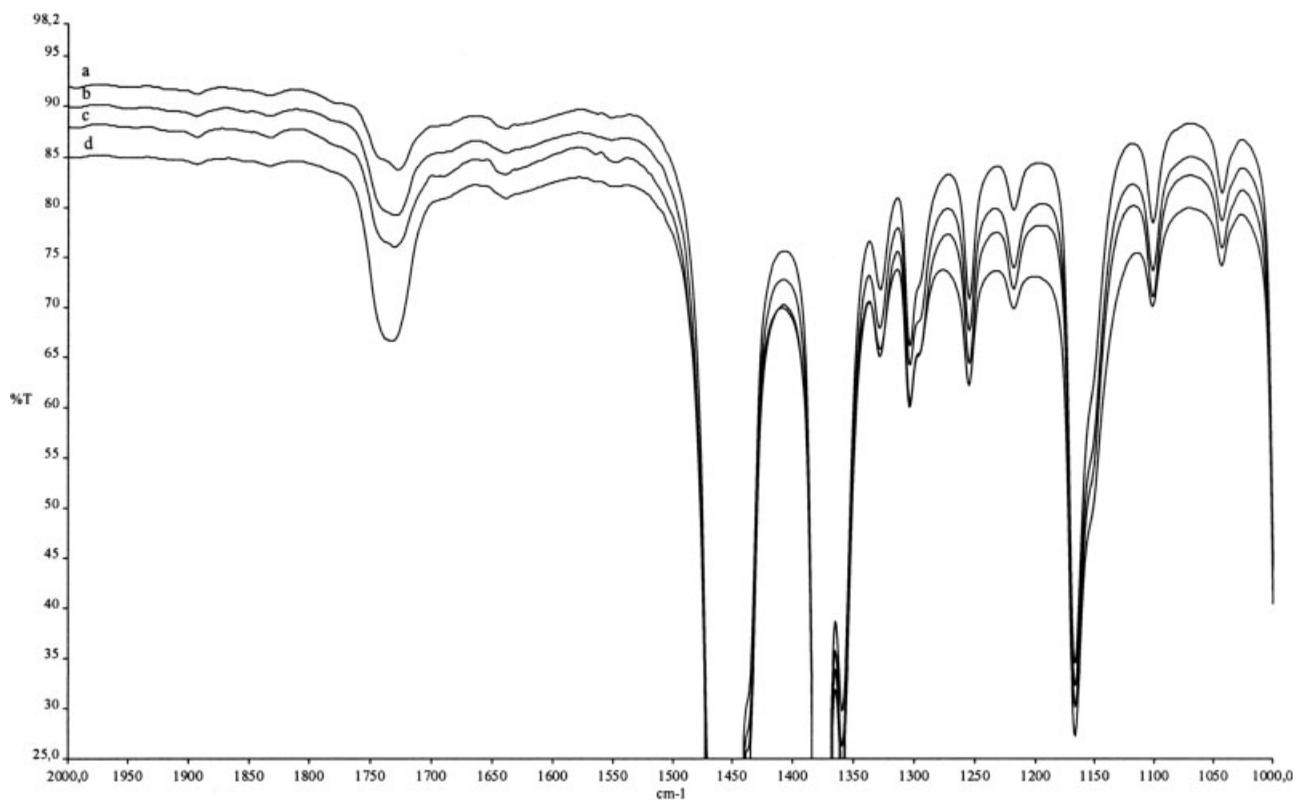


Figure 4 FTIR spectra of the carbonyl stretching regions of (a) sample 2, (b) sample 4, (c) sample 5, and (d) sample 6 obtained with a constant amount of peroxide but with an increasing amount of the monomer.

TABLE II
GPC and MFI Results for Functionalized PP

Sample	TMPTMA (mol %)	DCP (mol %)	R^a	MFI (g/10 min at 190°C)	$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n
Neat PP	—	—	—	4.6	61	336	5.5
1	0.074	0.012	6.17	35.8	39	171	4.4
2	0.074	0.023	3.22	40.4	37	158	4.3
3	0.074	0.079	0.94	50.2	39	120	3.0
4	0.124	0.023	5.39	24.0	50	217	4.3
5	0.186	0.023	8.09	16.2	55	196	3.6
6	0.372	0.023	16.17	9.3	58	236	4.1
7	0.372	0.140	2.66	— ^b	— ^b	— ^b	— ^b
8	0.084	0.012	7.00	10.8	71	239	3.3

^a Molar ratio of TMPTMA to DCP.

^b Not determined because of the presence of the gel fraction.

DCP/TMPTMA ratios (samples 5 and 6). Afterwards, extraction with xylene was performed; there was no xylene residue, and thus gel formation was not observed. This result rejects the occurrence of crosslinking reactions except for high concentrations of both the monomer and peroxide (sample 7). FD was strongly dependent on the feed compositions and monomer/DCP molar ratio. At a constant low concentration of TMPTMA of 0.074 mol % (samples 1–3), the conversion of the monomer and FD increased with a decreasing monomer/peroxide ratio (R), whereas the efficiency values decreased as expected from the results collected for the radical functionalization of polyolefins with maleic derivatives.²² By keeping constant the amount of DCP (samples 2 and 4–6) and by increasing R , we increased both the FD and efficiency values; particularly for sample 6, a very good efficiency value was obtained, and this indicated that the process could be adjusted and optimized with a high R value (16.17 for sample 6). The sample produced in the extruder showed an IR spectrum and FD value very similar to those of sample 1 (obtained in the mixer) with lower efficiency.

Molecular weight of functionalized PP and its dependence on the feed composition

An increase in MFI and a decrease in the molecular weights with respect to the neat PP were generally observed during the reaction (Table II). This result can be attributed to the well-known degradation by β scission of PP in the presence of radical initiators.²³

Even taking into account this consideration, we found that both MFI and GPC produced trends depending on the feed composition. Indeed, MFI increased with an increasing initiator concentration at high (samples 6) and low concentrations (samples 1–3) of the monomer (Fig. 5), corresponding to the occurrence of β -chain scission, which rose at a high level of DCP.²⁴ At the same time, MFI decreased with an increasing TMPTMA concentration and a constant

amount of DCP (samples 2 and 4–6; Fig. 5); branching/crosslinking reactions promoted by the grafting of TMPTMA (Scheme 1) reduced the degradation effects and positively affected the MFI behavior.

Very similar trends could be observed for the number-average molecular weight (M_n) and weight-average molecular weight (M_w), despite the generally observed polydispersity decrease (M_w/M_n), in agreement with the degradation effect. For high R values (samples 4–6), the M_n data were similar to those of neat PP, and M_w showed a certain control, thus highlighting that the β -scission effect could be partially hindered or offset by a branching reaction due to the grafting of the monomer. The best results in terms of molecular weight control were obtained for sample 6, which was characterized by a high FD. As for the crosslinking extent, the gel content tests summarized in Table I indicated that all samples were gel-free, except for the sample with high amounts of the monomer and initiator (sample 7), in which a gel fraction of less than 5% was detected. This suggested that under all conditions tested, branching and grafting reactions

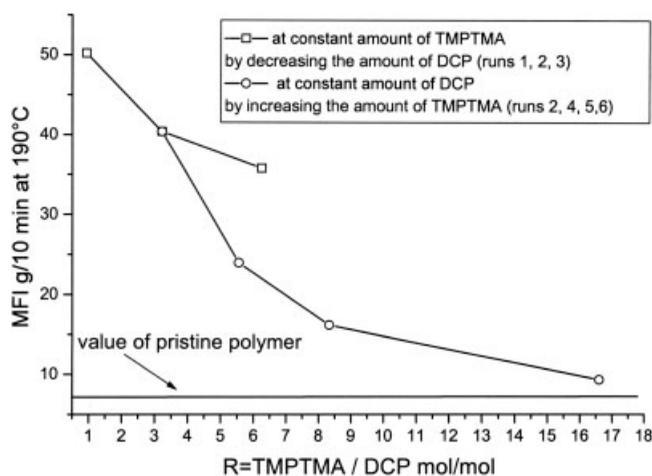


Figure 5 MFI behavior at different TMPTMA/DCP molar ratios.

TABLE III
Thermal Properties of Modified PP

Sample	R^a	FD (mol %)	T_m (°C)	T_c (°C)	ΔH_c (J/g)	Onset-of-degradation temperature (°C)
Neat PP	—	—	162.1	107.6	94.2	433
1	6.17	0.055	161.3	114.5	96.0	431
2	3.22	0.056	159.1	112.6	96.2	420
3	0.94	0.073	156.7	113.7	93.6	427
4	5.39	0.077	161.0	116.9	98.6	435
5	8.09	0.080	161.9	118.1	98.2	428
6	16.17	0.148	162.4	118.8	100.7	430
7	2.66	0.248	158.4	119.2	93.2	425
8	7.00	0.047	161.0	115.8	100.2	431

^a Molar ratio of TMPTMA to DCP.

overcame crosslinking. Also, the insoluble part in sample 7 could be a mixture of crosslinked PP and a TMPTMA homopolymer macrogel^{16,17,25} experimentally difficult to separate.

The sample modified in the extruder showed a lower MFI value and higher M_n and M_w values than sample 1 modified in the internal mixer under very similar feed conditions. This may be related to the different machine efficiency and residence time, which could influence polymer degradation and the probability of polymer branching.

Thermal, thermomechanical, and tensile properties of modified PP

The melting temperature (T_m), crystallization temperature (T_c), and enthalpy of crystallization (ΔH_c) for the neat PP were 162.1°C, 107.6°C, and 94.2 J/g, respectively. All the modified samples showed melting peak temperatures slightly lower than or equal to T_m of the neat polymer but increased crystallization peak temperatures and ΔH_c values (Table III). These results can be discussed on the basis of molecular weight reduction due to the β -scission effect (Table II) and on the

basis of grafting and branching reactions affecting chain regularity. Generally, for degraded PP, a slight increase in T_c was observed without a substantial variation of the crystallinity.²⁶ Short-chain branching due to the grafting with the functional monomer generated defects causing a decrease in both the polymer crystallinity and T_m .²⁷ The presence of a low number of long-branched^{28–31} or crosslinked^{29,31} chains in the polymer structure could result in an increased nucleation density promoting polymer crystallization along with increased T_c . T_c and ΔH_c of the samples at a low concentration of the grafting monomer (samples 1–3) slightly increased over those of neat PP (Table III) or remained constant. Under these feed conditions, the grafting of TMPTMA was accompanied by significant chain degradation. The increases in the T_c and ΔH_c values were even higher than those of neat PP at $R > 5$ (samples 4–6 and 8). Sample 7, characterized by the presence of about 5% crosslinked chains, had the highest T_c value at 119.2°C. The last result is in agreement with characterization data found for branched PP.²⁹

The TGA curves of the modified samples and the related degradation temperatures indicated that the

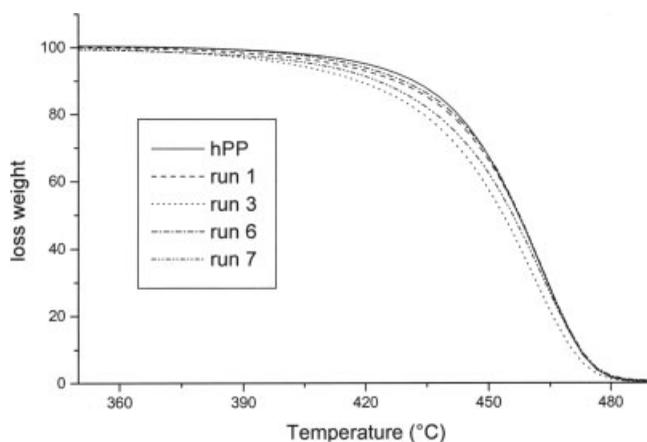


Figure 6 TGA of selected samples.

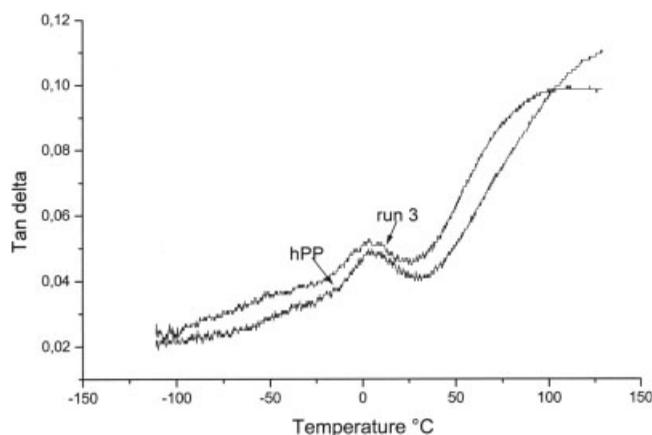


Figure 7 Tan δ versus the temperature for run 3 and an untreated sample (hPP).

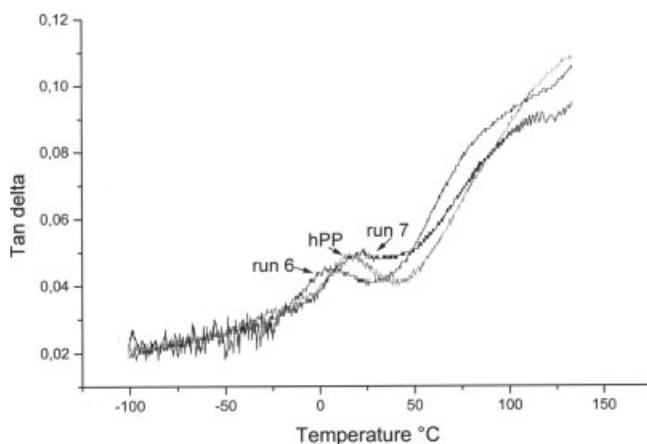


Figure 8 Tan δ versus the temperature for runs 6 and 7 and an untreated sample (hPP).

polymer thermal stability was not substantially affected by the grafting process. Only a slight decrease in the onset temperature was observed with an increasing amount of DCP (Fig. 6) in accord with increased degradation.²⁷

DMTA was used to determine the tan δ behavior of modified and unmodified PPs (Figs. 7 and 8) and showed three peaks associated with α , β , and γ relaxations. The α relaxation, between 50 and 100°C, is related to the crystalline phase and melting transition; the β relaxation, describing the amorphous phase, where the peak position is generally considered associated with the glass-transition temperature, was around 0–10°C; and the γ relaxation in PP, associated with the onset of local mode relaxation,³² appeared very weak and in a few samples at about –60°C. The temperatures of the main transitions seemed to be substantially unchanged according to a comparison of the different modified samples with neat PP. The peak intensity associated with the β relaxation was weakly increased in sample 3 with respect to neat PP (Fig. 7) in agreement with reports³³ on polyethylenes with short (C4–C8) branches.

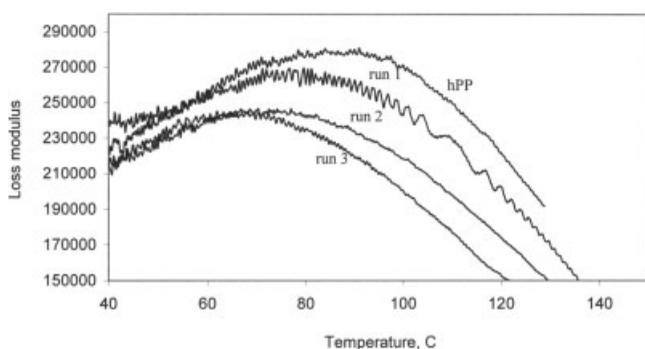


Figure 9 Loss modulus versus the temperature in the α -relaxation range for runs 1–3 and an untreated sample (hPP).

TABLE IV
Tensile Properties of the Modified Samples

Sample	Break		E (Young Modulus) (MPa)	Yield	
	Elongation (%)	Tensile stress (MPa)		Elongation (%)	Tensile stress (MPa)
hPP	179	28.0	1275	5	31.2
1	4	24.3	1647	3	24.8
2	4	22.5	1609	3	25.0
3	3	28.5	1624	— ^b	— ^b
4	4	30.5	1593	4	30.9
5	5	27.3	1612	4	31.0
6	5	29.7	1544	4	30.0
7	3	27.9	1649	— ^b	— ^b
8 ^a	5	32.8	1583	4	33.8

^a The run was performed in the extruder.

^b Not determined.

The β -relaxation peak intensity of partially cross-linked sample 7 decreased with respect to sample 6, which also had a lower glass-transition temperature; this suggested a higher branching level in this last sample (Fig. 8). The temperature dependence of the loss modulus indicated that the α -relaxation temperature moved to a lower temperature, and its intensity decrease was consistent with the DSC results (Fig. 9).

The modified samples showed a dramatic decrease in the elongation at break (Table IV) due to the reduced molecular weight in a similar fashion and to a similar extent as the samples obtained by electron-beam-initiated grafting of 1,1,1-trimethylolpropane triacrylate.^{17,18,22} At the same time, an increase in the tensile modulus due to polymer branching/crosslinking was observed, with the highest value for partially crosslinked sample 7.

The increased percentage of the monomer in the process feed from run 2 to runs 4–6 enhanced the polymer toughness. The tensile stress and elongation at yield were comparable for all the samples, with a moderate reduction of the stress for the samples that were characterized by a lower T_m value and crystallinity: accordingly, the yielding point for samples 3 and 7 could not be determined with certainty.

CONCLUSIONS

Isotactic PP was bulk-modified by a free-radical melt process carried out in the presence of a trifunctional reagent (TMPTMA) at different feed ratios with the objective of evaluating the relative extent of grafting, branching, and crosslinking reactions and their effect on the thermomechanical properties. The accurate FTIR characterization performed with a calibration curve allowed us to determine the structure of the grafted groups and to quantitatively evaluate the number

of grafted groups and their dependence on the TMPTMA/peroxide ratio. The FD values increased with an increasing TMPTMA/DCP molar ratio. At the same time, solvent-extraction, MFI, and GPC measurements confirmed that β -scission and grafting/branching reactions occurred simultaneously and could be adjusted on the basis of the feed conditions. Degradation reactions predominated at high amounts of peroxide, whereas at high levels of TMPTMA, grafting and branching processes became competitive. DSC, TGA, and DMTA indicated that the thermal properties of the polymers were not substantially changed by the performed reactions. However, the crystallization results hinted at the presence of grafted chains (branching) with an increased percentage of TMPTMA. Finally, the tensile properties showed stress values comparable to those of the unmodified PP.

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