

## Radical reactions on polypropylene in the solid state

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### Abstract

The chemical modification initiated by radicals and the grafting of isotactic polypropylene (i-PP) in the solid state are reviewed.

The attack of a radical onto the polypropylene mainchain is led by abstraction of a hydrogen atom to a *tert*-carbon radical. The *tert*-carbon radical of the polypropylene mainchain is unstable and overcomes with the so-called  $\beta$ -scission-reaction.

During the  $\beta$ -scission-reaction, the mainchain is broken into two parts with a double bound on the one and a primary radical on the other chain end.

The resulting degradation of the molecular weight is one limitation of the radical modification of i-PP in the melt and is the main reason for the development of radical reactions in the solid state.

It is well known that the  $\beta$ -scission-reaction depends strongly on the temperature. Below 60 °C, the recombination reactions of the i-PP-radicals predominate so that a cross-linking results.

Above 60 °C, the  $\beta$ -scission-reaction increases and the molecular weight of the i-PP decreases in a logarithmic scale.

The first part of our paper deals with the mechanism of the grafting reactions of different monomers onto i-PP below the melting point of i-PP and the special processing conditions related to it.

To start the grafting at low reaction temperatures,  $\gamma$  or electron-ray scattering or special peroxides are used. As monomers different methacrylates, acrylates, acrylonitrile, styrene, divinylbenzene, maleic anhydride, butadiene, dimethylbutadiene, vinyltrimethoxysilane and other silanes to PP-graft copolymers are investigated.

The influence of the resonance stability ( $Q$ -value of the  $Q_e$ -schema) of the monomer radicals in the process will be discussed. From this knowledge, we will further discuss a special process for the long chain branching of the melting temperature of i-PP in an extruder. The properties of the resulting materials are an important part of our review. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Polypropylene; Radical reactions; Solid state; Grafting; Branching; Cross linking

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## 1. Introduction

The synthesis of polyolefine graft copolymers by reactive extrusions is excellently reviewed by Moad [1] so that it is not necessary to discuss the radical grafting reactions under melt conditions in this review.

One important basis of the possibility to modify isotactic polypropylene (i-PP) in the solid state is the morphology of the native powder from the polymerization reactor. The porous macroparticles have a diameter of 1–3  $\mu\text{m}$  inside of the holes with a summary density between 0.87 and 0.856  $\text{g}/\text{cm}^3$  in comparison with the compact material (granulate) with 0.91  $\text{g}/\text{cm}^3$ . An exact densitometric measurement of the porosity is not possible because of a closing film on the surface. The crystallinity of the i-PP in the powder particles is between 40.5% (82.7 J/g) and 43.3% (86.9 J/g) (by DSC-measurements) depending on the polymerization technology and the reaction conditions in comparison with the crystallinity after melting and re-cooling with 48.1% (98.2 J/g).

The measurements of the density and the crystallinity of the powders would be carried out by Gierlinger [2] of Borealis GmbH, Linz, Austria. The knowledge of the crystallinity is of interest for a chemical modification because there is every reason to believe that the initiator and monomers are only condensed in the holes and dissolved in the amorphous phase, so that the crystallinity can be neglected.

The second important factor for the use of the native reactor granule is their inertness. The role of oxygen in all radical reactions is well known. The native reactor granules absorb the oxygen and react in high rates to hydroperoxides and build up all the well-investigated following oxidation products. This reaction is accelerated by the residues of the polymerization-catalysts [5].

So, the best way of modifying i-PP in the solid state is to transport the powder under inert conditions directly from the polymerization reactor(s) into the modification reactor.

One of the first research groups recognizing the possibilities and chances of the i-PP powder modification was from Montecatini/Himont/Montell [3,4] in the beginning of the 1990s. They developed the 'HIVALLOY' reactor alloy process of i-PP by activating the powder by e-beam radiation or with special peroxides. 1996 PCD/Borealis Linz published [6] as the second company the results of an i-PP powder modification development into the own 'DAPLOY'-process.

Previous modification of i-PP in the solid state was done by grafting of acrylic monomers on polypropylene (PP) fibres of Russian scientists in the 'Baumwoll-Institute of Moscow' by  $\gamma$ -radiation activation at 30–60  $^{\circ}\text{C}$  and in different other research groups f.e. by ultraviolet initiation of hydroxyethylacrylate [7] at 50  $^{\circ}\text{C}$ .

The targets are changing the surface properties (adhesion, dyability) of the PP-fibres.

The third important basis for the solid state modification of i-PP is the reduction of the  $\beta$ -scission-reaction by the temperature.

In Part 4, we will demonstrate that below 60 °C the cross-linking reactions and above the degradation reactions dominate.

The grafting of monomers reduces the decrease in the molecular weight in different amounts. Lamba and co-workers [8,9] found a reduction of the molecular degradation by adding styrene (S) to a free radical grafting of glycidyl methacrylate on i-PP at >200 °C in an extruder.

To reduce the  $\beta$ -scission-reaction during the grafting in the extruder, the initiator was selected so that this main decomposition range is between 160 and 180 °C, which means before or during the melting of the i-PP crystallites [10].

A mechanochemical initiation of grafting i-PP with maleic anhydride (MAH) at 180 °C is published by Russian scientists [11].

The chemistry of free radical graft copolymerization, initiated with *t*-butoxy radicals, has been investigated using 3-methylpentane and 2,4-dimethylpentane as models for LLDPE and PP, respectively, by Dokolas et al. [17].

Mitsutani and co-workers published the development of microporous films and fibres containing finally dispersed cross-linked vinylpolymers on i-PP-powder in *n*-Hexan at 70–80 °C with AIBN as an initiator [12], without solvent at 90–95 °C and with BPO as initiator [13] and at 170–200 °C in a twin screw extruder with 1,1-bis(*t*-butylperoxy)cyclohexane as the initiator [14]. In this case, the bifunctional monomer divinylbenzene (DVB) compensates the degradation reactions by coupling reactions.

Hawker and co-workers [15] reported a synthesis of PP grafted PS by an interesting combination of a metallocene catalyst co-polymerization and the living free radical polymerization.

Mirawa et al. [16] reported the living radical grafting of S on a modified i-PP-chain. The nitroxide stable free radical polymerization leads to a controlled grafting with a uniform PS chain-length.

## 2. Diffusion and sorption

### 2.1. Morphology of PP-powder

The idea for a model, first developed by Yermakov et al. [18], contents that the catalysts consist of particles which break up fast into small parts at the beginning of the polymerization. During the polymerization reaction, the small catalyst parts grow to the microparticle, which form macroparticles by the interpenetration of the polymer chains of the microparticles.

This idea has been acknowledged by the practical results and is now the basis of the multigrain model [19,20]. Electron microscopic examinations confirm the correctness of these ideas. In Figs. 1 and 2, the multigrain structure of PP-synthesis products is demonstrated.

The size of microparticles and the extensions of the holes can be estimated from Fig. 2. The diameter of the microparticles is between ca. 0.5 and 1.0  $\mu\text{m}$ , the visible hole measures about 0.8  $\mu\text{m}$ . These dimensions are only examples and not valid for all products.

The following processes determine the transport of the components to the place of reaction:

- diffusion in porous regions of the PP-grain (macroparticle)
- mass transfer from the gas to the surface of the microparticles

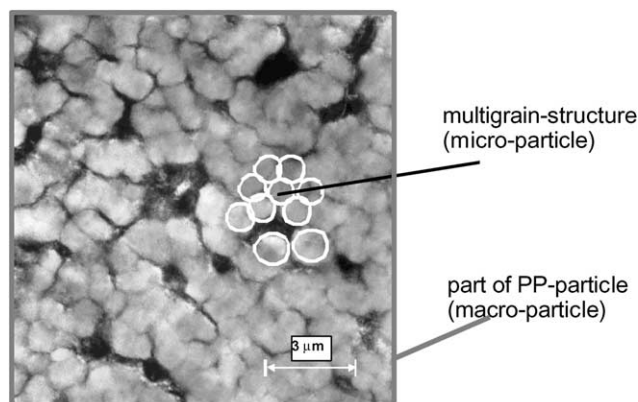


Fig. 1. Electron micrograph of PP particle (multigrainstructure).

- absorption in the amorphous phase
- diffusion in the amorphous phase.

These processes are demonstrated in Fig. 3.

The diffusion coefficient determines the rate to obtain the equilibrium conditions. The sorption determines the concentration of the modifiers in the solid phase.

Basic examinations of different authors [21] indicated that sorption and diffusion in crystalline areas can be ignored, i.e. according to the process of solid state grafting, the reactive modification can be realized only in the amorphous areas.

The influence of crystallinity on the equilibrium concentration of styrene in PP-films is demonstrated in Fig. 4.

The equilibrium concentration of styrene increases from about 16% with a crystallinity of approximately 63% (129.4 J/g) to about 35% with a crystallinity of 53% (108.7 J/g).

The experiments demonstrate that the higher the crystallinity of the i-PP the lower is the absorbed styrene. From these results, the conclusion is that the radical initiated grafting reaction of i-PP with styrene (and the other monomers) in the solid state can only take place in the amorphous regions.

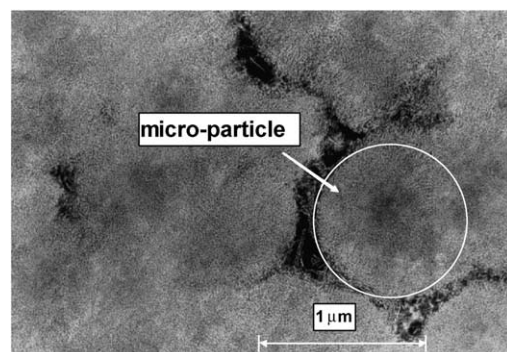


Fig. 2. PP particle (part of macroparticle and microparticle).

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