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

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ABSTRACT

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.

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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(P-*ter*-(p-MS)-*ter*-E)/*n*-BuLi	P(E-*co*-(*p*-MS)-*g*-PS [11]; P(E-*co*-(*p*-MS)-*g*-P(MS) [12] 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.

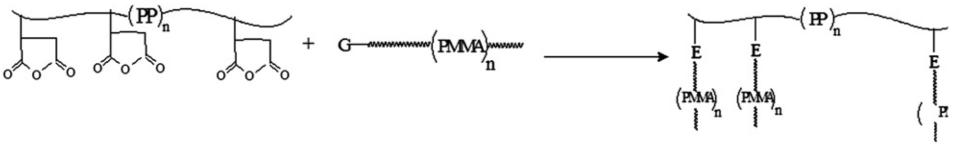
However, these grafting reactions were achieved in solution, knowing that PP or PE presents a poor solubility, i.e. only soluble in aromatic and halogenated solvents. During these last years, industrial companies tried to develop reactions in the melt avoiding the use of solvent for ecological and economical 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.