Radical Grafting of Polar Monomers onto Polypropylene by Reactive Extrusion

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ABSTRACT: Polypropylene (PP) was functionalized in the melt by grafting polar monomers using an internal mixer and a corotating twin-screw extruder. 2,5-Bis(tertbutylperoxy)-2,5-dimethylhexane (Luperox 101) and dicumyl peroxide (DP) were the used radical initiators. The polar monomers were itaconic acid (IAc), 2-octen-1-ylsuccinic anhydride (OY), 2-hydroxyethyl methacrylate (HEMA), and 3-allyloxy-1,2-propanediol (AP). Grafting was quantified by FTIR combined to Elemental Analysis. Grafting degree depends mainly on monomer and initiator natures and concentrations. Grafting degree maxima were 3.9, 2, 9.5, and 3.9 wt %, respectively, for IAc, OY, HEMA, and AP. Some properties of the modified PP were evaluated. Thermal analysis indicated that the polarity of PP increased by grafting reaction and size-exclusion chromatography showed that the grafting was not accompanied by a significant M_w and viscosity decrease. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2177–2188, 2013

INTRODUCTION

The modification of polymers, especially polyolefins through the grafting of functional monomers via free-radical reaction, has led to wide industrial applications and has continually gained scientific interest. Functionalized polyolefins[1–4] and more particularly functionalized PP were used to compatibilize a large number of polar polymers such as polyesters and polyamides thus improving the properties and stability of immiscible polymer blends.[5–19] Polypropylene (PP) has been one of the polymers that present great commercial interest, since some properties of ordinary PP such as adhesion, dyeability, and compatibility can be improved thanks to its modifications.[20–28] PP compatibilization with polar polymers either can be due to specific interactions such as hydrogen bonding or to the formation of graft copolymers by reactions between the functions grafted onto the PP and others existing in polar polymers.

Reactive extrusion is a favorable process to obtain modified polymers continuously in molten state. Radical functionalization of PP by reactive extrusion is a very challenging industrial process. The occurrence of side reactions such as chain scission makes the grafting process quite critical for the production of grafted polymers with high graft contents while preserving the

mechanical properties or processability of PP.[29,30] Besides, another challenge is to control the chemical structure of the grafts during processing, and the coexistence of several types of grafts is usually observed in commercial products.[31] Among reactive monomers, the most important ones for PP modification by free-radical mechanisms are unsaturated organic compounds having oxygen-containing functional groups. The best known modification is performed with maleic anhydride. It generally improves the adhesion of PP to metals, glass fibers, or other polymers such as polyamides. The grafting of maleic anhydride to PP is usually carried out in the presence of radical initiators in solution,[1,32–34] in the solid state[35,36] or directly in the melt.[20,22,25,26,37–43] Generally, the grafting reaction is accompanied by chain scissions then the grafting degree and efficiency are relatively low. In the case of acrylic acid, grafting is accompanied by homopolymerization.[29] Other polar monomers such as unsaturated carboxylic acid derivatives and vinyl or acrylic substances containing more than one functional group have also been investigated.[25,39,43–59] Coagents like styrene were used to assist the PP radical functionalization and also to reduce molar mass decrease during grafting.[57,60–63] The literature clearly shows that maleic anhydride can be grafted onto PP leading to various grafting degrees going up to 5 wt %. A high grafting is
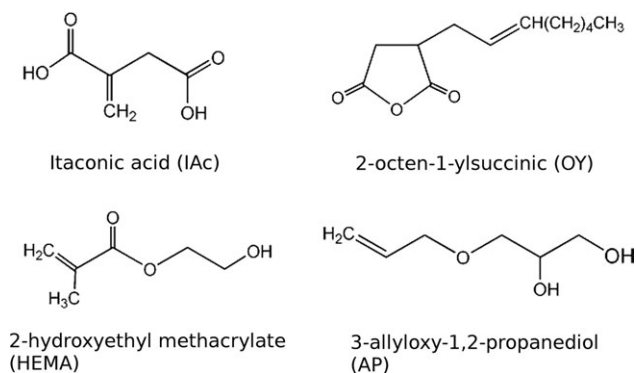
Scheme 1. Chemical structures of the used polar monomers.

accompanied by a dramatic decrease in PP molar masses and consequently a low viscosity and crystallinity. The use of a coagent can reduce molar mass decrease.

The purpose of this work is the melt functionalization of PP with various polar monomers without the use of coagents while obtaining relatively high grafting degrees without significant degradation of the PP and thus keeping PP viscosity and crystallinity high. Grafting reactions were first carried out in melt using free radical initiators in an internal mixer. The polar monomers were itaconic acid (IAc), 2-hydroxyethyl methacrylate (HEMA), 3-allyloxy-1,2-propanediol (AP), and 2-octen-1-ylsuccinic anhydride (OY). The structures of these monomers are shown in Scheme 1. Three of these monomers, IAc, AP, and OY have allyl structures. Their reaction with a chain-bearing radical, leads to stable radicals that do not lead to further polymerization. Only one monomer is grafted from one radical. In addition, considering that the radical issued from allyl reaction with a PP backbone radical is stable, the activation energy for the addition of allyl monomer is low, making the competition between the grafting reaction and β-scission favorable to grafting; consequently high grafting is expected. The effects of monomer and initiator concentrations and natures on the grafting degree were analyzed, as well as the structural and crystallinity modifications of PP. Afterward, grafting reactions were carried out in a corotating twin-screw extruder.

EXPERIMENTAL

Materials

PP homopolymer Moplen HF500R was kindly supplied by LyondellBasel Industries (MFI = 25 g/10 min; 230°C/2.16 Kg). IAc, HEMA, AP, and OY were purchased from Sigma Aldrich. Free radical initiators were 2,5-bis(tertbutylperoxy)-2,5-dimethylhexane (Luperox® 101), generously supplied by Arkema and the dicumyl peroxide (DP) initiator was purchased from Aldrich. Toluene was analytical grade. All reagents were used without further purification.

Grafting Reactions

PP was functionalized with IAc, HEMA, AP, and OY with 5-bis(tertbutylperoxy)-2,5-dimethylhexane or DP as initiators in a reactive melt polymer processing by using a Haake Rheomix internal mixer.

The studied monomer concentrations for IAc, AP, and OY were 5, 10 and 20 mol % (mol %= a mole of component × 100 over the total moles of all components).

For HEMA, only a concentration of 5 mol % was studied. The initiator concentration depends on that of monomer:

$$\frac{[\text{initiator}]}{[\text{monomer}]} = 10^{-2}$$

The mixer chamber was heated to 180°C. PP and functionalizing monomer were first mixed and 1 min later the peroxide was added to the molten system. The screws' speed was fixed at 80 rpm. The reaction was carried out for 6 min.

Prior to any analysis, to remove unreacted monomer and homopolymer formed during grafting reactions, a sample of 2 g was dissolved in 100 mL of boiling toluene for 30 min. The hot solution was precipitated in 400 mL of acetone at room temperature. Grafted polymers were recovered by filtration and washed several times with acetone and finally dried at 60°C under vacuum to reach a constant weight. For PP modified by HEMA, after precipitation and filtration, samples were also purified by Soxhlet-extraction using ethanol for 24 h to remove any poly-HEMA homopolymer before being dried. Thin films of thepurified samples were prepared under pressure at 180°C for 45 s.

Reactive Extrusion. A modular fully intermeshing corotating twin-screw extruder Clextral BC 21 was used. The screw diameter was 25 mm, the total barrel length 900 mm and the center-line distance 21 mm. The obtained polymers were extruded through a cylindrical die. The extruder screw's profile is given in Figure 1.

A colorimetry technique was used for residence time distribution (RTD) measurements in the extruder. PP-carbon black master-batch was used as a color detectable tracer. Typically, 0.5 g of this mixture was added as a pulse in the feeder. Extrudates were collected for 18 min; a specimen was taken every 30 s for analysis. The samples were scanned as an image using an Epson Scan form of photos. Then the grayscale was determined using image processing software. The gray intensity in the sample is proportional to the carbon black concentration; then, the value of the black intensity is directly correlated to the concentration of the tracer in the sample.

The RTD can be described quantitatively with the function, $E(t)$. This function represents the exit age distribution of the polymer in the extruder:

$$E(t) = \frac{C_i}{\sum_0^\infty C_i \Delta t} \tag{1}$$

where C_i is the concentration of the tracer in each sample and Δt is the time between successive samples. To compare different distributions, the distribution's first moment, also called the mean residence time, $\bar{t}_m$, and the variance, σ^2, are used:

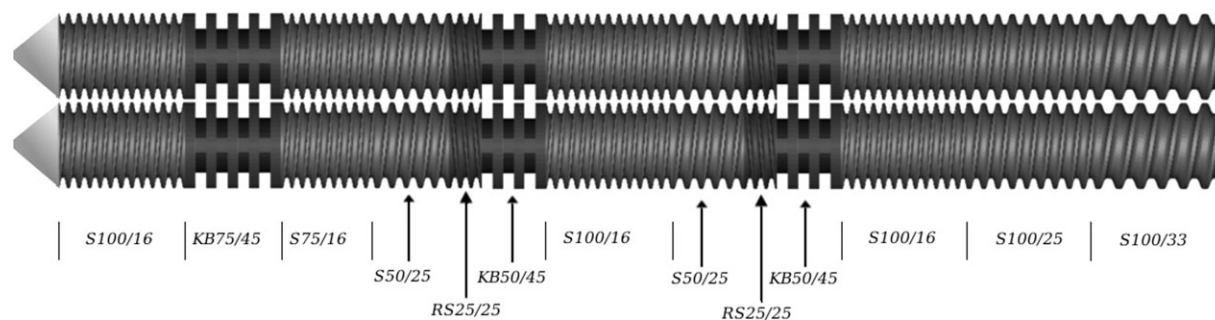$$\bar{t}_m = \sum_0^\infty t E(t) \Delta t \tag{2}$$

Figure 1. Screw profile used in reactive extrusion for grafted PP synthesis. S, Screw; RS, Reverse Screw; KB, Kneading-Block.

$$\sigma^2 = \frac{\sum_0^\infty t_i^2 C_i \Delta t_i}{\sum_0^\infty C_i \Delta t_i} - \bar{t}_m^2 \qquad (3)$$

which in dimensionless form is:

$$\sigma_\theta^2 = \frac{\sigma^2}{\bar{t}_m^2} \qquad (4)$$

Grafting Degree Determination. The grafting degree was quantified by FTIR spectroscopy combined with elemental analysis. Indeed, elemental analysis was done for the oxygen content determination by a total combustion of a sample of grafted PP at 1080°C under nitrogen. The obtained oxygen of the combustion compounds is transformed to carbon monoxide by passing over activated carbon at 1120°C. Carbon monoxide is quantified with a specific infrared detector and then the percentage of oxygen is calculated. Only modified PP with the highest grafting degree were analyzed by elemental analysis. For each grafted PP, the highest grafting degree is represented with the largest area of the characteristic peak of grafting (CPG). Grafting degree is proportional to the area of CPG; knowing the grafting degree, which corresponds to the area of the CPG, grafting degrees of the other modified PP can be calculated by integrating their CPG area.

Characterizations

FTIR Spectroscopy. FTIR spectra were recorded from compression-molded films on a Nicolet-Nexus 670 FTIR apparatus, from 4000 to 400 cm^{-1}.

Size Exclusion Chromatograph. Molecular weights and intrinsic viscosity were determined by high temperature size-exclusion chromatography (SEC; Waters Alliance GPC 2000) equipped with three columns Shodex, HT 803, HT 804, and HT 805 along with a differential refractometer coupled to a viscometer used as detectors. This coupling is mainly used with the universal calibration. Viscometric data allow calculating the mean intrinsic viscosity as well as changes on the instantaneous intrinsic viscosity as a function of the molecular weight. This allows to determine K and a Mark-Houwink coefficients and to calculate the molar masses of polymers using the universal calibration. The eluent was 1,2,4-trichlorobenzene (TCB) at 1 mL min^{-1} and 135°C. The concentration of the samples was 1-1.4 mg mL^{-1} in TCB and dissolution was achieved by shaking at 145°C for 2 h.

Differential Scanning Calorimetry. Differential Scanning Calorimetry (DSC) was carried out with a Q10 TA Instruments with heating or cooling rates of 10°C min^{-1} under nitrogen. This consisted of a first heating scan from 40 to 200°C, followed by a cooling scan down to −70°C. Melting points and enthalpies were measured from the second heating ramp.

The PP crystallinity rates (χ_c) were determined by using the following equation:

$$\chi_c(\%) = Degree\ of\ cristallinity\ (\%) = \left(\frac{\Delta H_m}{\Delta H_m^0}\right) \times 100 \qquad (5)$$

where ΔH_m is the measured PP melting enthalpy and ΔH_m° is the enthalpy of 100% crystalline PP ($\Delta H_m = 209$ J g^{-1}).

RESULTS AND DISCUSSION

The modification reactions of PP macroradicals depend on the temperature. The grafting reaction of PP with monomers after radical generation is significant due to radical reactions in a narrow temperature range from 80 to 150°C. In the temperature range up to 180°C, branching and crosslinking are predominant and at temperatures above 180°C the degradation reaction is dominant.[64] Taking into consideration these results, radical-initiated grafting onto PP was carried out at 180°C.

Grafting of Acid or Anhydride Function onto PP
Grafting of IAc. Compared with the other used monomers for PP grafting, for example maleic anhydride, IAc is much less toxic. In addition, its production has been set up on a commercial scale, whereas functionalized polyolefins prepared by IAc grafting are authorized for food contact.[65,66]

FTIR spectroscopy of PP-g-(IAc). The FTIR spectra of the neat PP and modified PP are displayed in Figure 2. The spectra are normalized with an internal standard peak at 1168 cm^{-1}, assigned to a vibration of methyl groups of PP.

The FTIR spectrum of the grafted PP with IAc (PP-g-IAc) showed two absorption bands in the carbonyl region that are absent in the spectrum of unmodified PP. The absorption band at 1712 cm^{-1} is due to stretching vibrations of the carbonyl groups in the carboxylic acid of the monomer. The second absorption band centered at 1770 cm^{-1} is due to a carbonyl absorption band, which
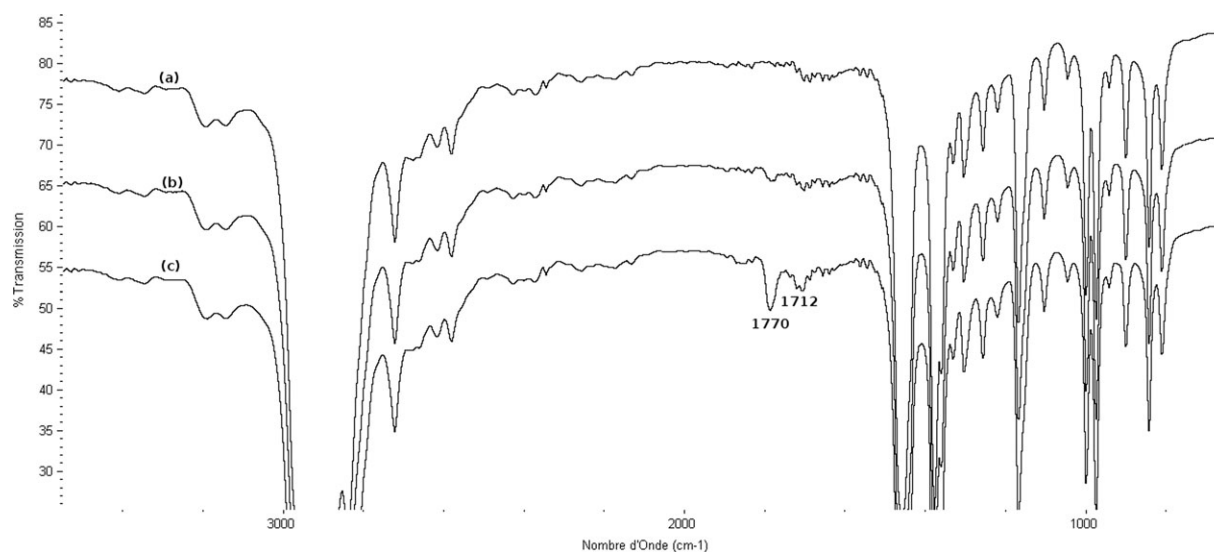
Figure 2. FTIR spectrum of neat PP and grafted PP with IAc (a) PP, (b) PP grafted with IAc (DP as initiator), and (c) PP grafted with IAc (Luperox 101 as initiator).

comes from the anhydride resulting from IAc dehydration. This result is in agreement with the results of Cowie et al. In their studies of the thermal stability of the corresponding polymonoesters, they reported the formation of anhydrides through dehydration/de-esterification reactions of monoesters of IAc. They concluded that the dehydration/de-esterification reactions were either intermolecular or intramolecular in nature.[67,68]

FTIR has been combined with elemental analysis to measure the grafting rate expressed as weight percentage. The obtained values of the grafting degree are grouped in Table I. The grafting degree is in close relation with the nature of the initiator; it is higher in the case where Luperox101 is used. Grafting degree increased from 0.85 wt % when the reaction was initiated by DCP to 3.85 wt % when Luperox 101 was used. Assoun et al.[69]

Table I. Summary Table of the Main Data Obtained by IRTF Combined to Elemental Analysis and DSC of the Modified PP at 180°C and 80 rpm for 6 min by Using Luperox101 as Initiator DP as Initiator

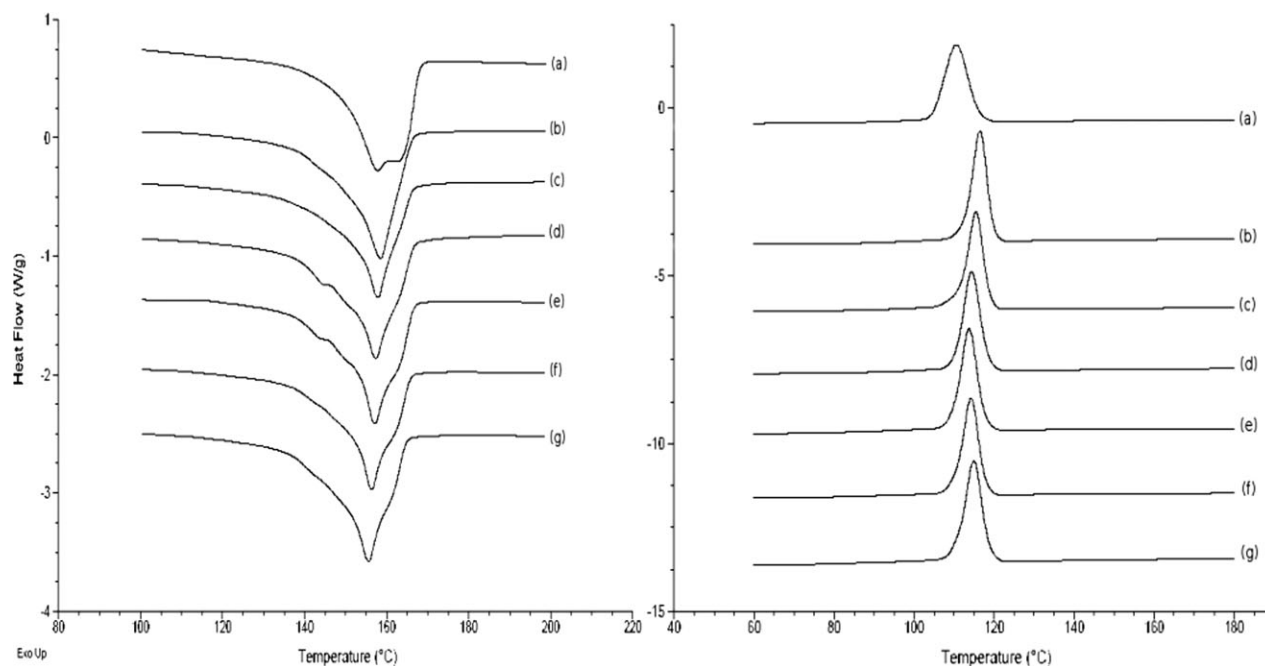| Initiator	Grafted monomer	Monomer content in feed (mol %)	Grafted monomer contents (wt %)	T_m (°C)	T_c (°C)	ΔH_m (j g^{-1})	χ_c (%)
Luperox 101	IAc	5	2.1	157.1	113.7	86.3	41.3
		10	1.98	156.3	114.2	83.7	40
		20	3.85	155.6	114.9	96.3	46.0
	AP	5	2.74	156.1	113.8	84.5	40.4
		10	2.77	155.8	114.9	86.1	41.12
		20	3.91	154.3	113.6	87.5	41.9
	OY	5	1.78	155.0	111.6	75.3	36
		10	2.01	155.6	112.7	85.6	40.9
		20	1.91	156.0	112.1	90.1	43.1
	HEMA	5	6.3	159.1	118.6	79.7	38.1
DP	IAc	5	0.5	158.6	116.5	84.1	40.2
		10	0.26	157.9	115.4	83.2	39.8
		20	0.85	157.4	114.4	88.9	42.5
	AP	5	0.22	157.2	113.8	79.6	38
		10	0.76	158.5	114.7	86.4	41.3
		20	1.74	156.7	114.2	82.3	39.4
	OY	5	0.92	158.4	112.5	82.4	39.4
		10	0.92	157.7	112.6	83.3	39.8
		20	1.35	156.8	112.4	84.6	40.5
	HEMA	5	9.46	160.3	121.1	76.7	36.7
Neat PP			–	157.9	110.6	81.3	38.9

Figure 3. DSC thermographs of the grafted PP with IAc at a heating/cooling rate of $10°C$ min^{-1} obtained from the second cycle: (a) Neat PP; (b) 5% of added IAc with DCP; (c) 10% of added IAc with DCP; (d) 20% of added IAc with DCP; (e) 5% of added IAc with Luperox101; (f) 10% of added IAc with Luperox101; (g) 20% of added IAc with Luperox101.

studied the influence of the peroxide nature on the kinetics of monomers grafting onto PP. Peroxides that are easily soluble in molten PP are preferable.[70]

In this study, the difference of the efficiency between the initiators is partly due to the solubility of Luperox 101 in PP that is higher than that of DCP. Therefore, created free radicals on PP, which are likely to react on the monomer double bond, outnumber those created by DCP, and consequently the grafting degree is higher. The second parameter that influences the grafting degree is the initiator's half-life $t_{1/2}$. For DCP $t_{1/2}$ is 49s at 180°C while for Luperox101, $t_{1/2}$ is equal to 87 s. In addition, concentration of active oxygen for Luperox101 is 11.03% while it is only 5.92% for DCP. The theoretical active oxygen content can be calculated with the following formula:

$$\%A(O) = \frac{(\text{number of available } O-O) \times 16 \times 100}{\text{molecular weight}} \quad (6)$$

according to Organic Peroxides—Product Bulletin—Peroxide Selection Guide for Molding Unsaturated Polyester Resins at Elevated Temperatures by Arkema.

It can be concluded that grafting degree is closely dependent on the chosen initiator and on its concentration but on the monomer's concentration.

Thermal analysis of PP-g-(IAc). Figure 3 displays the DSC thermograms of unmodified PP and of the grafted one. The thermograms showed sharp endotherms during heating. Grafted PP has a lower T_m than ungrafted ones. The PP chain degradation during grafting may result in a reduction of T_m. The effect of the variation of grafted monomer content on the melting

temperature (T_m) and crystallinity is given in Table I. The ΔH_m results show that the crystallinity of grafted PP is higher than that of neat PP. Crystallinity depends on the contents of the polar functions of the grafted PP. The observed differences between crystallinity rates for grafted PP are related to the grafting degree of IAc onto PP backbone. The functionalization caused an increase in the polarity of the polymer, intensifying the interaction between the PP chains; consequently, it increased the polymer's crystallinity.

Molecular weight of PP-g-(IAc). In the presence of free radicals, PP undergoes primarily a β-chain scission, via the tertiary macroalkyl radicals, leading to a reduction in the molar masses and viscosity of the polymer.[22,64] The sequence of reactions leading to grafting and possible homopolymerization of the monomer could be postulated by considering that organic peroxide used as initiator in grafting reactions undergoes homolytic rupture generating the primary radicals. The radicals generated by thermal decomposition of the peroxide can abstract the tertiary hydrogen atoms from PP chains, leading to the formation of PP macroradicals as has been shown by De Roover et al. and Sclavons et al.[30,37] The resulting macro-radicals can then undergo a β-scission where two new PP chains of lower molecular weights are generated. Consequently, one PP chain ended with a radical site is generated as the result of each β-scission event, together with a second PP chain ended with a double bond. This has been discussed by De Roover et al. and Sclavons et al. when they studied the mechanism of melt functionalization of PP with maleic anhydride.[30,37] They stated that the β-scission is a fast intramolecular reaction, taking place predominantly in the presence of organic peroxides in the melt phase.

Table II. Summary Table of the Main Data Obtained by IRTF Combined to Elemental Analysis and SEC Analysis of the Modified PP at 180°C and 80 rpm for 6 min by Using Luperox101 as Initiator DP as Initiator

Initiator	Grafted monomer	Monomer content in feed (mol %)	Grafted monomer contents (wt %)	$M_n \times 10^{-3}$ (Dalton)	$M_w \times 10^{-3}$ (Dalton)	M_w/M_n	$[\eta]$ (dL g^{-1})
Luperox 101	IAc	5	2.1	91	330	3.6	0.52
		10	1.98	83	292	3.5	0.48
		20	3.85	85	293	3.4	0.44
	AP	5	2.74	97	226	2.3	0.39
		10	2.77	87	218	2.5	0.3
		20	3.91	58	200	3.4	0.28
	OY	5	1.78	107	301	2.8	0.63
		10	2.01	85	374	4.4	0.56
		20	1.91	80	327	4.1	0.5
	HEMA	5	6.3	131	301	2.3	0.4
DP	IAc	5	0.5	94	420	4.5	0.7
		10	0.26	85	372	4.4	0.68
		20	0.85	84	590	7	0.63
	AP	5	0.22	95	321	3.4	0.56
		10	0.76	96	210	2.2	0.4
		20	1.74	71	358	5.0	0.35
	OY	5	0.92	118	373	3.1	0.62
		10	0.92	149	435	2.9	0.63
		20	1.35	123	390	3.1	0.63
	HEMA	5	9.46	132	433	3.3	0.51
Neat PP			–	96	713	7.4	0.75

The major molecular weight averages, $\overline{M_n}$ and $\overline{M_w}$ and intrinsic viscosity $[\eta]$ were determined and results are given in Table II.

Figure 4 displays the molecular weight variations of modified PP compared to neat PP. The presented results are those obtained for maximum grafting degree for both initiators. Figure 4(A) displays grafting reactions initiated with Luperox 101 while Figure 4(B) displays those initiated with DCP. When reac-

tions were initiated by Luperox 101, the molecular weight decrease is higher than that observed for the system initiated by the DCP. This is due to the higher solubility of Luperox 101 and consequently to higher radical concentration in the molten polymer. These radicals are responsible of β-scission. The new macroradical resulting from the β-scission could in turn react on a double bond of the monomer to form a smaller chain of
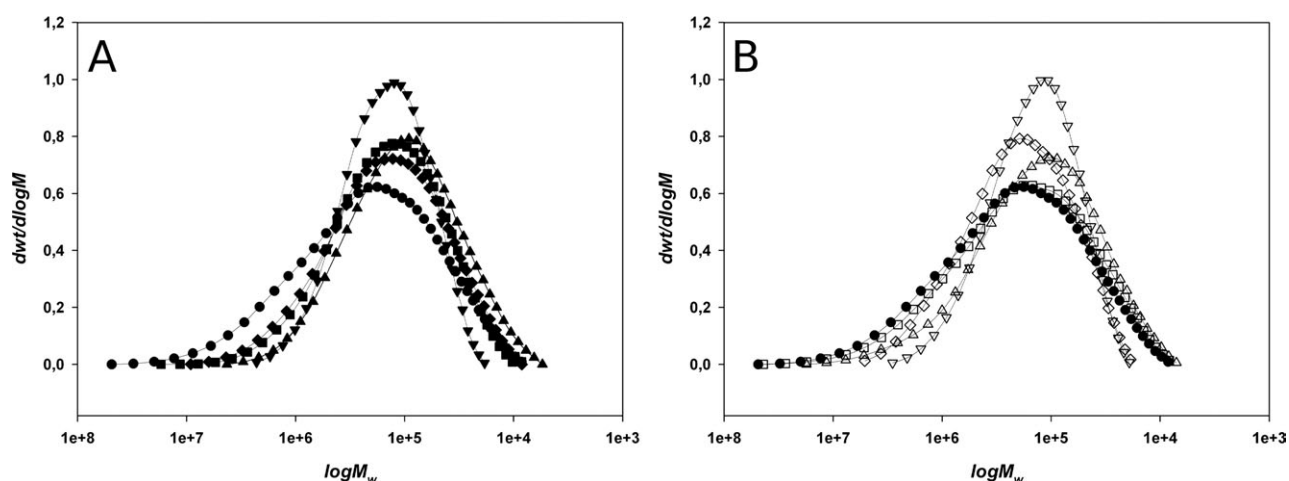

Figure 4. SEC analysis of neat and grafted PP, M_w, molecular weight; dwt/d(logM): differential weight distribution. (a) with Luperox 101 as initiator; ●: neat PP, ■: PP-*g*-IAc, ▲: PP-*g*-AP, ◆:PP-*g*-OY, ▼:PP-*g*-poly(HEMA); (b) with DCP as initiator; ●: neat PP, □: PP-*g*-IAc, △: PP-*g*-AP, ◇:PP-*g*-OY, ▽: PP-*g*-poly(HEMA).
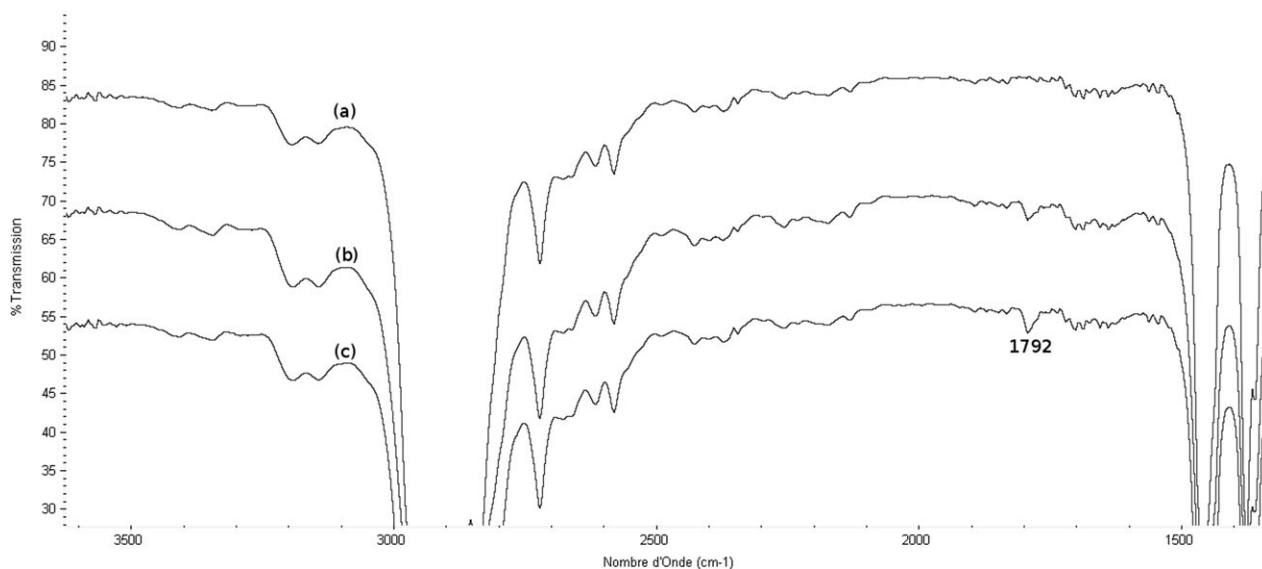
Figure 5. FTIR spectrum of neat PP and grafted PP with OY: (a) PP, (b) PP grafted with OY (DP as initiator), and (c) PP grafted with OY (Luperox 101 as initiator).

PP ended with a grafted function. This is coherent with the results presented in Table I. Increasing initiator concentration results in a molecular weight decrease and an increase of the grafting degree. The grafting degree reaches its maximum for the highest initiator concentration.

Grafting of OY. As in the previous case, grafting of OY onto PP was investigated in the same conditions and all the obtained results are reported in Tables I and II.

FTIR spectroscopy of PP-g-(OY). Figure 5 displays the evidence of grafting by comparing the FTIR spectra of the nongrafted PP with the grafted one. The appearance of a low absorption band near 1792 cm^{-1} is assigned to symmetrical $C = O$ stretching of anhydride function grafted on PP.

In the same way as in the previous case, grafting degree is obtained by combination of FTIR spectroscopy and elemental analysis of the polymer; obtained values are reported in Table I. It is observed that the nature of the initiator has always a high influence on the grafting degree. Luperox 101 leads to a higher grafting degree than that obtained for initiated reactions by the DCP. The grafting degree increased from 1.35 wt % for the reactions initiated by DCP to 2 wt % for that initiated by Luperox 101. It is also observed that the grafting degree increases with the initial concentration of the monomer as well as with that of the initiator.

Thermal analysis of PP-g-(OY). From the presented results in Table I, a decrease in the T_m of the grafted PP compared with that of the ungrafted one can be observed. The differences between crystallinity values for grafted PP are related to the grafting degree of OY onto PP backbone. There is a slight increase of grafted PP crystallinity due to the grafting of polar functions on the PP backbone intensifying the interaction forces between the grafted PP molecules and then increased the polymer's crystallinity.

Molecular weight of PP-g-(OY). Figure 4 displays the molecular weight variation of modified PP compared to neat PP and the results obtained by SEC are summarized in Table II. The grafting of OY is not as high as the grafting of IAc on the PP although used initiators are the same and at the same concentrations. This can be due to a better affinity between OY and the used initiator than that between IAc and initiators.[69] Therefore, the free radicals created by decomposition of peroxide are less reactive on the PP than in the previous case.

IAc and OY can be successfully grafted onto PP in the melt at 180°C by using Luperox 101 or DCP as free radical initiators with an acceptable decrease of molecular weights. Compared with the grafting of IAc onto PP, the grafting of OY is lower.

Grafting of Alcohol Functions onto PP

Grafting of AP. As in the first studied cases, the grafting reaction of AP onto PP was studied. The influences on the grafting degree of the initial concentration of initiator as well as its nature were investigated. All the values obtained after characterization of the modified PP are reported in Tables I and II.

FTIR spectroscopy of PP-g-(AP). Figure 6 compares the nongrafted PP FTIR spectrum with that of grafted PP. The FTIR spectrum of PP-g-AP displays an absorption band in the range of 3200 and 3600 cm^{-1}, which is due to stretching vibrations of the hydroxyl groups $O - H$ of the alcohol.

FTIR spectroscopy combined to the elemental analysis allows to calculate values of the grafting degree of AP onto PP, which are reported in Table I. The grafting degree is higher for the systems initiated by Luperox 101 than for those initiated by DCP. The explanation is the same as that given before. Grafting degree increased with the initial concentration of the monomer and subsequently with that of the initiator. The grafting degree increased from 1.7 wt % when the reaction was initiated by DCP to 3.9 wt % for that initiated by Luperox 101.
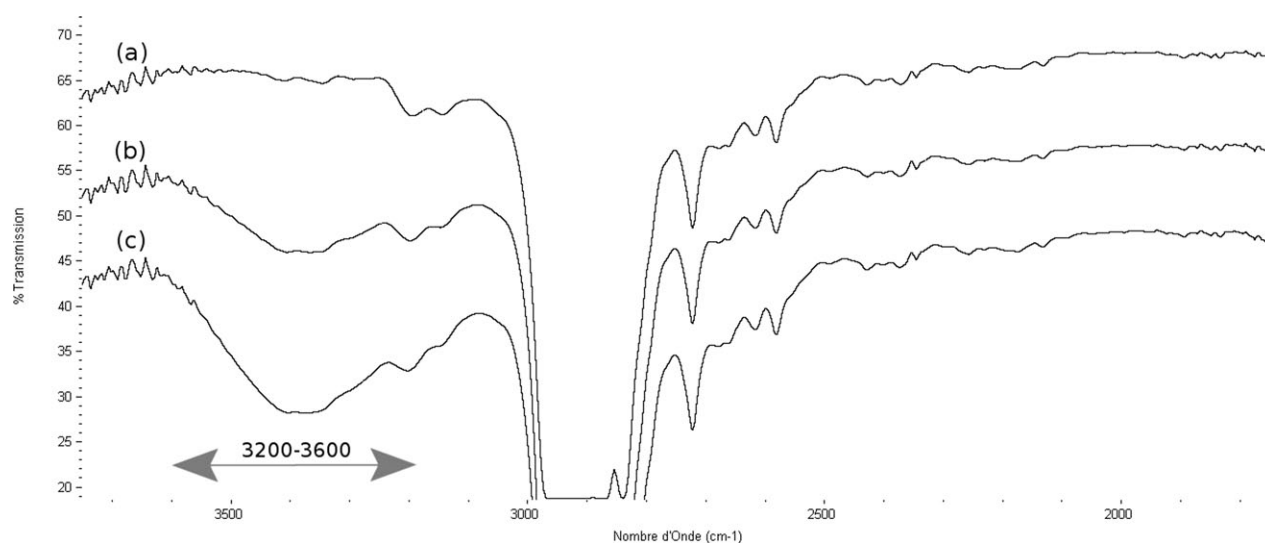
Figure 6. FTIR spectrum of neat PP and grafted PP with AP: (a) PP, (b) PP grafted with AP (DP as initiator), and (c) PP grafted with AP (Luperox 101 as initiator).

Thermal analysis of PP-g-(AP). Results equivalent to those of the previous cases were obtained for the grafting of AP onto PP as shown in Table I. A decrease in the grafted PP's melting point compared with that of the ungrafted one is observed. The observed differences between crystallinity values for grafted PP are related to the grafting degree of AP onto PP backbone. There is a slight increase of grafted PP crystallinity due to the grafting of polar functions on the PP backbone.

Molecular weight of PP-g-(AP). Figure 4 displays the variation in molecular weights of modified PP compared with neat PP and more details are grouped in Table II. In comparison with the molecular weights obtained for the grafting of the other monomers onto PP, the molecular weight decrease is more significant in this case. The intrinsic viscosity was reduced by half for modified PP with the best grafting degree compared with the neat PP. Otherwise, the same behavior as a function of the concentration of initiator was observed. Here, in the case of the reactions initiated by Luperox 101, the molecular weight decrease is higher than that observed for those initiated by the DCP.

Grafting of HEMA. Several studies have investigated the grafting of poly(HEMA) on the surface of PP microporous membranes because of its possible technological applications, that include enzyme immobilization,[71–73] hydrophilicity,[74,75] biocompatibility,[76,77] and antifouling properties.[77–79] Due to the presence of hydroxyl groups in the polymer side chain, versatile modifications of poly(HEMA) using its primary alcohol are possible and provide a wide range of poly(HEMA) derivatives for various purposes. This grafting was induced by plasma, irradiation and ozonation. Grafting of poly(HEMA) onto PP in the molten state has not been widely reported in literature. However, Chun Xu et al. have studied the influence of different parameters on the melt grafting of HEMA onto PP in the presence of DCP.[80]

FTIR spectroscopy of PP-g-poly(HEMA). Figure 7 shows the evidence of grafting by comparing the nongrafted PP FTIR spectrum with that of PP-g-poly(HEMA). The absorption band in the range of 3200 and 3600 cm^{-1} is due to the $O — H$ stretching vibration gradually enhanced as the grafting degree increases, indicating the appearance of $O — H$ groups. An additional intense absorption at 1730 cm^{-1} is ascribed to the $C = O$ stretching vibration of esters which is the major characteristic of poly(HEMA).

The obtained values of grafting degree are grouped in Table I. It is observed in this case, unlike all the previous cases, that the highest grafting degree was obtained when the initiator was DCP. This singular result can be attributed to the fact that all the monomers used for PP functionalization do not undergo homopolymerization except for HEMA. For the monomers that do not undergo homopolymerization, grafting efficiency is proportional to the concentration of radicals. This concentration being related to the initiator $t_{1/2}$, solubility and oxygen index, it is higher when Luperox 101 was used leading to higher grafting degrees than when DCP was used.

When HEMA was used, relatively long grafted chains were obtained. The grafting degree does not only depend on radical concentration, but also on other kinetic constants. Obviously, in the heterogeneous system used, where DCP is the initiator instead of Luperox 101 for HEMA grafting, the combination of all parameters leads to higher grafting. The grafting degree reaches 9.4 wt % for the reactions initiated by DCP while it is 6.3 wt % when Luperox101 is used.

Thermal analysis of PP-g-poly(HEMA). The melting and crystallization behaviors of the neat and grafted PP are displayed in Figure 8. The results are not similar to the previous cases. For exothermic thermograph a small shoulder on the left part of the curves was observed. The T_c is higher than all other grafted PP and the T_m increases. Melting-crystallization was observed particularly for PP.
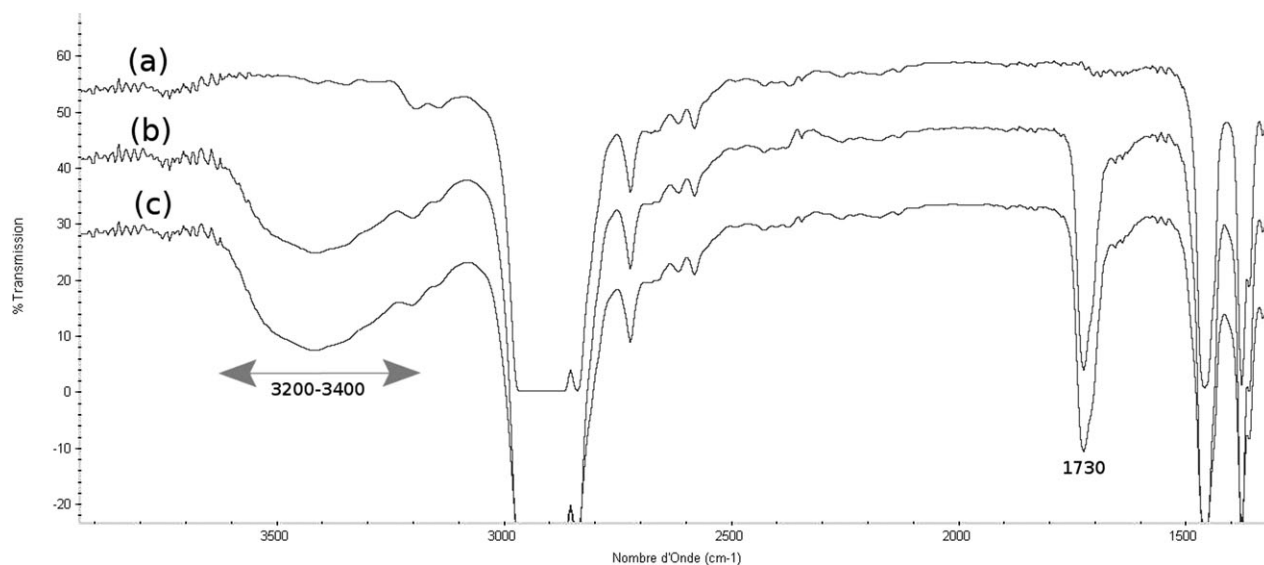
Figure 7. FTIR spectrum of neat PP and grafted PP with HEMA at 180°C and 80 rpm for 6 min: (a) PP, (b) PP grafted with HEMA (Luperox 101 as initiator), and (c) PP grafted with HEMA (DP as initiator).

Nevertheless, the shape of the other melting graphs seems different than the one of PP. This does not exclude that a recrystallization occurred, but it can reasonably be said that if a recrystallization cannot be excluded, it is smaller for grafted PP than for neat PP. The absolute values of melting enthalpy are maybe approximate, but are given here as indicative value. The conclusions that crystallinity increased with grafting in this document seems correct. (i.e., Figures 3 and 8).

Molecular weight of PP-g-poly(HEMA). Figure 4 displays molecular weight distributions of pure PP and PP-*g*-poly(HEMA) and more details are grouped in Table II. The first observation is the narrow distribution of grafted PP compared with neat PP and therefore the low polydispersity index. The effect of the nature of the initiator is the same as the previously studied cases. It can support our reasoning about the higher grafting degree obtained by using DCP because it is clearly shown that Luperox

101 has a better miscibility in the PP, meaning that the obtained grafting degree should be the best when using this initiator.

The absence of a shoulder on the grafted PP curves and the narrow distribution of molecular weight confirm the purity of the modified PP and the absence of poly(HEMA) homopolymer. The thermographs also show that the grafted chains have almost the same length.

It is also important to note that for all the grafted PP, the PDI decreased dramatically to half and even one third. This reduction is often obtained when a random scission occurs for long polymer chain distribution.

Parameters Influencing Intrinsic Viscosity

It was shown in the previous paragraph that the intrinsic viscosity of grafted PP depends on the nature of the initiator used for grafting reactions. Figure 9 displays the evolution of the
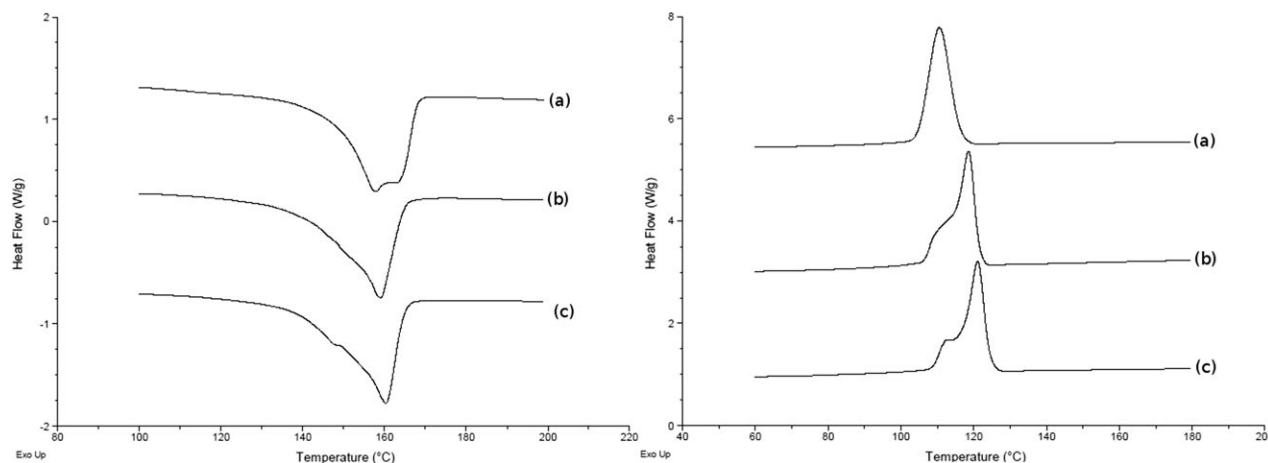

Figure 8. DSC thermographs of the neat PP, grafted PP with 2-hydroxyethyl at a heating/cooling rate of 10°C min^{-1}: (a) Neat PP; (b) 5% of added HEMA with DCP; (c) 5% of added HEMA with Luperox101.
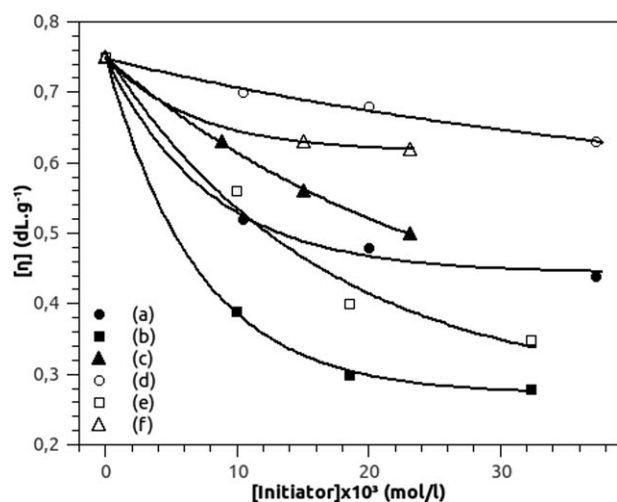
Figure 9. Intrinsic viscosity as a function of the concentration of initiator: (a) PP-*g*-(IAc) synthesized with Luperox101; (b) PP-*g*-(AP) synthesized with Luperox101; (c)PP-*g*-(OY) synthesized with Luperox101; (d) PP-*g*-(IAc) synthesized with DCP; (e) PP-*g*-(AP) synthesized with DCP; (f) PP-*g*-(OY) synthesized with DCP.

intrinsic viscosity as a function of the initial concentration of initiator for the used monomers.

Knowing that initiator concentration depends on monomer concentration by the following relation:

$$\frac{[\text{initiator}]}{[\text{monomer}]} = 10^{-2}$$

Then for each initial concentration of monomer, there is a corresponding initiator concentration. From this figure, the intrinsic viscosity depends on the type of initiator used and on its concentration. Intrinsic viscosity follows the equation:

$$f(x) = y_0 + A \times \exp(\frac{-x}{t})$$

where y_0, A, and t are constants related to the nature of the initiator as well as to the nature of the grafted monomer.

For the system synthesized by Luperox 101, the molecular weight decrease is higher than that observed for the system initiated by DP. This is due to the high solubility of Luperox 101 in the molten polymer. Then, the radicals generated by thermal decomposition of Luperox 101 could abstract the tertiary hydrogen atoms from PP chains leading to the formation of PP mac-
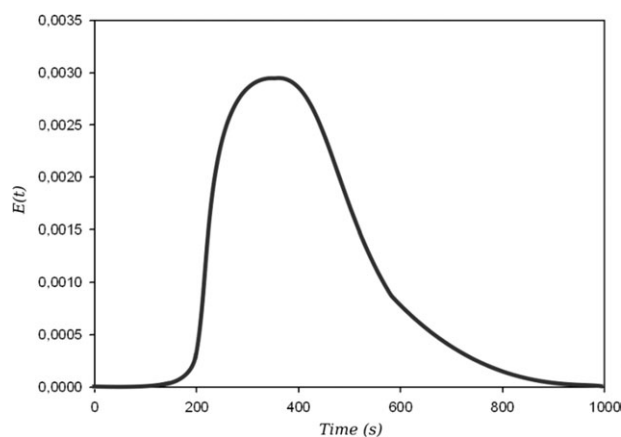

Figure 10. E(t) for extruded PP-*g*-(IAc). Throughput = 1.2 Kg h^{-1}, regulated barrel temperature =180°C, IAc content in feed = 5 mol %, screw rate = 80 rpm.

roradicals. As it has already been explained, the resulting macroradicals could react directly on the double bond of the monomer or undergo β-scission resulting in a decrease in molecular weight. The new macroradical resulting from the β-scission could in turn react on a double bond of the monomer to give birth to a smaller chain of PP ended with a grafted function. This is confirmed by results presented in Table II, which show that the molecular weight decreases with increasing concentration of initiator and that it is accompanied by an increase of the grafting degree.

The influence of the monomer's nature on the intrinsic viscosity is probably due to the affinity between the monomer and the initiator because the closer the peroxide affinity is to the monomer, the lower the grafting efficiency is.[67] Therefore, free radicals created by thermal decomposition of peroxide are less reactive on the PP. Consequently, fewer free radicals are created on the PP backbone leading to a low grafting degree and PP undergoes fewer β-scission.

PP Modification by Reactive Extrusion
As we know, reactive extrusion is an interesting route for cost-effective one-step preparation of polymer materials allowing us to obtain modified polymers continuously in a molten state. For these reasons, this second part is devoted to the modification of PP in the molten state by reactive extrusion using a twin screw extruder. The aim was to have an idea on the grafting degree obtained for modified PP by twin screw extruder in the same conditions as previously studied.

Table III. Summary Table of the Main Data Obtained by IRTF Combined to Elemental Analysis and Thermal Analysis Obtained by DSC of the Modified PP by Using Twin Screw Extruder

Initiator	Grafted monomer	Monomer content in feed (mol %)	Grafted monomer contents (wt %)	T_m (°C)	T_c (°C)	ΔH_m (j g^{-1})	χ_c (%)
Luperox 101	IAc	5	1.7	161.4	116.4	90.5	43.3
	AP	5	1.2	160.1	118.8	86.8	41.5
	HEMA	5	6.7	162.8	124.8	89.4	42.8
Neat PP				157.9	110.6	81.3	38.9

Luperox 101 was used as initiator and studied monomers were IAc, AP, and HEMA. Initial monomer concentration was fixed at 5 mol % and profile temperature was kept constant at 180°C. Finally, the feed rate was set to 1.2 Kg h^{-1}.

The extruder screw profile is given in Figure 1. Each zone of the screw profile in the extruder was chosen according to the desired functions. A relatively long compression step, 300 mm, was needed to assure a correct feeding and melting of the reactants introduced by the volumetric feeder. Three kneading block areas with a neutral configuration (staggering angle: 90°) were used; the first and the second disc areas were directly followed by reverse pitch screw elements to fill these zones. This relatively severe screw profile was chosen to obtain an intensive mixing and high residence time.

The RTD of the reactive extrusion of PP-g-(IAc) is given as an example and displayed in Figure 10. In this experiment, the mean residence time is 440 s and σ_θ^2 is equal to 0.17.

FTIR Spectroscopy of Grafted PP

Grafted PP prepared by REX was analyzed by FTIR and Elemental Analysis. The degree of grafting obtained was 1.7% by weight of PP for IA, 1.2% for AP, and 6.7% for HEMA; more details are presented in the Table III. Grafting degree was a bit lower than that obtained with internal mixer for grafted PP with IAc and AP; that is probably due to lower reaction times. For HEMA, the RTD is sufficient to obtain a grafting degree equivalent to that obtained in an internal mixer. The main aim of this paragraph was to compare the grafting degree obtained by reactive extrusion and that obtained when grafting reactions were carried out in an internal mixer.

CONCLUSION

It is concluded from this study that IAc, OY, AP, and HEMA can be successfully grafted onto PP in the melt at 180°C by using Luperox 101 or DCP as free radical initiators. Two ways have been explored; the first one was PP modification using an internal mixer and the second one using a twin screw extruder. The combination of FTIR with elemental analysis to determine the obtained extent of grafting, it was found that the percentage of grafting depends on both monomer and initiator concentrations as well as on the nature of the initiator used. A maximum of 3.9 wt % of grafting was reached when IAc was used as functional polar monomer. A similar value was found for grafting of AP where a maximum of 3.9 wt % of this monomer was incorporated in PP, 9.5 wt % for HEMA and 2 wt % for OY. It was found that the grafting degree increases by increasing both monomer and initiator concentrations. Grafting degree is closely related to the solubility of the initiator in PP. Thermal analysis indicates an increase of the polarity of PP due to the grafting reaction.

ACKNOWLEDGMENTS

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