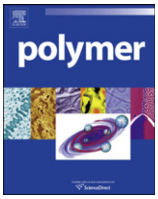
Polymer 49 (2008) 4519–4528

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Synthesis and properties of polyolefin graft copolymers by a grafting “onto” reactive process

Jean Jacques Robin*, Cyrille Boyer, Bernard Boutevin, Cedric Loubat

Institut Charles Gerhardt Montpellier UMR5253 CNRS-UM2-ENSCM-UM1, Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier II, Bat 17, cc17-02, Place Eugène Bataillon 34095 Montpellier Cedex 5, France

A R T I C L E I N F O

Article history:
Received 14 April 2008
Received in revised form 3 August 2008
Accepted 4 August 2008
Available online 13 August 2008

Keywords:
Graft polymers
Functional polymers
Molten state

A B S T R A C T

The synthesis of graft copolymers by the grafting “onto” process in the molten state was described. Functional oligomers obtained by telomerization or by ATRP were reacted onto maleic anhydride grafted polypropylene (PP-g-MAH) and poly(ethylene-*ter*-maleic anhydride-*ter*-methyl acrylate) (P(E-*ter*-MAH-*ter*-MeA)) to obtain PP-g-PMMA and P(E-*ter*-MAH-*ter*-MeA)-g-PMMA graft copolymers, respectively. The grafting of different mono-functional oligomers bearing hydroxyl, aliphatic amine or aromatic amine functions was investigated at 180 °C and at 200 °C. The grafting efficiency was very low in the case of hydroxyl-terminated PMMA, while the amine-terminated PMMA led to high yields. In the last part, PP-g-PMMA and P(E-*ter*-MAH-*ter*-MeA)-g-PMMA graft copolymers were synthesized by the reaction of aliphatic amine functional PMMA oligomers onto PP-g-MAH and P(E-*ter*-MAH-*ter*-MeA), respectively. The influence of the molecular weight of PMMA oligomers was investigated and showed that he grafting efficiency slightly decreases with the increasing molecular weight. However, this process allows the synthesis of PP-g-PMMA graft copolymers containing 6–45 wt% of PMMA side chains. The microstructure of the nanostructured PP-g-PMMA and P(E-*ter*-MAH-*ter*-MeA)-g-PMMA graft copolymers was investigated by TEM and SEM. This was established that the addition of PP-g-PMMA in PP/PMMA binary blends allows to control their morphologies and stabilities.

1. Introduction

Polyethylene (PE) and polypropylene (PP) are the most widely used commercial polymers, with over 24 billion tons/year in 2004. The excellent combination of mechanical resistance and chemical stability explains the commercial success. Although physical blending with other polymers is a versatile and economical way to modify polyolefin by combining properties of the two polymers, compatibilizing agents are necessary because blending polyolefin (PP, PE…) with other polymers usually leads to phase segregation. Indeed, its high crystallinity and low surface energy (due to the lack of chemical functionality) explain the incompatibility with other polymers. Usually, block and graft copolymers based on polyolefins are used as compatibilizers. In this paper, the synthesis of polyolefins based graft copolymers is reported.

Graft copolymers can be synthesized according to three possible approaches: (i) grafting “through” [1], (ii) grafting “from” [2], (iii) grafting “onto” [3]. The first approach deals with the copolymerization of macromonomers with different olefins, such as propene or ethylene described in the publications [4–9]. On the other hand, the “grafting from” method is the most used in industry to obtain graft polyolefins. In this way copolymers containing functional comonomers are prepared using a metallocene [10–17] catalyst, and in a second step, these comonomers can initiate a polymerization to give graft segments. Unfortunately, some difficulties, such as catalyst poisoning and side reactions, have prevented serious consideration of this direct process for commercial applications. However, many research activities [12,18–26] have been focused on the prevention of catalyst poisoning by protecting sensitive functional groups or employing new catalysts. The third approach consists of the chemical modification of pre-irradiated polymers by ionizing radiation (γ-ray, X-ray and electron beam) in the presence of air [27–29] or ozone treatment [30–35] to produce the polymeric peroxides on the chains [31]. These peroxides can initiate radical polymerization in the presence of monomers to lead to graft copolymers. However, these methods are not suitable for preparing well-defined graft copolymers. Indeed, side reactions such as β-scission induce some degradations of the polyolefin. Moreover, these techniques do not allow a satisfactory control on the molecular weights (M_n) of the grafts.

---

* Corresponding author. Institut Charles Gerhardt Montpellier UMR5253 CNRS-UM2-ENSCM-UM1, Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier II, Place Eugène Bataillon, batiment 17, case courrier 17-02, 34296 Montpellier Cedex 5, France. Tel.: +33 4 6714 4157; fax: +33 4 6714 7220.

E-mail address: jean-jacques.robin@univ-montp2.fr (J.J. Robin).

0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.08.011

Table 1
Overview of graft polyolefin copolymers synthesized from different radical methods

	Methods	Initiator, catalyst or chain transfer agent	Structure of graft copolymers
Metallocene	Radical	PE-*co*-DVB	PE-*g*-PS [22]
	Anionic	PE-*co*-(*p*-MS)/*n*-BuLi [11]	P(E-*co*-(*p*-MS)-*g*-PS [11]; P(E-*co*-(*p*-MS)-*g*-P(MS) [12]
		P(P-*ter*-(p-MS)-*ter*-E)/*n*-BuLi	P(P-*ter*-(*p*-MS)-*ter*-E)-*g*-PS [12]
	Borane	PP-g-Borane [13], PE-*g*-Borane [13]	PP-g-PMMA [14,15]; PP-g-PMA [14]; PP-g-SMA [16]; PE-*g*-PMMA [17]
Radical polymerization	Irradiation/O$_2$	γ or UV irradiation	PP-g-P(NIPAAm) [27,28], PE-*g*-PMMA; PP-*g*-PMMA
	Ozonization	PE-g-OOH [28,29]	PE-g-P(DMAEMA) [35]; PE-*g*-PAA [35]; PE-*g*-P(VPA) [35]; PE-*g*-PMMA [31]; PE-*g*-PS [31]; PE-*g*-PVC [31]; PE-*g*-HEA [29]; PE-*g*-P(VAC) [32–34]
Controlled Radical Polymerization	ATRP	PE-*g*-bromoisobutyrate [39]	PE-*g*-PnBA [37,38]; PE-*g*-PMMA [38]
		PE-*g*-chloroacetate	PE-*g*-PS [41]; PE-*g*-PMMA [41]
		PE-*g*-(Br-methyl Styrene)	PE-*g*-PMMA [40], PE-*g*-PS [42]; PE-*g*-PMMA [42]
	RATRP	PE-g-OOH/FeCl$_3$/PPh$_3$ [36]	PE-*g*-PMMA [36]
	NMP	PP-OOH or PE-OOH/TEMPO, PE-*g*-TEMPO [51]	PP-g-PS [49,50]; PP-*g*-PnABu [49], PE-*g*-PS [51,52], PE-*g*-P(AN) [51]

AA: acrylic acid; AN: acrylonitrile; DVB: divinylbenzene; S: styrene; DMAEMA: 2-dimethylaminoethyl methacrylate; MMA: methyl methacrylate; MA: methyl acrylate; MA: methyl acrylate; GMA: glycidyl methacrylate; *n*-BA: *n*-butyl acrylate; PE: polyethylene; PP: polypropylene; PA-6: polyamide-6; VPA: vinyl phosphonate; VC: vinyl chloride; HEA: 2-hydroxyethylacrylate; *n*-BuLi: *n*-butyllithium; NIPAAm: *N*-isopropylacrylamide; VAC: vinyl acetate; ATRP: atom transfer radical polymerization; RATRP: reversible atom transfer radical polymerization, RAFT: reversible addition–fragmentation transfer; NMP: nitroxide mediated polymerization.

Some authors proposed the combination of the previously described methods with controlled radical polymerization (CRP), such as reversible atom transfer radical polymerization (RATRP) [36], atom transfer radical polymerization (ATRP) [4,37–42], reversible addition–fragmentation transfer (RAFT) [43–46] and nitroxide mediated polymerization (NMP) [47–52] (Table 1).

For example, Yamamoto et al. [47] used the RATRP technique to obtain poly(methyl methacrylate) grafted polyethylene (PE-*g*-PMMA). In the first step, PE was irradiated by γ irradiation in the presence of air to obtain PE bearing hydroperoxide groups (PE-*g*-OOH) that were used in a second step as macroinitiators in the presence of FeCl$_3$/PPh$_3$ catalyst for RATRP of methyl methacrylate (MMA). Matyjaszewski et al. [38,41] modified a PE bearing epoxide functions in the presence of chloroacetate or 2-bromoisobutyroyl bromide to give PE-*g*-Cl [38] or PE-*g*-Br [41]. These polymers were used as a macroinitiators initiating the polymerization of styrene in the presence of CuBr/HMTETA (CuBr/1,1,4,7,10,10-hexamethyltriethylene tetramine) or CuBr/dNbpy (CuBr/4,4′-Di(5-nonyl)-2,2′-bipyridine) to obtain PE-*g*-PS. Thus, the authors showed good control of the polymerization until 60–70% conversion. After, some cross-linking reactions were observed by coupling reactions for high conversion, i.e. >70%. Cao et al. [42] synthesized novel poly(E-*co*-divinylbenzene) copolymers by copolymerization of 1,4-divinylbenzene and ethylene in the presence of a metallocene catalyst. The graft copolymer obtained with pendant styrene moiety was modified by the addition of HCl to give an ATRP initiator. In a last step, the grafting of styrene or MMA was performed in the presence of CuCl/*N*,*N*″,*N*‴-pentamethyldiethylenetriamine.

Miwa et al. [49, 50], Baumert et al. [51] and Robin et al. [52] proposed the synthesis of polystyrene grafted polypropylene (PP-*g*-PS) and poly(methyl methacrylate) grafted polyethylene (PE-*g*-PMMA) in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to control the polymerization, the graft lengths and grafts' molecular weights.

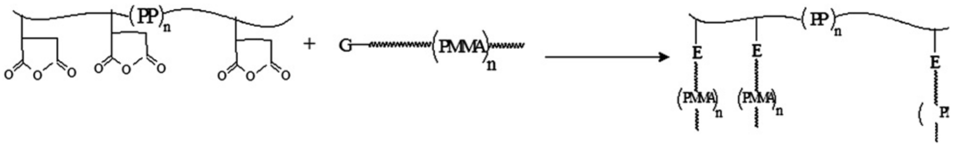
However, these grafting reactions were achieved in solution, knowing that PP or PE presents a poor solubility, i.e. only soluble in aromatic and halogenated solvents. During these last years, industrial companies tried to develop reactions in the melt avoiding the use of solvent for ecological and economical reasons. In the literature, only few studies propose the use of the grafting "onto" method to obtain graft copolymers. For example, graft copolymers of poly(methyl methacrylate) and polyamide-6 (PA-6) were prepared by reactive blending of amino-terminated PA-6 and glutaric anhydride units randomly distributed along the backbone of PMMA [53]. PE-*g*-PA-6 was also synthesized by the reaction between PE bearing reactive sites such as maleic anhydride [54–56] or glycidyl methacrylate [54,55,57] and amino-terminated PA-6.

In conclusion, this paper is focused on the grafting "onto" process in the molten state of alpha-functional PMMA oligomers onto functional polyolefin to obtain PP-*g*-PMMA (Scheme 1). This approach is very original since, to our knowledge, no study in the literature describes the synthesis of well-defined graft copolymers according to this route, i.e. with good control of M_n and PDI.

2. Experimental section

2.1. Materials

Methyl methacrylate (99%, Aldrich) was distilled under vacuum (20 mm Hg, 60 °C). 2-Mercaptoethanol (98%, Aldrich), ethanethiol (98%, Aldrich), anisole (99%, Aldrich), 2-aminoethanethiol hydrochloride (AET·HCl) (98%, Aldrich), 12 M HCl solution (99%, SDS), *N*,*N*′-dimethyl formamide (DMF) (99%, SDS), acetonitrile (99%, SDS), dichloromethane (DCM) (99%, Aldrich), chloroform (99.5%, SDS), dioxane (99%, SDS), and salicylaldehyde (99%, Aldrich) were used without other purifications. 2,2′-Azobisisobutyronitrile (AIBN) (98%, Fluka) was purified by recrystallization from methanol and vacuum dried (20 mmHg, at 20 °C). Water was demineralised and degassed before use. Cu^{I}Br was washed with glacial acetic acid to remove any soluble oxidized species, filtered, washed with ethanol and dried under vacuum. 2-Bromoisobutyroyl bromide (98%, Aldrich), 4-nitrophenol alcohol (99%, Aldrich), 3-amino-1-propanol (99%, Aldrich), di-*tert*-butyl dicarbonate (97%, AVOCADO), triethylamine (99.5%, SDS Society), CHCl$_3$ (99%, SDS Society), silica (60 ACC, SDS Society), hexamethyldisilazane (HMDS) (99%, Aldrich),



Scheme 1. Principle of the chemical reactions between functional oligomers and PP-g-AM.

zinc powder (3 μm, 99%, Aldrich), 1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA) (97%, Aldrich) were used without further purification. Polypropylene-*g*-MAH (Q500E) was purchased by Mitsui Company ($M_n = 53\,000\ \mathrm{g\,mol^{-1}}$, PDI = 3.2, and 2 maleic anhydride functions per chains determined by titration). Poly(ethylene-*ter*-maleic anhydride-*ter*-methyl acrylate) (P(E-*ter*-MAH-*ter*-MeA), composition 81.69/0.31/18.00 w/w/w%) was purchased from Arkema (Lotader, 4403, melting point 77 °C).

2.2. Analytical techniques

The molecular weights were measured by SEC (Size Exclusion Chromatography) using PMMA standards (Polymer Laboratories). The chromatograms were recorded on a Spectra-Physics apparatus equipped with a pump SP 8850 and a differential refractometer Spectra Physics SP 8430 RI, Phenogel columns of Polymer Laboratories (Mixed D, 500 Å, 100 Å). THF was used as eluent at a flow rate of $0.8\ \mathrm{mL\,min^{-1}}$ at 30 °C.

^{1}H NMR experiments were carried out on a BRUKER AC 400 apparatus with tetramethylsilane (TMS) as internal reference and $CDCl_3$ as solvent.

Gas Chromatography (GC) was performed with a Delsi Instruments 330 apparatus equipped with a Shimadzu C-R6A integrator and a 2 m long Carbowax 20 M (poly(ethylene glycol)) column. Nitrogen was used as the carrier gas (vector) at a pressure of 1 bar. The analysis was performed at an oven temperature of 150 °C. GC was used to determine the monomer conversion throughout the polymerization. Solvent (DMF) was used as internal standard.

The FTIR analyses were performed on a Nicolet Nexus apparatus at $2\ \mathrm{cm^{-1}}$ resolution. Samples were analyzed in transmission mode.

Glass transition temperatures were determined by differential scanning calorimetry on a Perkin Elmer Pyris 1 calibrated with indium. The samples (about 10 mg) were heated from 50 to 200 °C at a heating rate of $20\ ^\circ\mathrm{C\,min^{-1}}$ to determine glass transition temperatures (T_g) and at $10\ ^\circ\mathrm{C\,min^{-1}}$ to determine melting temperatures (T_m).

The grafting reactions in the molten state were performed in a HAAKE Polylab Rheometer batch mixer (chamber volume = 50 mL) at 180 °C or 200 °C.

The amine functionalities were titrated by using a pH meter calibrated with buffer solutions pH = 4, 6, and 7. A sample of 2 g of oligomer was dissolved in 25 mL THF/water (85/15 v/v%) solution for 30 min. This reaction mixture was titrated by acid standard solution ($0.01\ \mathrm{mol\,L^{-1}}$) of perchloric acid diluted in THF (85/15 v/v%). The amine functionality was determined using the following equation:

$$F = \left(n_{\mathrm{amine}}^{\mathrm{total}} \times \overline{M}_n\right) \tag{1}$$

where F = amine functionality; $\overline{M}_n$ = molecular weight ($\mathrm{g\,mol^{-1}}$); $n_{\mathrm{amine}}^{\mathrm{total}}$ = primary and secondary amine function content per gram of product determined by titration ($\mathrm{mol\,g^{-1}}$).

2.3. Synthesis of telomers and functional oligomers

We name oligomers the polymers obtained by ATRP and telomers the polymers obtained by telomerization.

Hydroxyl-functionalized telomers or amine-functionalized telomers were obtained by telomerization of MMA in the presence of 2-mercaptoethanol or 2-aminoethanethiol hydrochloride (AET·HCl), respectively. Amine-functionalized oligomers were synthesized by ATRP using a protected initiator. The synthesis of non-functional oligomers was carried out in the presence of ethanethiol.

2.4. Synthesis of non-functional PMMA telomers

For example for $\overline{DP}_n = 20$, 20 g (0.2 mol) of methyl methacrylate (MMA), 0.62 g (0.01 mol) of ethanethiol, 0.164 g (10^{-3} mol) of 2,2′-azobisisobutyronitrile (molar ratio [monomer]/[AIBN] = C_0 = 0.5) were dissolved in 80 mL of acetonitrile in a round-bottom flask fitted with a condenser. The mixture was degassed for 15 min at 0 °C, and then the temperature was raised to 70 °C for 14 h. At the end of the reaction, the polymer was precipitated twice in methanol and finally dried in an oven at 60 °C under vacuum (48 h). The same procedure was used for the synthesis of all the telomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.5 (CH_3O, 3H), 2.5 (CH_2S, 2H), 1.8 (CH_2, 2H), 0.8 (CH_3, 3H).

2.5. Synthesis of hydroxyl-terminated PMMA telomers

For example for $\overline{DP}_n = 20$ with R_0 = molar ratio [telogen]/[monomer] = 0.05, 20 g (0.2 mol) of methyl methacrylate (MMA), 0.78 g (0.01 mol) of 2-mercaptoethanol, 0.164 g (10^{-3} mol) of 2,2′-azobisisobutyronitrile ([monomer]/[AIBN] = C_0 = 0.5) were dissolved in 80 mL of acetonitrile in a round-bottom flask fitted with a condenser. The mixture was degassed for 15 min at 0 °C, and then the temperature was raised to 70 °C for 14 h.

At the end of the reaction, the telomer was precipitated in pentane, separated from the liquid phase by filtration. The telomer was precipitated, and finally dried in an oven at 60 °C under vacuum (48 h). The same procedure was used for the synthesis of all the telomers.

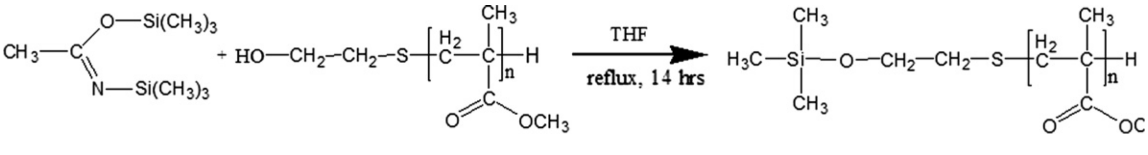
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.6 ($HOCH_2$, 2H), 3.5 (broad signal, CH_3O, 3H), 2.5 (CH_2S, 2H), 1.8–1.5 (CH_2 (backbone), 2H), 1.2–0.8 (broad signal, CH_3, 3H).

2.6. Determination of the functionality of hydroxyl-functionalized PMMA telomers by silylation

Hydroxyl functions were reacted with bis-(trimethylsilylacetamide) (BTMSA) (Scheme 2) according to the well-known method of silylation (for details, see Supporting information). The presence of hydroxyl function was confirmed by the presence of $(CH_3)_3Si$ signal appearing at 0.1 ppm. Functionality of telomers was calculated with the following equation:

$$\text{functionality} = \frac{\frac{\int 0.1\ \text{ppm}}{9}}{\frac{\int 1.8\ \text{ppm}}{(2\overline{DP}_n)}} \tag{2}$$

where DP_n corresponds to the average degree of polymerization determined by SEC analysis.



Scheme 2. Determination of functionality by silylation.

2.7. Synthesis of aliphatic amine-terminated PMMA telomers

For example for $\overline{DP}_n = 20$, 20 g (0.2 mol) of methyl methacrylate (MMA), 1.13 g (0.01 mol) of 2-aminoethanethiol hydrochloride (AET·HCl), 0.164 g (10^{-3} mol) of 2,2′-azobisisobutyronitrile ($[\text{monomer}]/[\text{AIBN}] = C_0 = 0.5$), and 1 g HCl solution (12 M) were dissolved in 200 mL of DMF in a round-bottom flask fitted with a condenser. The mixture was degassed for 15 min at 0 °C, stirred and heated at 70 °C for 14 h. At the end of the reaction, the polymer was precipitated in basic water (pH > 9), separated from the liquid phase by filtration, and washed several times with demineralised water. The polymer was precipitated twice in methanol and finally dried in an oven at 40 °C under vacuum (48 h). The same procedure was used for the synthesis of all the telomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.5 (broad signal, CH_3O, 3H), 2.8 (m, NH_2CH_2, 2H), 2.5 (t, CH_2S, 2H), 2.0–0.6 (broad signal, CH_2 (backbone), 2H), 1.2–0.8 (broad signal, CH_3, 3H).

2.8. Synthesis of the initiator: p-nitrophenyl 2-bromoisobutyrate

10 g (6.5×10^{-2} mol) of *p*-nitrophenol, 6.50 g (6.5×10^{-2} mol) of triethylamine and 200 mL of anhydrous chloroform were introduced in a double-necked round-bottom flask (500 mL) equipped with a condenser. Then 16.42 g (7.2×10^{-2} mol) of 2-bromoisobutyroyl bromide were added dropwise under stirring for 1 h at 0 °C. After 4 h at room temperature, the reaction medium was filtered to eliminate the insoluble quaternary ammonium salt. The filtrate was washed with an aqueous solution of hydrochloric acid (0.1 N) and then with water until pH = 7 of the aqueous phase. The organic phase was dried over anhydrous Na_2SO_4, concentrated by evaporation of the solvent to recover the initiator (brown solid, yield = 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.25 (d, 2H, aromatic H), 7.25 (d, 2H, aromatic H) and 1.95 (s, 6H, CH_3).

2.9. Synthesis of methyl methacrylate oligomers with aromatic nitro function

For example for $\overline{DP}_n = 20$ (molar ratio [monomer]/[initiator]/[CuBr]/[ligand] = 100/4/1/1), in a 50 mL Schlenk flask, 10.0 g (1×10^{-1} mol) of methyl methacrylate, 1.16 g (4×10^{-3} mol) of *p*-nitrophenyl 2-bromoisobutyrate, 0.14 g (1×10^{-3} mol) of CuBr, 0.23 g (1×10^{-3} mol) of HMTETA and 12.8 g of anisole were introduced. The solution was degassed for 10 min with argon. The Schlenk was then placed in an oil bath previously heated at 90 °C.

The polymerization was stopped at about 70% of conversion ($DP_{n\ \text{targeted}} = 20$). The solution was cooled to room temperature, dissolved in THF and filtered on silica to eliminate CuBr and ligand. Solvent and non-reacted monomers were evaporated under vacuum (0.1 mmHg at 90 °C for 2 h). The product was dissolved in THF and precipitated in cold methanol. After filtration on Buchner, the polymer was dried in oven at 40 °C for 24 h to lead to a white product (yield = 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.25 (d, 2H, aromatic H), 7.25 (d, 2H, aromatic H), 3.50 (broad signal, 3H × n, CH_3O), 1.8–1.2 (broad signal, $2H \times n + 1H \times n$, CH and CH_2 backbone), 1.15 (s, 6H, CH_3).

2.10. Reduction of the nitro function of the methyl methacrylate oligomer

5 g (2.5×10^{-3} mol) of nitro-functionalized methyl methacrylate oligomer ($DP_n = 20$), 1.65 g (2.5×10^{-2} mol) of Zn(0) and 100 mL of ethanol were introduced in a two-necked round-bottom flask (250 mL) equipped with a condenser. Then 20 mL of acetic acid were added dropwise under nitrogen atmosphere at 0 °C. After the addition, the mixture was stirred at ambient temperature for 24 h. The solution was filtered on Celite, then solvent and acetic acid were eliminated under vacuum. The obtained mixture was dissolved in THF and precipitated in NaOH solution (0.1 N). Then the solid was washed with demineralised water and dried in a vented oven at 40 °C for 24 h. The product was precipitated twice in methanol (same process described previously) to lead to a white-yellow powder. The aromatic amine-functionalized PMMA oligomer was analyzed by ^{1}H NMR (yield = 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.1 (d, 2H, aromatic H), 6.77 (d, 2H, aromatic H), 3.50 (broad signal, $2H \times n$, CH_3O), 1.8–1.2 (broad signal, $2H \times n + 1H \times n$, CH and CH_2 backbone), 1.15 (s, 6H, CH_3).

2.11. Synthesis of the aliphatic amine-functionalized methyl methacrylate oligomer

For example for $\overline{DP}_n = 20$ (molar ratio [monomer]/[initiator]/[CuBr]/[ligand] = 100/5/1/1), 10.0 g (1×10^{-1} mol) of methyl methacrylate, 1.63 g (5×10^{-3} mol) of *t*-Boc-aminopropyl 2-bromoisobutyrate, 0.14 g (1×10^{-3} mol) of CuBr, 0.23 g (1×10^{-3} mol) of HMTETA and 12.8 g of anisole were introduced into a 50 mL round-bottom flask. The solution was degassed for 10 min with argon. The round-bottom flask was then sealed by a septum and was placed in an oil bath at 90 °C. The conversion rate was monitored by GC. The polymerization was stopped at about 70% of conversion. The solution was cooled at ambient temperature, dissolved in THF and filtered on silica to eliminate CuBr and ligand. Solvent and non-reacted monomer were evaporated under vacuum (0.1 mmHg at 90 °C for 2 h). The solution was concentrated after the polymer was precipitated in methanol and then dried in oven at 40 °C to give a white powder (yield = 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.00 (s, 1H, NH–Boc), 4.00 (t, 2H, $–CH_2–O$), 3.50 (broad signal, 3H, $CH_3–O$), 3.10 (t, 2H, $–CH_2–NH–$), 1.8–1.2 (broad signal, $2H \times n + 1H \times n$, CH and CH_2, backbone), 1.4 (s, 9H, $(CH_3)_3C–$), 0.80 (t, 6H, CH_3).

2.12. Deprotection of the aliphatic amine function of the methyl methacrylate oligomer

10 g (5×10^{-3} mol) of *t*-Boc amine-functionalized oligomer ($M_n = 2.0 \times 10^3$ g mol^{-1}), 4 g (3.5×10^{-2} mol) of trifluoroacetic acid (TFA) and 25 mL of $CHCl_3$ were introduced in a one-necked round-bottom flask (50 mL). The solution was stirred at room temperature for 24 h. Then solvent and TFA were evaporated under vacuum. The obtained mixture was dissolved in diethyl ether and washed with a NaOH aqueous solution (0.1 N). Then solvent and TFA were evaporated under vacuum. The obtained mixture was dissolved in DCM and precipitated in a NaOH aqueous solution (0.1 N). Then the polymer was removed by filtration and dried in oven at 40 °C for 24 h. The polymer was precipitated in cold methanol. After filtration, the product was dried to lead to the aliphatic amine-functionalized PMMA oligomer (yield 90%, white-yellow powder).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.20 (broad signal, 1H, $–NH_2$), 4.00 (t, 2H, $–CH_2–O$), 3.10 (t, 2H, $–CH_2–NH_2$), 1.8–1.2 (broad signal, $2H \times n + 1H \times n$, CH and CH_2, backbone), 0.80 (t, 6H, CH_3).

2.13. Characterization of PP-g-MAH

Functionality in anhydride groups was determined by the Sclavons' method [58]. For example, 0.5 g of PP-*g*-MAH was dissolved in 50 mL of xylene at 130 °C for 30 min. 1 mL of water was added to the mixture which was titrated by a standard solution (NaOH 0.005 N) in a methanol/benzylic alcohol mixture (1/9 v/v% in the presence of phenolphthalein as indicator (from colourless to pale pink)). Titrations were repeated 10 times. The functionality in anhydride is close to 2 anhydrides per chain.

2.14. Synthesis of graft copolymers by coupling reaction in the molten state

Blends were prepared in a batch mixer by mixing at 180 °C or 200 °C for 15 min the functionalized polyolefin in the presence of functionalized telomers or oligomers obtained by ATRP.

2.15. Synthesis of PP-*g*-PMMA graft copolymers

An example of reaction is given: 25 g of PP-*g*-MAH (4.7×10^{-4} mol, 9.4×10^{-4} mol of anhydride function, $M_n = 53\,000$ g mol^{-1}) and 25 g of amine-functionalized telomers (10.4×10^3 g mol^{-1}, 2.5×10^{-3} mol, amine functionality close to 0.55, 1.4×10^{-4} mol of amine function) were introduced into the pre-heated batch mixer at the desired temperature. The product was mixed at 32 rpm. At the end of the reaction, the mixture was collected from the mixer and cooled to room temperature.

The blend mixture was purified by dissolution in xylene at 140 °C for 30 min and precipitation in THF at 0 °C. This operation was repeated three times and the copolymer was recovered by filtration, and then washed with acetone to eliminate free PMMA. The graft copolymers were dried in a vented oven for 48 h. In the same time, the filtrate solution was condensed to recover the non-grafted PMMA oligomers. These non-reacted oligomers were analyzed by SEC and by titration. The PP-*g*-PMMA graft copolymers were analyzed by FTIR. The weight fraction of PMMA was determined by the intensity of the carbonyl band by using a calibration curve (Supporting information).

2.16. Synthesis of PE-*g*-PMMA graft copolymers

The methodology used for the synthesis of PP based copolymers was applied to polyethylene (PE) based ones. The synthesis of PE-*g*-PMMA graft copolymers was carried out by reactive coupling of aliphatic amine functional PMMA onto poly(ethylene-*ter*-maleic anhydride-*ter*-methyl acrylate) (P(E-*ter*-MAH-*ter*-MeA)). The composition of P(E-*ter*-MAH-*ter*-MeA) was equal to 81.69/0.31/18.00 in w/w/w%. Different oligomers with M_n ranging from 4×10^3 to 10×10^3 g mol^{-1} were grafted onto the polyolefin. After reaction, the copolymers were precipitated in acetone to eliminate the presence of free unreacted PMMA. The obtained copolymers presented a good solubility in toluene at 100 °C after reaction. Thus, several analyses (^1H NMR, FTIR, and elemental analysis) were carried out to confirm the effective reaction of the oligomers with the anhydride functions.

2.17. Preparation of scanning electron microscopy (SEM) samples

The reaction mixtures of the copolymers were compression molded to obtain bars. These bars were plunged in liquid nitrogen for 20 min, and then broken to obtain smooth surfaces. The samples were analyzed by SEM to visualize the morphology of the blends of PP-*g*-MAH/NH_2-PMMA. Prior to analysis, samples were covered with platinum. Three consecutive metallization were necessary to reach a coating resistant to the electron beam. SEM analyses were performed on a JEOL 5400 apparatus (Tokyo, Japan) with a resolution of 5 nm. Heavy elements could be differentiated from light elements by chemical contrast, lighter ones appear darker.

2.18. Transmission electron microscopy

The morphologies of the blends were also examined by Transmission Electron Microscopy. After compression molding of the graft copolymers between two sheets of Teflon®, an ultrathin (ca. 100 nm) section was cut on a Reica Ultracut microtome equipped with a diamond knife at low temperature and then stained with RuO_4. TEM was obtained using a Hitachi H-7000 transmission electron microscope at an acceleration voltage of 75 kV and at a magnification of $\times 10^5$. PMMA phase was selectively stained with RuO_4. The PMMA phases appeared in black and the PE ones in white. Annealing was achieved at 180 °C for 20 h.

3. Results and discussion

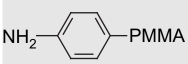
The synthesis of graft copolymers by condensation of terminally functional oligomers onto anhydride grafted polypropylene (PP-g-MAH) was achieved in the molten state. The reactivity of functions like hydroxyl and amine in the presence of anhydride is well known in solution, but there are only few studies [59] that compare the reactivity of these functions in the molten state. In our case, the grafting was performed in a temperature ranging from 180 °C (PP melting point is close to 170 °C) to 220 °C (starting thermal decomposition temperature of PMMA). The stability of PMMA ($M_n = 5.07 \times 10^3$ g mol^{-1}, PDI = 1.75) in our conditions of grafting was checked by TGA at 200 °C and only low weight loss was observed after 2 h (inferior to 2 wt%). This experiment proves that the conditions used for the grafting does not degrade the PMMA. The mono-functional oligomers were prepared either by telomerization or by ATRP according to general methods previously described by our team [60–62] and the characterizations are described in Supporting information. Five types of oligomers presenting molecular weights close to 2×10^3 g mol^{-1} and functionalities in the range of 0.8–1 (Table 2) were used as reagents. At the end of the reaction, the crude products were dissolved in xylene and precipitated three times in tetrahydrofuran to remove unreacted oligomers. The copolymers were dried in a vented oven for 48 h. To determine the yield of grafting, the copolymers were characterized by ^{13}C NMR, FTIR and elemental analysis.

The elemental analysis allowed to calculate the presence of PMMA grafts in the copolymers after the purification step and to evaluate the grafting efficiency (Eq. (3)) using the oxygen content.

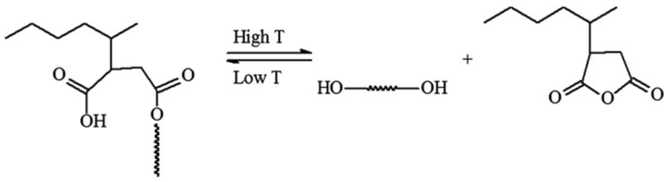
$$\text{Grafting efficiency} = \frac{\text{wt\%}_{\text{experimental oxygen}}}{\text{wt\%}_{\text{theoretical oxygen}}} \times 100 \qquad (3)$$

where wt% theoretical oxygen and wt% experimental oxygen correspond to the oxygen content in the graft copolymers for a grafting efficiency equal to 100% and experimental values measured by elemental analysis, respectively. This equation does not take into account the oxygen present on the backbone of PP-g-AM. Indeed, the value of AM is inferior to 0.2 wt% (determined experimentally).

Table 2
Comparison of the anhydride conversion for different functional oligomers 15 min ($t = 15$ min, shear rate was 50 s^{-1})

Chemical structure of the terminal function	Method of polymerization	M_n (g mol^{-1})	PDI	f[a]	T (°C)	Grafting efficiency (%)
HO–CH_2–PMMA	Telomerization	2.2×10^3	1.70	0.85	180	0.0
					200	0.0
NH_2–CH_2–PMMA	Telomerization	2.0×10^3	1.75	0.80	180	97.0
					200	98.0
	ATRP	2.2×10^3	1.15	0.95	180	40.0
					200	55.0
NH_2–CH_2–PMMA	ATRP	2.3×10^3	1.23	0.95	180	94.0
					200	96.0
HO–CH_2–PMMA	ATRP	2.1×10^3	1.25	1.00	180	0.0
					200	0.0

[a] Corresponds to the functionality per chain.



Scheme 3. Cyclisation of the hemiester functions at high temperature.

The w% of theoretical oxygen was calculated by the Eqs. (4a) and (4b) with the assumption the anhydride was totally reacted.

$$\%\text{PMMA} = \frac{n^{(\text{anhydride})}\overline{M}_{\text{n}}^{\text{oligomer}}}{\overline{M}_{\text{n}}^{\text{PP}} + n^{(\text{anhydride})}\overline{M}_{\text{n}}^{\text{oligomer}}} \qquad (4a)$$

where $\overline{M}_{\text{n}}^{\text{oligomer}}$ and $\overline{M}_{\text{n}}^{\text{PP}}$ correspond to the oligomer and polypropylene molecular weights ($\overline{M}_{\text{n}}^{\text{PP}} = 53 \times 10^3$ g mol^{-1}, $n^{(\text{anhydride})} =$ 2 per chain), respectively.

$$\%\text{O} = 0.32 \times \%\text{PMMA} \qquad (4b)$$

where % O and 0.32 correspond to wt% of theoretical oxygen in the copolymer and percentage of oxygen present in the PMMA, respectively.

The grafting efficiency of hydroxyl-terminated oligomers was close to 0 (Table 2). This result shows that the hydroxyl functions present a low reactivity in the molten state with the anhydride groups. It confirms also the results and conclusions obtained with the model molecules [60]. This result can be explained by the reversibility of the reaction of hydroxyl-anhydride at high temperature (Scheme 3) and by steric hindrance. Aromatic amine-terminated oligomers can be grafted onto PP-*g*-MAH but yields are lower than in the case of aliphatic amine-terminated oligomers. However, aliphatic amine-functionalized PMMA obtained by telomerization or by ATRP gives excellent grafting efficiency (close to 100%) and displays similar results for low molecular weight. It is interesting to note that the grafting efficiency is not dependant on the temperature in the case of aliphatic amine. Whatever the temperature 180 or 200 °C, the grafting efficiency is close to 100% for low molecular weight. This result is consistent with a previous result obtained in the case of model compounds [60]. However, in the case of aromatic amine, the efficiency was slightly improved for high temperature.

In the following part, the influence of the molecular weights of aliphatic amine-functionalized oligomers on the grafting efficiency is described taking into account the two methods used to synthesize the oligomers. The characteristics of the different oligomers that have been grafted are summarized in Table 3. The grafting efficiencies decrease versus the molecular weights of oligomers. The grafting efficiency of telomers is inferior to that of oligomers prepared by ATRP for high molecular weight (Table 4). This behavior is explained by their difference in functionality. Indeed, the functionality of telomers is clearly lower than that of oligomers obtained by ATRP (close to 0.9 whatever the molecular weight), while for $M_{\text{n}} > 15.0 \times 10^3$ g mol^{-1}, the telomers present a functionality inferior to 0.4.

The grafting efficiencies were also determined by FTIR analysis using the characteristic band of the ester function close to 1730 cm^{-1} (Fig. 1). Thus, it is possible to evaluate the PMMA weight content in the copolymers by using a calibration curve obtained by calculating the ratio $\text{RI} = A^{1730\text{cm}^{-1}}/A^{2722\text{cm}^{-1}}$ of different mechanical blends obtained by melt mixing of PP with non-functional PMMA (where $A^{1730\text{cm}^{-1}}$ is the ester band area of PMMA and $A^{2722\text{cm}^{-1}}$ is the reference one belonging to PP (C–H band at 2722 cm^{-1})). The values obtained by FTIR and elemental analysis are in good agreement (Table 4) and confirm the effective grafting of PMMA oligomers onto the PP backbone chain.

The PP-*g*-PMMA graft copolymers were analyzed by ^{13}C NMR (Fig. 2) (after selective precipitation). The broad signal centered at 50–55 ppm which corresponds to the tertiary carbon (*C*) of PMMA backbone and O*C*H$_3$, and at 175–180 ppm (carbonyl *C*=O) confirmed the presence of PMMA. The presence of broad signals can be explained by the difference of conformation of atactic PMMA chains. The others signals centered at 22, 28 and 40–45 ppm correspond to *C*H$_3$, *C*H$_2$, and *C*H carbon of polypropylene. In the case of the copolymers obtained by grafting of hydroxyl-functionalized PMMA oligomers, no characteristic peaks of PMMA were observed in solid NMR. This proves the efficiency of the purification.

Table 3
Characteristics of the different oligomers used for the grafting reaction with PP-*g*-MAH

Runs	Exper. Cond.	$M_{\text{n}}^{\text{theo}}$ (g mol^{-1})	$M_{\text{n}}^{\text{exp}}$ (g mol^{-1})	PDI	*f*
Telomerization	[M]$_0$/[telogen]$_0$/[initiator]$_0$				
TELO-1	100.0/12.5/1.0	8.7×10^3	1.6×10^3	1.50	0.91
TELO-2	100.0/10.0/1.0	1.07×10^3	2.0×10^3	1.58	0.85
TELO-3	100.0/8.3/1.0	1.27×10^3	2.1×10^3	1.60	0.84
TELO-4	100.0/6.6/1.0	1.57×10^3	2.3×10^3	1.60	0.80
TELO-5	100.0/5.0/1.0	2.07×10^3	3.0×10^3	1.70	0.75
TELO-6	100.0/2.0/1.0	5.07×10^3	5.6×10^3	1.75	0.71
TELO-7	100.0/1.3/1.0	7.57×10^3	8.0×10^3	1.75	0.67
TELO-8	100.0/1.0/1.0	10.07×10^3	10.4×10^3	1.80	0.55
TELO-9	100.0/0.66/1.0	15.1×10^3	14.0×10^3	1.8	0.4
TELO-10	100.0/0.5/1.0	20.07×10^3	18.0×10^3	1.9	0.25
TELO-11	0	–	35.0×10^3	2.10	0
ATRP	[M]$_0$/[CuBr]$_0$/[ligand]$_0$/[initiator]$_0$				
ATRP-1	100/1/1/5.0	1.7×10^3	2.3×10^3	1.08	0.95
ATRP-2	100/1/1/3.3	2.1×10^3	3.1×10^3	1.15	0.92
ATRP-3	100/1/1/2.0	3.5×10^3	3.8×10^3	1.06	0.88
ATRP-4	140/1/1/2	6.0×10^3	6.0×10^3	1.16	0.90
ATRP-5	100/1/1/0.8	10.0×10^3	9.7×10^3	1.17	0.90
ATRP-6	100/1/1/0.7	11.4×10^3	10.4×10^3	1.18	0.92
ATRP-7	100/1/1/0.5	15.2×10^3	16.0×10^3	1.07	0.88
ATRP-8	100/1/1/0.3	23.3×10^3	21.0×10^3	1.16	0.90
ATRP-9	100/1/1/0.3	32.3×10^3	30.0×10^3	1.16	0.90
ATRP-10	120/1/1/0.2	53.0×10^3	50.0×10^3	1.16	0.90

f, PDI, [M], [CuBr], [Ligand] and [Initiator] correspond to the oligomer functionality, polydispersity index, monomer, CuBr, ligand and initiator molar concentrations, respectively.

Table 4
Characteristics of the PP-g-PMMA graft copolymers

Runs	Functional oligomers synthesized by	M_n (g mol^{-1})	Elemental Analysis		FTIR	Grafting efficiency (FTIR) (%)
			Theoretical PMMA (w%)	Experimental PMMA (w%)	PMMA (w%)	
Copo 1	Telomerization	2.0×10^3	7.01	6.6	6.6	95
Copo 2	Telomerization	3.0×10^3	10.2	9.4	8.6	93
Copo 3	Telomerization	5.6×10^3	15.9	14.1	14.0	89
Copo 4	Telomerization	7.0×10^3	20.9	18.2	16.4	87
Copo 5	Telomerization	8.0×10^3	23.4	19.7	17.9	84
Copo 6	Telomerization	10.4×10^3	27.4	21.6	20	79
Copo 7	Telomerization	14.0×10^3	29.3	22.6	20.7	76
Copo 8	ATRP	2.3×10^3	7.01	6.6	6.6	95
Copo 9	ATRP	3.1×10^3	10.2	9.4	9.5	93
Copo 10	ATRP	3.8×10^3	13.1	12.1	12.0	92
Copo 11	ATRP	6.0×10^3	18.5	17.2	17.2	93
Copo 12	ATRP	9.7×10^3	24.1	21.4	21.4	89
Copo 13	ATRP	10.4×10^3	28.1	24.5	24.4	87
Copo 14	ATRP	16.0×10^3	36.1	30.3	30.0	84
Copo 15	ATRP	21.0×10^3	44.2	36.3	35.0	82
Copo 16	ATRP	30.0×10^3	53.1	41.4	41.0	78
Copo 17	ATRP	50.0×10^3	65.4	49.0	45.0	70

3.1. *Study of the unreacted oligomers after grafting reaction*

When the crude PP-g-PMMA graft copolymers were precipitated in THF, the free PMMA oligomers were separated and analyzed to determine their functionalities and their molecular weights. The objective of theses analyses was to determine which oligomers are grafted in priority, i.e. low or high molecular weight. Free PMMAs collected were analyzed by Size Exclusion Chromatography (SEC) and by titration. As expected, the free telomers separated showed a lower functionality than the initial telomers used for the coupling reaction. For example, in the case of Copo 3, the functionality of initial telomers of $M_n = 5.6 \times 10^3$ g mol^{-1} was close to 0.71 and after coupling reaction it was equal to 0.66. The same result was obtained for Copo 6 with telomer of $M_n = 10.4 \times 10^3$ g mol^{-1} (with functionalities equal to 0.55 and to 0.43 before and after coupling reaction, respectively). Indeed, only functional oligomers are consumed during the coupling reaction while the non-functional telomers cannot react onto anhydride groups of polyolefin. Different result was obtained in the case of oligomers obtained by ATRP. In this case, as an example, the functionality of oligomer of

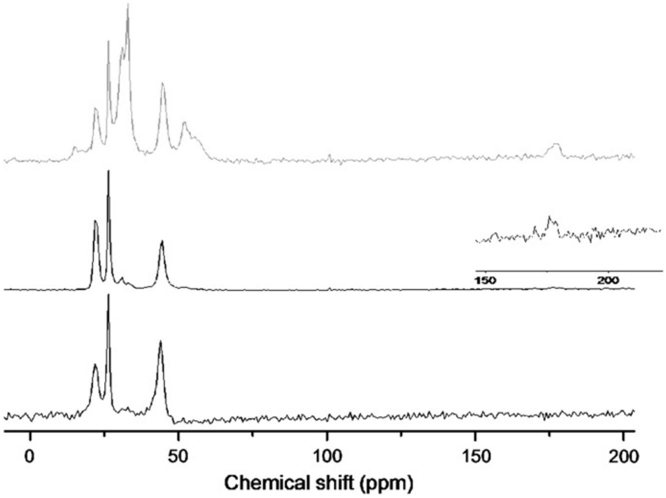


Fig. 2. ^{13}C NMR spectra of graft copolymers after purification by precipitation in THF: (A) PP-g-MAH; (B) PP-g-PMMA from with $M_n^{PMMA} = 2.0 \times 10^3$ g mol^{-1}; (C) PP-g-PMMA from with $M_n^{PMMA} = 10.4 \times 10^3$ g mol^{-1}.

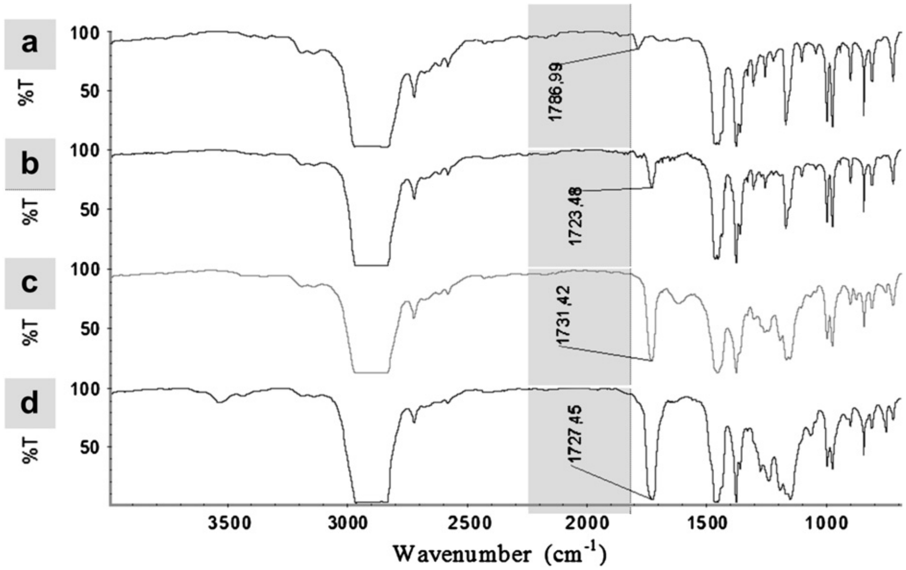


Fig. 1. FTIR spectra of PP-g-PMMA graft copolymers after purification (precipitation in THF): (a) PP-g-MAH; (b) PP-g-PMMA from PMMA with $M_n = 2.0 \times 10^3$ g mol^{-1}; (c) PP-g-PMMA from PMMA with $M_n = 5.0 \times 10^3$ g mol^{-1}; (d) PP-g-PMMA from PMMA with $M_n = 10.4 \times 10^3$ g mol^{-1}.

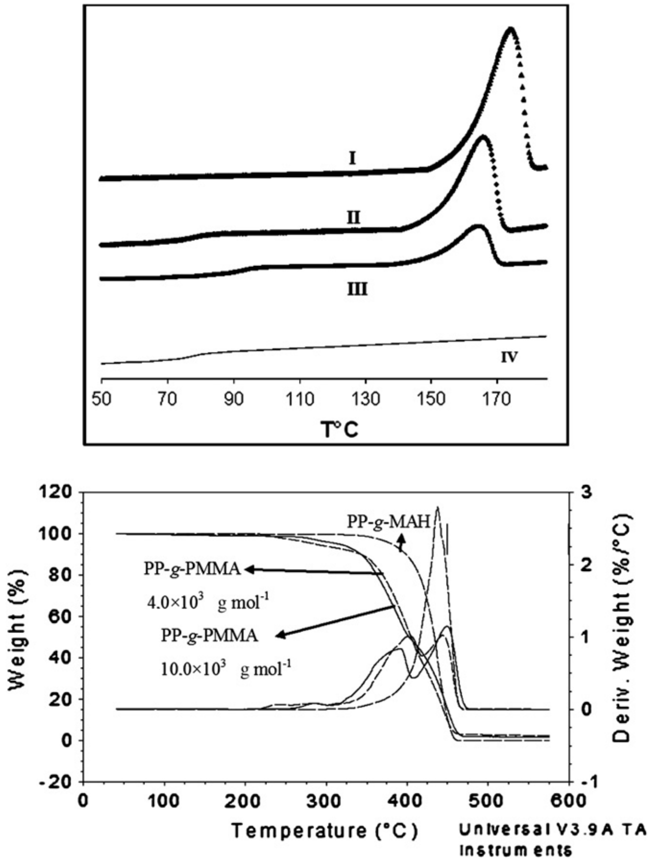


Fig. 3. A) Differential scanning calorimetry (DSC) of different graft copolymers: (I) PP-g-MAH; (II) PP-g-PMMA with $M_n^{PMMA} = 2.0 \times 10^3$ g mol^{-1}; (III) PP-g-PMMA with $M_n^{PMMA} = 4.0 \times 10^3$ g mol^{-1}; (IV) PP-g-PMMA with $M_n^{PMMA} = 10.0 \times 10^3$ g mol^{-1}; (V) PMMA oligomer ($M_n = 2.0 \times 10^3$ g mol^{-1}). (B) TGA thermograms of PP-g-MAH, PP-g-PMMA with $M_n^{PMMA} = 4.0 \times 10^3$ g mol^{-1} and PP-g-PMMA with $M_n^{PMMA} = 10.0 \times 10^3$ g mol^{-1} (under nitrogen).

$M_n = 9.70 \times 10^3$ g mol^{-1} before and after reaction remained close to 0.90.

3.2. Thermal properties

The thermal properties of the purified graft copolymers have been investigated by differential scanning calorimetry (DSC) (Fig. 3A) and thermal analysis (Fig. 3B). Initial PP-g-MAH presents only a melting point of about 160–170 °C whereas a new transition temperature was observed for PP-g-PMMA, which should correspond to the glass transition of PMMA graft. The existence of both T_m of the backbone and T_g of the PMMA graft indicates a microphase-separated morphology (Table 5). The intensity of the melting peak depends on the PMMA chain content in the copolymer and it can be observed that the PMMA grafts disturb the crystallinity of PP.

Table 5
Summary of the thermal properties of PP-g-PMMA copolymers

Samples	M_n of PMMA grafts (g mol^{-1})	T_g[a] (oligomer) (°C)	T_g[b] (°C)	Melting point (°C)	ΔH (J g^{-1})	T_{dec}[c]
PP-g-MAH	–	–	–	168	80	410
Copo 1	2.0×10^3	76	78	165	51	370
Copo 3	4.0×10^3	94	95	162	34	360
Copo 6	10.4×10^3	102	105	160	22	360
Copo 8	2.0×10^3	78	81	165	50	380
Copo 12	8.4×10^3	100	102	160	28	360
Copo 13	10.4×10^3	102	105	160	20	360

[a] Glass transition of PMMAs before coupling reactions.

[b] Glass transition of the PMMA segments in PP-g-PMMA copolymers after purification.

[c] Decomposition temperature (10% lost) under nitrogen.

The thermogravimetric analysis (TGA) of PP-g-MAH, purified PP-g-PMMA copolymers and PMMA oligomers was performed under nitrogen and oxygen (Fig. 3B). The PP-g-MAH presents a good thermal stability until 410 °C (under nitrogen) and 360 °C (under oxygen), while PP-g-PMMAs present an inferior thermal stability until 360 °C (under air) and 380 °C (under nitrogen).

3.3. Effect of PP-g-PMMA copolymers on the morphology of PP/PMMA blends

The effects of PP-g-PMMA graft copolymers on binary PP/PMMA blends were studied by SEM (Fig. 4). In simple homopolymer blend (PP/PMMA, 50/50 w/w%), sharp phase separation was observed. Indeed, PMMA component exhibited poorly dispersed domains (with a size nodules of around 4–8 μm), typically characteristic of poor interfacial adhesion. When a small amount of graft copolymer was added in the blend (PP/PMMA/PP-g-PMMA, 45/45/10 wt% (with $M_n^{PMMA\ graft} = 10.0 \times 10^3$ g mol^{-1})), a totally different morphology appeared (Fig. 4). The interface between the PP and PMMA domains became blurred, indicating that compatibility between the PP and PMMA was improved (size of nodule inferior at 1 μm). Fig. 4C exhibits the SEM micrograph of purified PP-g-PMMA which appears as an extremely fine dispersion of nodules (size <50 nm).

3.4. Synthesis of PE-g-PMMA graft copolymers

The methodology used for the synthesis of PP based copolymers was applied to polyethylene (PE) based ones. The synthesis of PE-g-PMMA graft copolymers was carried out by reactive coupling of aliphatic amine functional PMMA synthesized by ATRP onto poly(ethylene-*ter*-maleic anhydride-*ter*-methyl acrylate) (P(E-*ter*-MAH-*ter*-MeA)). The composition of P(E-*ter*-MAH-*ter*-MeA) was 81.69–0.31–18.0 in w/w/w%. Different oligomers with M_n ranging from 4.0×10^3 to 10.0×10^3 g mol^{-1} were grafted onto the polyolefin. After reaction, the graft copolymers were precipitated in acetone to eliminate the presence of free unreacted PMMA. The obtained copolymers presented a good solubility in toluene at 100 °C after reaction which allows ^{1}H NMR analysis. Thus, several analyses (^{1}H NMR, FTIR, and elemental analysis) were carried out to confirm the effective reaction of the oligomers with the anhydride functions. The composition of the obtained copolymers is given in Table 6.

^{1}H NMR spectra of P(E-*ter*-MAH-*ter*-MeA)-g-PMMA (after purification by precipitation) synthesized from $M_n^{PMMA} = 4.0 \times 10^3$ and 10.0×10^3 g mol^{-1} in toluene-d_8 at 100 °C are presented in Fig. 5. A broad singlet is observed at 1.2 ppm attributed to PE segments (CH_2–CH_2). Besides, the others signals at around 3.5–3.4 ppm, 2.0 ppm and 0.8 ppm correspond to the –OCH_3 of methyl acrylate and methacrylate, –CH_2– of methyl acrylate and methacrylate and –CH_3 of methyl methacrylate, respectively. The signal which appears at 4.1 ppm is attributed to –CH_2–N– in adjacent position of the imide group. This analysis confirms the effective grafting of PMMA in the different copolymers.

The morphologies after purification were examined by transmission electron microscopy (TEM) of P(E-*ter*-MAH-*ter*-MeA)-g-PMMA copolymer containing $M_n^{PMMA\ graft} = 10.4 \times 10^3$ g mol^{-1} (Fig. 6). The technique of staining the PMMA phases with ruthenium (RuO_4) was used to underscore the different phases between the PE and the PMMA. Indeed, these two polymers are not compatible. The size of included objects remains smaller than

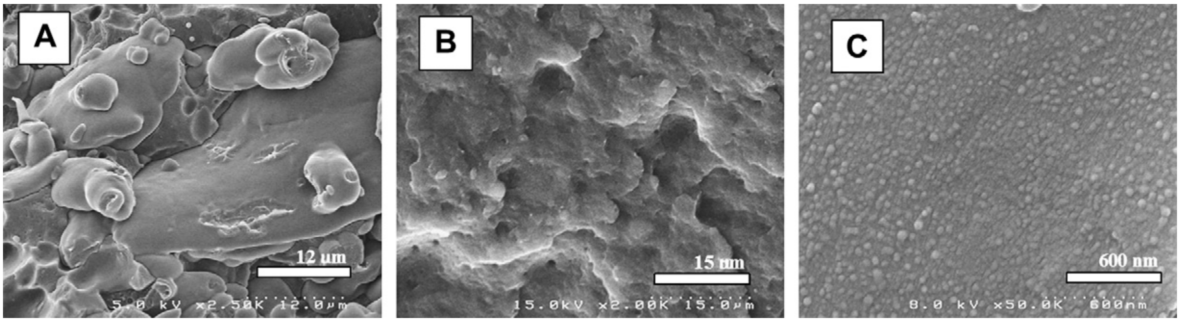


Fig. 4. SEM of PP/PMMA blends (50/50 w/w%) with or without copolymer: (A) blend with no added functional polymer (nodules >2 µm); (B) blend with incorporation of PP-*g*-PMMA copolymers in the mixture (PP/PMMA/PP-*g*-PMMA, 45/45/10 w/w/w%) (PMMA graft $M_n^{PMMA} = 10.4 \times 10^3$ g mol^{-1}, nodules <1 µm); (C) PP-*g*-PMMA graft copolymer alone after purification (PMMA graft $M_n^{PMMA} = 10.4 \times 10^3$ g mol^{-1}, nodules <50 nm). The SEM micrographs were obtained by annealing at 180 °C for 20 h.

Table 6

Characteristics of P(E-*ter*-MAH-*ter*-MeA)-*g*-PMMA graft copolymers

Copo	M_n of PMMA grafts (g mol^{-1})	PDI	f[a]	PMMA theoretical content[b] (w%)	PMMA experimental content (w%)
Copo PE-1	4.0×10^3	1.18	0.95	11.1	10.0
Copo PE-2	6.0×10^3	1.21	0.92	16.0	15.1
Copo PE-3	10.2×10^3	1.15	0.95	23.0	20.0

The reaction was carried out at 180 °C for 15 min, molar ratio $[\text{anhydride}]_0/[NH_2\text{–PMMA}]_0 = 1/1$.

[a] Corresponds to the amine functionality of PMMA oligomer reagents synthesized by ATRP.

[b] PMMA theoretical content $= M^{PMMA}/[M^{P(E\text{-ter-MAH-}ter\text{-MA})} + M^{PMMA}]$; where $M^{PMMA} = [\%\ \text{anhydride} \times M^{P(E\text{-ter-MAH-}ter\text{-MA})}/M^{\text{anhydride}}] \times M^{PMMA}$ with M^{PMMA}, $M^{P(E\text{-ter-MAH-}ter\text{-MA})}$, $M^{\text{anhydride}}$, M^{PMMA}, % anhydride correspond to weight of grafted PMMA, weight of P(E-ter-MAH-*ter*-MA), molecular weight of maleic anhydride and molecular weight of PMMA oligomers, respectively.

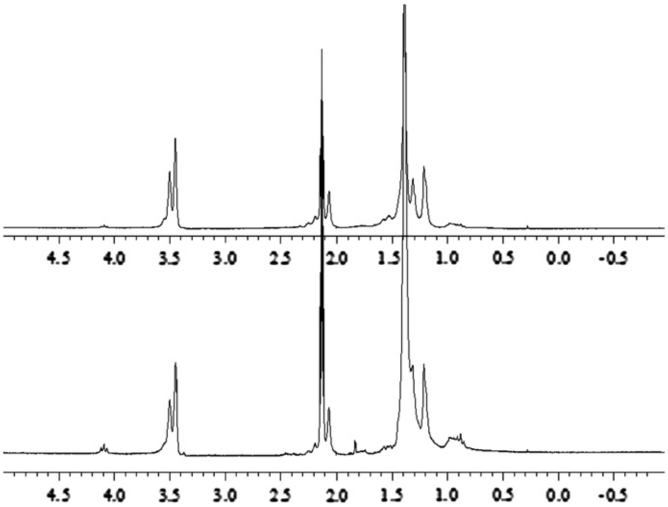


Fig. 5. ^1H NMR spectra of PE-*g*-PMMA graft copolymers with different molecular weights of PMMA graft (above $M_n = 6000$ and under 10.4×10^3 g mol^{-1}) (recorded in toluene-d_8 at 100 °C, 250 MHz).

50 nm, in agreement with the visual aspect of the film, which appears transparent after annealing.

4. Conclusion

The synthesis of graft copolymers by the grafting "onto" process in the molten state was reported. Different mono-functional oligomers bearing terminal hydroxyl, aliphatic or aromatic amine were grafted onto PP-*g*-MAH at 180 °C and at 200 °C. In the case of hydroxyl functional oligomers, the grafting efficiency was nil while with the aliphatic amine-terminated PMMA a good yield was observed (about 0.95). The grafting efficiency increased with the increase of molecular weight oligomers. The grafting efficiency was higher in the case of oligomers synthesized by ATRP since they present a better functionality. In using different aliphatic amine functional oligomers and PP-*g*-MAH or P(E-*ter*-MAH-*ter*-MA), different graft copolymers were synthesized with PMMA contents ranging from 6% to 45%. These PP-*g*-PMMA and P(E-*ter*-MAH-*ter*-MA)-g-PMMA copolymers exhibited phase segregation with very small nodules (nodule size <100 nm) observed by SEM and TEM. PP-*g*-PMMA graft copolymers added to binary PP/PMMA blends exhibited a compatibilizing effect.

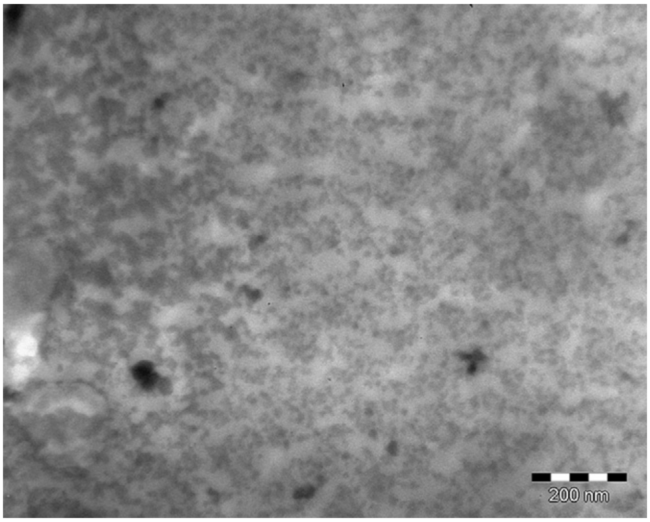


Fig. 6. Transmission electron micrograph of the morphology of PE-*g*-PMMA with PMMA graft $M_n^{MMA} = 10.0 \times 10^3$ g mol^{-1}, annealed at 180 °C for 20 h. TEM micrograph was obtained by staining ultrathin section with RuO_4 vapor which selectively stains the PMMA.

Acknowledgment

The authors thank Solvay S.A. company for financial support.

Appendix. Supporting information

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.08.011.

References

[1] Boutevin B, David G, Boyer C. Adv Polym Sci 2007;206:31–135.
[2] Sauguet L, Boyer C, Ameduri B, Boutevin B. Macromolecules 2006;39(26):9087–101.
[3] Hadjichristidis N, Pitsikalis M, Pispas S, Iatrou H. Chem Rev 2001;101(12):3747–92.
[4] Kaneyoshi H, Inoue Y, Matyjaszewski K. Macromolecules 2005;38(13):5425–35.
[5] Cherian AE, Lobkovsky EB, Coates GW. Macromolecules 2005;38(15):6259–68.
[6] Kaneko H, Kojoh S-i, Kawahara N, Matsuo S, Matsugi T, Kashiwa N. Macromol Symp 2004;213:335–45.
[7] Gaynor SG. Macromolecules 2003;36(13):4692–8.
[8] Hong SC, Jia S, Teodorescu M, Kowalewski T, Matyjaszewski K, Gottfried AC, et al. J Polym Sci Part A Polym Chem 2002;40(16):2736–49.
[9] Zheng L, Farris RJ, Coughlin EB. Macromolecules 2001;34(23):8034–9.
[10] Chung TC. Prog Polym Sci 2002;27:39–85.
[11] Chung TC. 56th annual technical conference, vol. 2. Society of Plastics Engineers; 1998. p. 1813–15.
[12] Chung TC, Lu HL, Ding RD. Macromolecules 1997;30(5):1272–8.
[13] Chung TC, Janvikul W, Lu HL. J Am Chem Soc 1996;118(3):705–6.
[14] Chung TC, Rhudright D, Jiang GJ. Macromolecules 1993;26(14):3467–71.
[15] Chung TC, Lu HL, Janvikul W. Polymer 1997;38(6):1495–502.
[16] Chung TC, Janvikul W, Bernard W, Jiang GJ. Macromolecules 1993;27:26.
[17] Chung TC. Macromol Symp 1995;89:151–62.
[18] Chung TC. Contemp Topics Polym Sci 1992;7:323–31.
[19] Chung TC, Kumar A, Chen F, Stanat J. New Adv Polyolefins 1993:87–99.
[20] Chung TC. Polym Prepr (Am Chem Soc Div Polym Chem) 1994;35(1):674–5.
[21] Chung TC, Xu G, Lu Y, Hu Y. Macromolecules 2001;34(23):8040–50.
[22] Chung TC. Abstr. Papers. 221st ACS National Meeting, San Diego, CA, United States; April 1–5 2001. PMSE-020.
[23] Chung TC, Dong JY. Abstr. Papers. 223rd ACS National Meeting, Orlando, FL, United States; April 7–11 2002. POLY-395.
[24] Chung TC. Isr J Chem 2003;42(4):307–32.
[25] Ramakrishnan S, Berluche E, Chung TC. Macromolecules 1990;23(2):378–82.
[26] Xu G, Chung TC. Abstr. Papers. 220th ACS National Meeting, Washington, DC, United States; August 20–24 2000. POLY-332.
[27] Bucio E, Arenas E, Burillo G. Mol Cryst Liq Cryst 2006;447:521–31.
[28] Bucio E, Burillo G, Adem E, Coqueret X. Macromol Mater Eng 2005;290(8):745–52.
[29] Boutevin B, Robin JJ. Eur Polym J 1990;26(5):559–64.
[30] Boutevin B, Pietrasanta Y, Robin JJ, Pollet T. Eur Polym J 1988;24(10):953–9.
[31] Boutevin B, Pietrasanta Y, Taha M, Sarraf T. Eur Polym J 1984;20(12):1131–5.
[32] Fargere T, Abdennadher M, Delmas M, Boutevin B. J Polym Sci Part A Polym Chem 1994;32(7):1377–84.
[33] Fargere T, Abdennadher M, Delmas M, Boutevin B. Eur Polym J 1995;31(10):923–30.
[34] Fargere T, Abdennadher M, Delmas M, Boutevin B. Eur Polym J 1995;31(5):489–97.
[35] Zouahri A, Assouag M, Robin JJ, Boutevin B, Elbachiri A, Elmidaoui A. J Appl Polym Sci 2006;101(6):4423–9.
[36] Yamamoto K, Miwa Y, Tanaka H, Sakaguchi M, Shimada S. J Polym Sci Part A Polym Chem 2002;40(20):3350–9.
[37] Okrasa L, Pakula T, Inoue Y, Matyjaszewski K. Colloid Polym Sci 2004;282(8):844–53.
[38] Inoue Y, Matsugi T, Kashiwa N, Matyjaszewski K. Macromolecules 2004;37(10):3651–8.
[39] Inoue Y, Matyjaszewski K. J Polym Sci Part A Polym Chem 2004;42(3):496–504.
[40] Hwu J-M, Chang M-J, Lin J-C, Cheng H-Y, Jiang G-J. J Organomet Chem 2005;690(26):6300–8.
[41] Matyjaszewski K, Teodorescu M, Miller PJ, Peterson L. J Polym Sci Part A Polym Chem 2000;38:2440–8.
[42] Cao C, Dong J, Hu Y. Chin Sci Bull 2005;50(10):1048–51.
[43] Lopez RG, Boisson C, D'Agosto F, Spitz R, Boisson F, Gigmes D, et al. Macromol Rapid Commun 2006;27(3):173–81.
[44] Nakamura H, Koshirai A. (Mitsubishi Rayon Co., Ltd., Jpn). Manufacture of vinyl-modified olefin polymers by efficient graft polymerization. Jpn Kokai Tokkyo Koho. 2003. 5 pp.
[45] De Brouwer H, Schellekens MAJ, Klumperman B, Monteiro MJ, German AL. J Polym Sci Part A Polym Chem 2000;38(19):3596–603.
[46] Barner L, Zwalneveld N, Perera S, Pham S, Davis TP. J Polym Sci Part A Polym Chem 2002;40:4180–92.
[47] Sugino Y, Yamamoto K, Miwa Y, Sakaguchi M, Shimada S. e-Polymers 2003. No pp. given, paper no. 7.
[48] Yamamoto K, Nakazono M, Miwa Y, Hara S, Sakaguchi M, Shimada S. Polym J (Tokyo, Jpn) 2001;33(11):862–7.
[49] Miwa Y, Yamamoto K, Sakaguchi M, Shimada S. Macromolecules 2001;34(7):2089–94.
[50] Miwa Y, Yamamoto K, Sakaguchi M, Shimada S. Macromolecules 1999;32(24):8234–6.
[51] Baumert M, Heinemann J, Thomann R, Mulhaupt R. Macromol Rapid Commun 2000;21(6):271–6.
[52] Bertin D, Boutevin B, Robin J-J. Graft copolymer obtained by free-radical polymerization with stable free radicals: its preparation and uses. Eur Pat Appl Ep: (Elf Atochem S.A., Fr), 1999. 17 pp.
[53] Freluche M, Iliopoulos I, Flat JJ, Ruzette AV, Leibler L. Polymer 2005;46(17):6554–62.
[54] Pan L, Chiba T, Inoue T. Polymer 2001;42(21):8825–31.
[55] Pan L, Inoue T, Hayami H, Nishikawa S. Polymer 2001;43(2):337–43.
[56] Li F, Chen Y, Zhu W, Zhang X, Xu M. Polymer 1998;39(26):6929–34.
[57] Koulouri EG, Georgaki AX, Kallitsis JK. Polymer 1997;38(16):4185–92.
[58] Sclavons M, Franquinet P. Polymer 2000;41:1989–99.
[59] Orr CA, Cernohous JJ, Guegan P, Hirao A, Jeon HK, Macosko CW. Polymer 2001;42(19):8171–8.
[60] Boyer C, Boutevin B, Robin JJ. Polym Degrad Stab 2005;90(2):326–39.
[61] Boyer C, Loubat C, Robin JJ, Boutevin B. J Polym Sci Part A Polym Chem 2004;42(20):5146–60.
[62] Boyer C, Otazaghine B, Boutevin B, Joly-Duhamel C, Robin J-J. J Polym Sci Part A Polym Chem 2005;43(18):4303–22.