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POLYPROPYLENE DERIVATIVES

E. Borsig[a]
[a] Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovak Republic

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POLYPROPYLENE DERIVATIVES

E. Borsig

Polymer Institute
Slovak Academy of Sciences
Dúbravská cesta 9
842 36 Bratislava, Slovak Republic
E-mail: upolebor@savba.sk

Faculty of Chemical Technology
Slovak University of Technology
Radlinského 9
812 37 Bratislava, Slovak Republic

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ABSTRACT

The paper brings a brief survey of the direct chemical methods for preparation of polypropylene (PP) derivatives, using mostly peroxides, UV or gamma irradiation and, in some cases, also strong acidic reagents for formation of precursors of binding the functional groups or side chains on the PP backbone. By this means, sulfonated, chlorinated, carboxylated, hydroperoxidated PP as the examples of functionalized PP's, can be prepared. As examples of binding side chains to the PP, the grafting of PP with unsaturated monomers like styrene, methyl methacrylate, acrylates, maleic anhydride, and its derivatives are described. The application of PP derivatives and their importance in preparation of polymer blends and composites is illustrated.

INTRODUCTION

Polypropylene is generally known as a polymer with a wide range of application in plastic industry, mainly in the production of different car parts (bumpers), water and waste pipe, household and kitchen utensils and appliances, package, toys, a variety of molds for sports equipments, furniture, machines, etc., but also as solid fiber.

It is due to relatively good mechanical properties of polypropylene, its low price and to another important property, ecologically friendly production and its waste processing. Further extension of the applicability of polypropylene requires, however, the combination of the properties with other polymers or materials, chiefly with polar polymers (in polymer blends) and with glass and metal (either as a filler or in the preparation of e.g., sandwich products). This can only be reached if part of polypropylene molecules will also contain polar groups or chains that will enable the combination of the properties with other, usually polar, material.

By introducing polarity into the polypropylene chain, an interfacial agent can be obtained for composite materials, where there improves the compatibility of PP with polar polymers, such as polyamide or polyester [1-5] or adhesion of PP to the glass or metal surface [6] but also the required properties like surface dyeability, hygroscopicity and surface conductivity (mainly of fibers) [7].

Chemical bonding of polar groups or chains to a PP molecule can, in principle, be achieved in two ways.

The first traditional way of binding to nonpolar popypropylene macromolecule without typical reactive sites uses a radical chain transfer reaction most often, a reaction site with active free radical being formed and this radical is used for binding the polar component [8]. The second newer way of obtaining the reaction center is the copolymerization of a monomer unit with an active group (most frequently with free double bond) into a polypropylene chain, which is then used for binding the required polar group [9].

To make the article more lucid, the methods of the chemical binding of polar components to PP were divided into two groups:

A) Functionalization of polypropylene (binding of low-molecular functional groups).

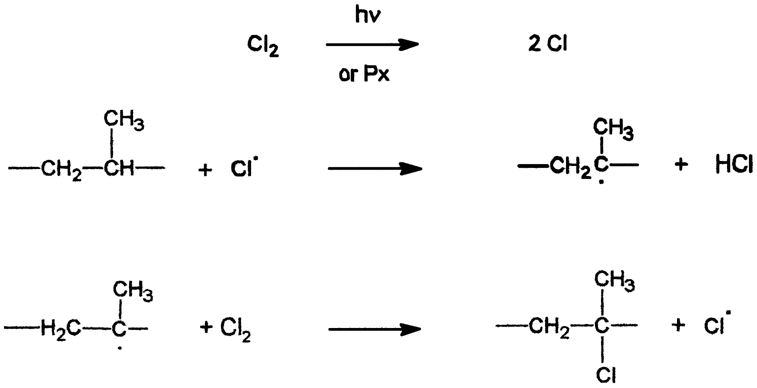
B) Grafting of polypropylene (binding of PP chains to the backbone of PP).

There is naturally no sharp boundary between the two groups and in the case of the binding of low-molecular functional groups to PP, they are often used for the consecutive polypropylene grafting. However, to justify this division all the same, the first group (A) will include the methods providing functionalized PP, which can be used separately for various purposes, such as e.g., polymer blends regardless of the fact whether it can be later used for grafting or not. The second group (B) will include only direct or indirect methods of PP grafting.

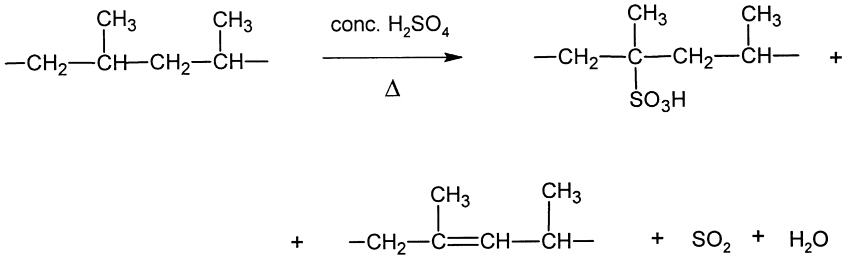
There are also other methods of the modification of polypropylene, e.g., PP crosslinking, which, however, was not been included into the article for practical reasons.

A. Functionalization of Polypropylene

The chlorination of PP belongs to the oldest and relatively simplest methods of introducing the polar heteroatom into the PP chain. The procedure is actually the same as the in the chlorination of low-molecular hydrocarbons using a radical chain reaction (Scheme 1). The chlorination is initiated by UV radiation or by thermal decomposition of peroxide and is carried out in a solution (mainly of atactic PP) in chlorinated solvents, e.g. CCl_4 or in a monomer slurry of PP. Chlorinated PP is used as a compatibilizer for the preparation of PP-EVA and PP-PMMA blends and as a secondary plasticizer for PVC. It can also be used for grafting with a cationic mechanism [10].



Scheme 1.

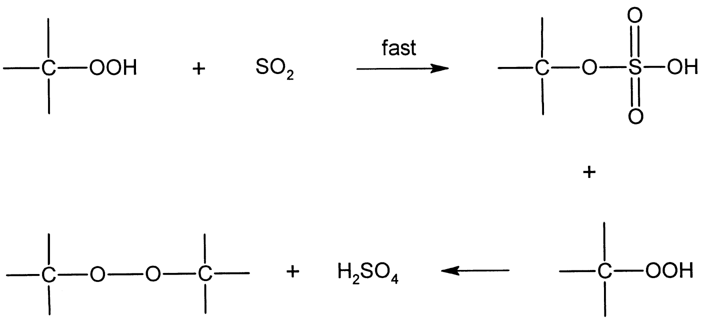


Scheme 2.

Sulfonation of PP is not successful in the measure required. There is always formed, in addition to a sulfonic group, unsaturated PP chain (Scheme 2). This process leads practically to dehydrogenation with the formation of olefinic bonds and, ultimately to charring. The planned use of sulfonated PP as ion-exchanger is thus very limited [11].

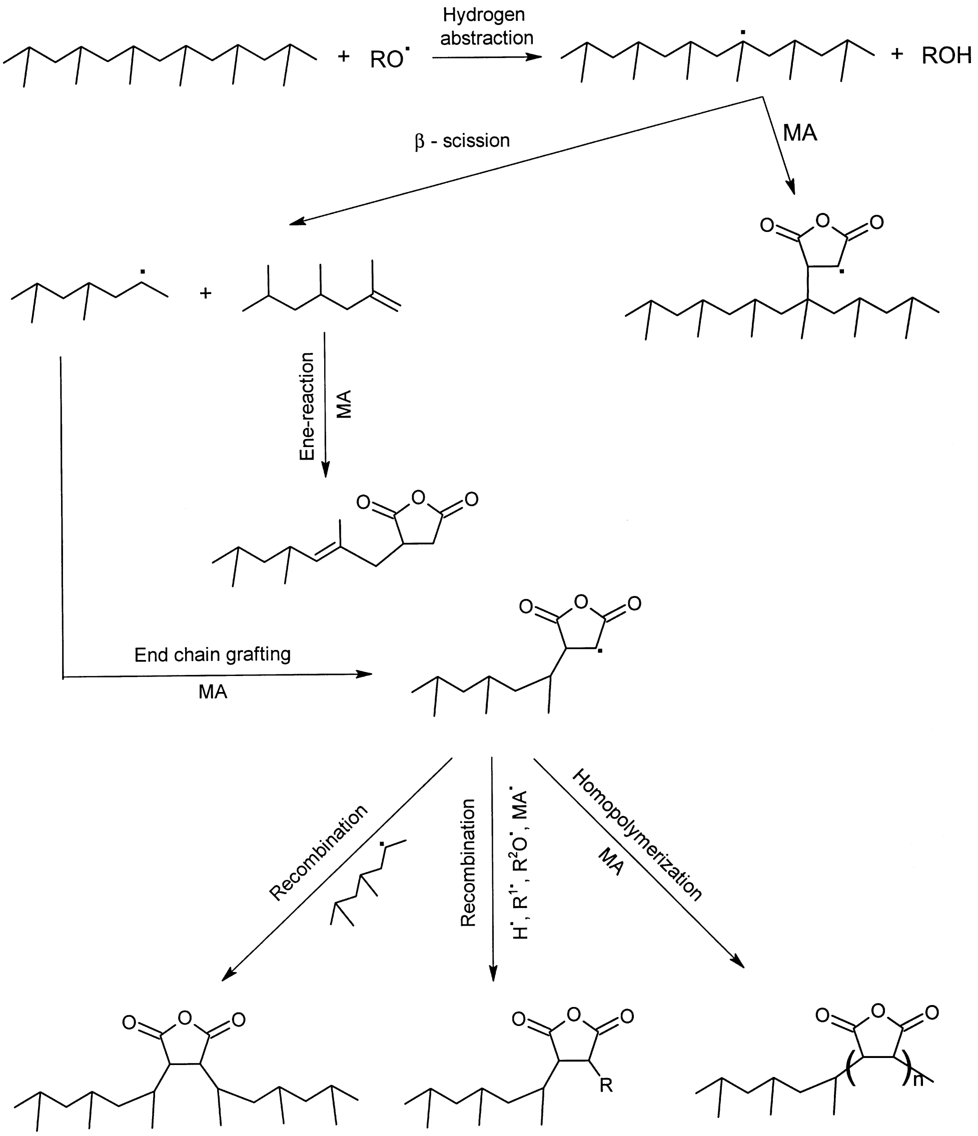
The reaction of hydroperoxidized PP with SO_2 does not yield a uniform product either. The sulfonic group formed reacts readily on a PP chain with the unchanged hydroperoxide group with the formation of the particular peroxide and with the release of sulfuric acid (Scheme 3) [11].

The binding of maleic anhydride to its polymer chains probably belongs to the most studied functionalization reactions of PP [6]. This follows from the



Scheme 3.

excellent compatibilizing properties of this modified PP for the preparation of PP blends and composites [2-5, 12]. There were published several mechanisms for this functionalization reaction. On the basis of the study of the kinetics and the reaction products of functionalization, its mechanism is currently described by the following Scheme (4) [13, 14].



Scheme 4.

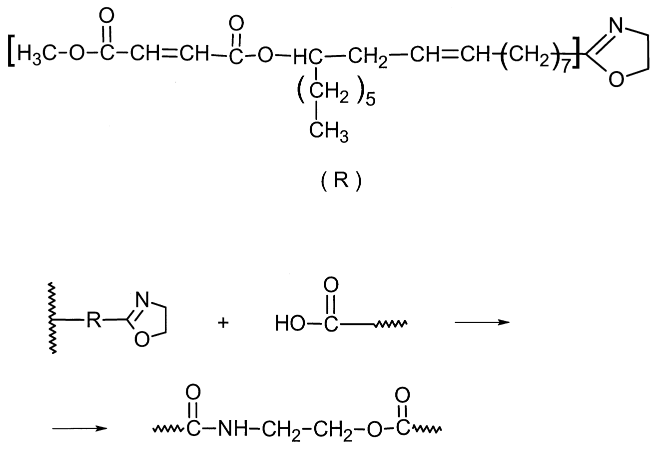
The reaction mechanism is derived from the principle of the majority of PP functionalization of the so-called chain transfer grafting using the free radical sources as initiator. This mechanism is particularly interesting (as has been experimentally confirmed) because the polymer radical being formed on the backbone of the PP chain during initiation is not responsible for direct reaction with maleic anhydride under formation of succinic radical on PP chain (see Scheme 4). The β-scission of PP chain takes place at first with the formation of end PP radical and a vinylidene group at the other end of PP chain. Both these fragments of PP chain formed are responsible for end-chain grafting of PP with maleic anhydride (MA). On the basis of the C^{13} NMR study, Heinen *et al.* [13] argue that the end succinic group has a double bond at the end of PP chain. The succinic radical formed at the end of PP chain is deactivated by one of the possible recombination reactions indicated in Scheme 4 [14]. The homopolymerization of MA is not real during grafting, mainly because the functionalization usually proceeds at the temperatures higher than the ceiling temperature of MA and because it is known that the procedure of MA homopolymerization itself under special conditions is difficult, not giving a uniform product [15, 16]. The model study of MA grafting on squalene and eicosane showed that even at the grafting temperature, i. e., 60-80°C, which is much lower than its ceiling temperature (150°C), grafting is preferred to homopolymerization [16]. Most grafts consist of single succinic anhydride units and this is ascribed to a relatively rapid intramolecular hydrogen abstraction by $P\text{-}MA^{\cdot}$ radicals.

The functionalization reaction of PP with MA can be conducted in three ways: in melt (reaction injection molding), in the solid phase, and in solution [17]. These procedures give conversions of mainly about 2 wt% of MA bound to PP. The grafting in the solid phase has certain advantages from the point of view of easier elimination of unchanged MA and about 1.5 wt% of binding of MA to PP is obtained [18-20]. MA-modified PP has been used longer in the reinforcement of glass of carbon fibers in PP. Recently, it has been used in the preparation of PP blends with polar polymers (PP-PET, PP-PAm), PP composites with inorganic fillers, and multilayer systems. Maleinated PP forms a very effective interface between the PP phase and the polar component of the system. It is strongly reflected in an increase of tensile strength, stiffness, and other mechanical properties. For example, isotactic PP grafted with MA was used as an adhesive bonding the cold-rolled steel sheets for the correlation of its bondability. It was found that the maximum adhesive strength 159 kg/cm^2 was obtained from a degree of grafting 0.217% [21]. In the case of the preparation of blends from PP and polar polymers, the reaction of succinic anhydride group bound to PP is used for direct spontaneous reaction between maleinated PP with end -OH groups in the case of polyester and with -NH- groups in the case polyamide 6 (PA6). In both cases, the covalent bond is formed between PP and PA6 chains, which has a positive effect on the mechanical properties of the mixture thus prepared - this way is also denoted as reactive extrusion [22].

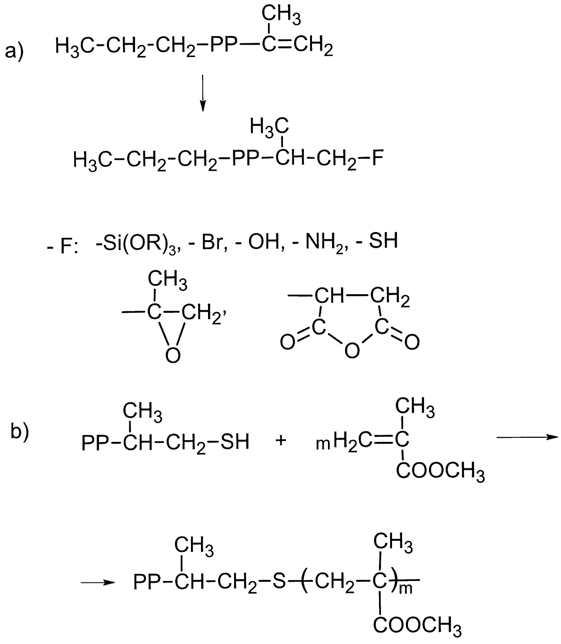
Another significant way of the functionalization of PP is the binding of oxazoline monomer groups e.g., in the form of ricinoxazoline maleinate [23]. The role of the relatively large ricino-maleate group is not only to apply at least one of the double bonds for binding to PP by the so-called "chain transfer" grafting (see Part Grafting of PP), but also to raise the boiling point and/or to lower the pressure of partial vapors of the monomer used at the reaction temperature.

Oxazoline group is known to react spontaneously with free carboxylic group which useful for the preparation of a mixture of PP with polar polymers or polymers of carboxylic groups (see Scheme 5) [23]. Great interest in the principle of the spontaneous reaction is documented by a number of references [24].

The functionalization of PP by the method of chain-transfer grafting has, however, also some disadvantages, e.g. a relatively lower reaction efficiency which often leads to PP degradation. A certain solution to these problems is the introduction of vinylidene groups into PP as early as during its preparation; this can be solved by using a Ziegler-Natta catalyst during the polymerization of



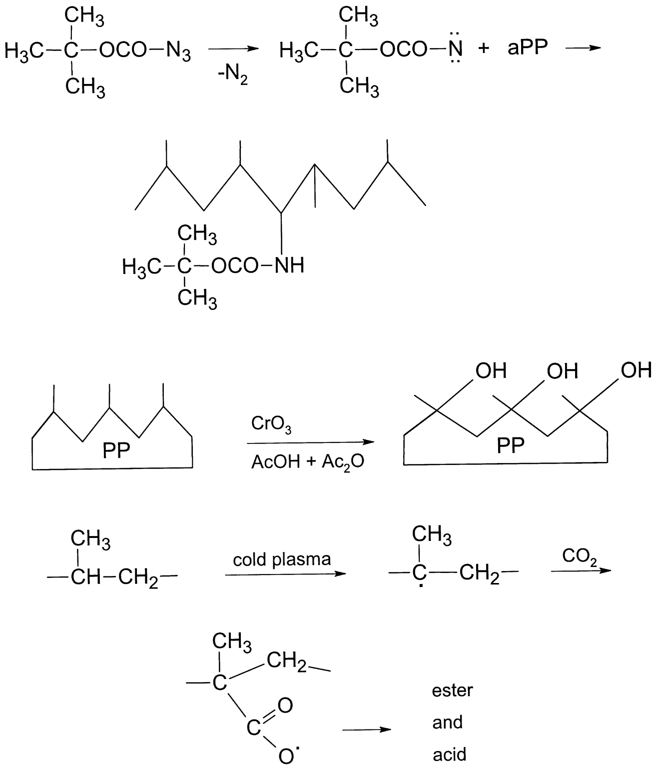
Scheme 5.



Scheme 6.

propene. It is then easy to bind various functional groups to he chain end such a PP type, e.g. -Si(OR)$_3$, -Br, -OH, NH$_2$, -SH, epoxide group but also the often required MA group [9, 24] (Scheme 6). The properly functionalized PP can also be used for PP grafting with various vinyl monomers. For instance, an anhydride-terminated PP was produced using a Lewis acid-catalyzed Alder Ene reaction. The MA incorporation onto the polymer was terminally positioned [25]. Anhydride-terminated PP is used e.g., for reactive blending of PP with polyamide 6, anhydride groups react with the amine-terminated polyamide 6 to yield polypropylene-block-polyamide 6 *in situ*. Such block copolymers are efficient dispersing agents [26]. In this way of functionalization and grafting of PP, there is undoubtedly expected a wider practical use from the viewpoint of both simplicity and the efficiency of this process.

Other reactions of PP functionalization which seem to be significant more from the perspective of getting to know rather than the near outlooks of their practical application are as follows.



Scheme 7.

A carbamate group can be bound to PP chain under the effect of the decomposition of azides, e.g. butylazoidoformate. Nitrene being formed during decomposition is able to insert into the C-H bond (Scheme 7) of PP chain. But the successfulness of this reaction is only about 30%; it is chiefly due to the fact that the greater part of azide is decomposed by radical mechanism [27].

A very successful procedure of the catalytic hydroxylation of PP surfaces under the effect of a CrO_3 mixture, a mixture of acetic acid and its anhydride was worked out; it increases the polarity of the PP surface to such an extent that the technically required adhesion to other polar surfaces is reached (Scheme 7 [28].

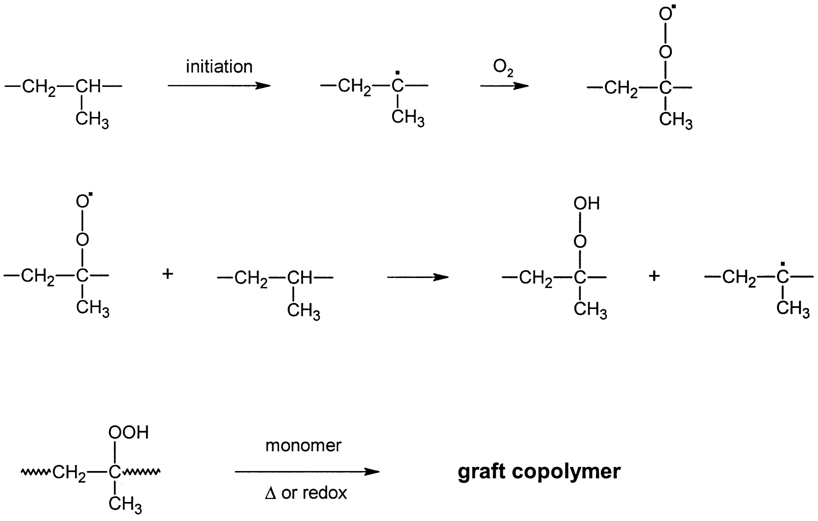
Cold plasma can be useful for an efficient modification of PP surfaces. In the presence of gas, CO_2 carboxylic or ester group can be bound to PP chains (Scheme 7).

B. Grafting of Polypropylene

The grafting of PP also belongs to the methods with similar aims-to insert the polar polymer chains, into the PP chains and thus to improve its compatibility with polar polymers or polar inorganic or organic fillers.

The development of these methods began shortly after launching the production of PP towards the end of the 1950s and at the beginning of the 1960s.

One of the first wider used grafting procedures was the method based on the principle of hydroperoxidized PP as an intermediate stage of grafting reaction itself. It solved the problem of the creation of a reactive site on PP chain. This reaction principle was also developed in several institutions [10, 29-32]. Hydroperoxidized PP, which is actually the product of PP oxidation, can be obtained in several ways. Ozonolysis of PP belonged to the first of them and was introduced by G. Natta and co-workers [29]. It represents a very efficient hydroperoxidization. Ozonolysis leads, however, to a considerable reduction of the molecular weight of PP, at 30°C it is even several times lower [30]. Hydroperoxidization of PP can also be carried out by using a cationic surfactant and potassium persulfate to achieve melting and initiate oxidation [31]. The oxidation reaction of PP can further be initiated by thermal decomposition of radical initiators, by UV or gamma radiation (Scheme 8).

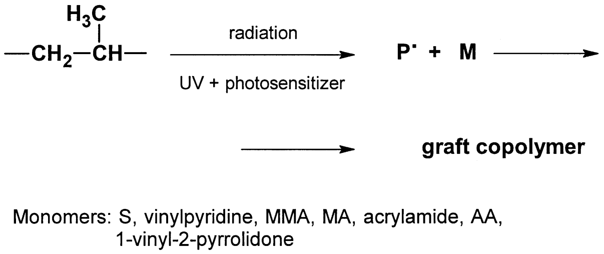


Scheme 8.

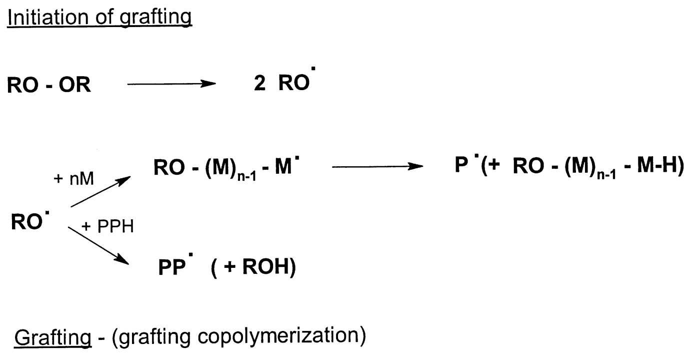
The grafting of hydroperoxidized PP can then be launched in the presence of vinyl monomer by adding a redox catalyst (e.g. ferric acetylacetonate or ferrous sulfate [32]) but also by the thermal decomposition of hydroperoxide [33]. The reaction can be done in an aqueous slurry (e.g. vinylpyridine, acrylamide) but also in a monomer slurry (e.g. S, MMA).

The PP grafting can also be carried out under direct irradiation (gamma or UV in the presence of a photosensitizer) of the polymer in the presence of a monomer, like styrene, vinylpyridine, MMA, MA, acrylamide, AA, 1-vinyl-2-pyrrolidone (Scheme 9). The presence of small amounts of polar solvents in the irradiated polymer was found to have a positive effect on grafting efficiency. This is explained by the effect of the polar solvent on the increase in the entanglements and by a lowering of the termination rate constants for propagating polymer radicals [34]. Radiation grafting is successfully used for the modification of the surface of PP products, e.g., for the grafting of PP fibers with methacrylic acid, acrylonitrile and vinyl acetate to increase the moisture content and to achieve the dyeing of grafted fibers [35]. Acrylic acid-modified PP fibers have the advantage of a softer hand and higher extension before breaking, but the disadvantage of a lower breaking strength [36]. UV radiation in the presence of benzoin ethyl ether as photoinitiator was used at grafting of 2-hydroxy-ethyl-methylacrylate onto PP [37]. Also, benzophenone was an efficient photoinitiator for photografting of PP film with acrylamide [38].

The grafting of PP initiated by thermal decomposition of radical initiator is called chain transfer grafting. This name denotes the principle of the method consisting in the transfer of the initiating center from the radical of the initiator (but it usually also proceeds by transfer from the propagating radical of the polymerizing monomer) onto the PP chain (Scheme 10). The radicals on the PP chain



Scheme 9.



Scheme 10.

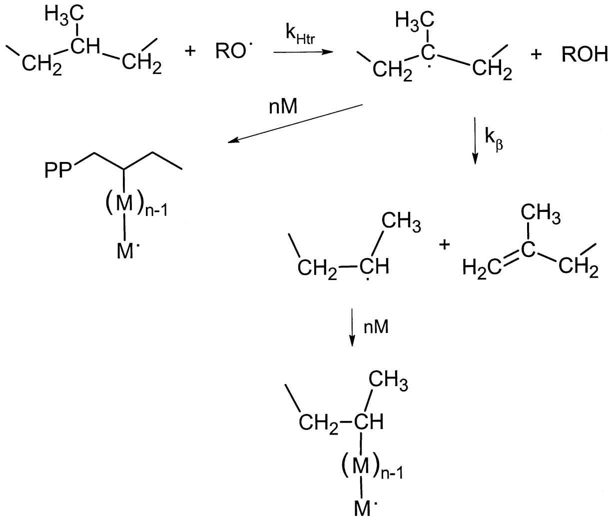
are used only partially for grafting since part of PP radicals is subjected to consecutive degradation and disproportionation. This method enables grafting of all common monomers of vinyl or vinylidene type but also polyfunctional monomers like glycidyl methacrylate [5, 39]. In view of the reaction conditions, this method of grafting can be performed in a polymer-monomer slurry, in a polymer-water slurry, PP in the form of powder or granulates, in a quasi solid state (monomer is absorbed in PP powder or granulates), and in melt. For example, in a polymer-monomer slurry PP was grafted with acrylonitrile [33]. An example of polymer-water slurry, where monomer is dissolved in the water phase, is grafting of vinyl chloride onto atactic polypropylene [40] or the grafting of butyl acrylate onto PP. This reaction mixture consists of a suspension of water and impregnated pellets with butyl acrylate [40]. Interesting results are obtained in the solid phase grafting (below melting point of PP), grafting efficiency reached being about 60% (i.e., about 60% of added monomer is grafted onto PP) [41-44] (Table 1). Another advantage of PP grafting in the solid phase is that the beta-scission of PP chains, which takes place to a considerable degree during the process in melt, can be significantly limited [44] (Scheme 11). A special type of PP grafting is cationic grafting of PP using siloxonium dication (DIC), which is able to transfer a cation to the PP chain. The PP^+ cation formed initiates the grafting of the cations of polymerizable monomers, such as e.g., tetrahydrofuran (Scheme 12). No crosslinking was observed and significant changes of molecular weight were noted [45].

TABLE 1. Grafting of PP with Various Monomers in the Solid Phase ([Monomer] =15 wt%, [Peroxide] = 37 mmol/1 kg Feed, Reaction Time = 210 minutes[a])

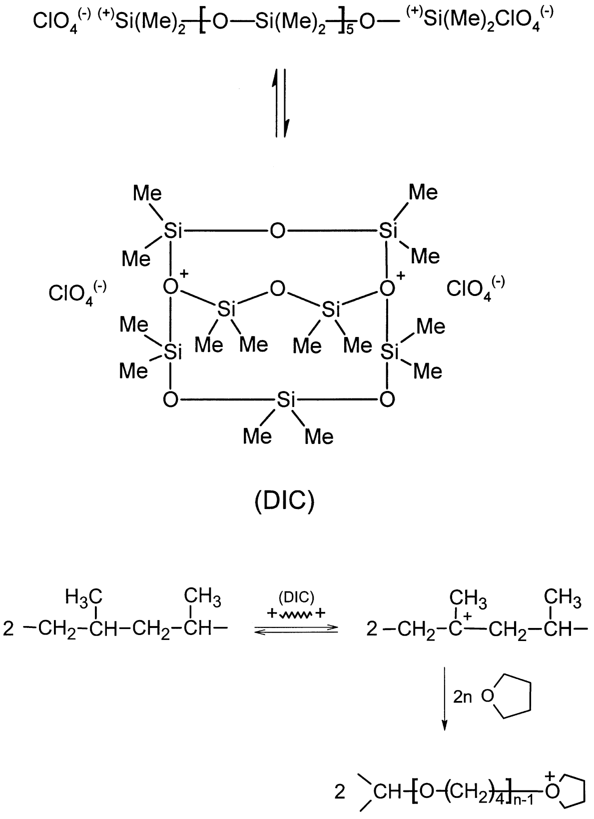
Initiator	Reaction temperature	Grafted amount of monomer		MFI
Type	[° C]	**Type**	[wt. %]	[g/10 min] b)
TBPEH	97	**BA**	10.1	0.15
TBPEH	97	**MMA**	11.3	0.39
TBEC	125	**MMA**	9.0	1.11
TBEC	125	**S**	8.2	0.07
TBIC	125	**MMA**	10.7	6.29

a) Reaction time was established from half life time of peroxides x 7
b) MFI_0 = 0.35 g/10 min
Half life time of peroxides used:

TBPEH = tert. butylperoxy ethylhexanoate $\tau_{1/2}$ = 30 min. at 97 °C
TBEC = tert. butylperoxy ethylhexylcarbonate $\tau_{1/2}$ = 30 min. at 125 °C
TBIC = tert. butylperoxy isopropylcarbonate $\tau_{1/2}$ = 30 min. at 125 °C



Scheme 11.



Scheme 12.

CONCLUSION

A series of chemical methods enabling an efficient binding of low-molecular polar functional groups and the polar polymer chains to PP has been worked out.

Radical reactions of the type of “chain transfer grafting” initiated by chemical initiators and by UV or gamma-radiation are most advantageous for PP modification.

Chemical modification of PP has two main goals: to improve compatibility of PP with polar polymers or with polar organic or inorganic fillers in the preparation of polymer blends and polymer composites and to better the processing properties of PP.

The most efficient PP compatibilizers in the preparation of PP blends are those having reactive functional groups and forming a covalent bond with the functional groups of polar polymer.

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