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REACTION MECHANISM TO LONG-CHAIN BRANCHED PP

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ABSTRACT

We have shown in the present article, starting from the high capacity PP´s on the market, the development of long-chain branched PP which means melt strength PP. As a basis, the radical mechanism were used to synthesize long-chain branched PP. Most known is the process at low temperature by using electron-beam-irradiation developed by Montell. It is shown that by using comonomers like styrene and vinylsiloxan also long-chain branched structures are produceable. To prove the melt strength, the melt rheology in dependence of shear rate, as well as the tensile force via velocity of the melt with the Rheotens-apparatus, are described.

INTRODUCTION

Polypropylen (PP) has quickly been promoted in the last 10 years. The amount of growth has an exceptional ratio of increase compared with other high capacity polymer materials. The trend is also being predicted by the producer and manufacturer for the coming years. The reason for this remarkable development is the constantly increasing level of properties. This was possible by new catalysts, comonomers, and chemical modifications.

Important increases could be reached concerning the modulus and the impact strength. Thus, PP made its way into the field of construction materials. On the other hand, new soft PP-polymers up to high molecular atactic and block

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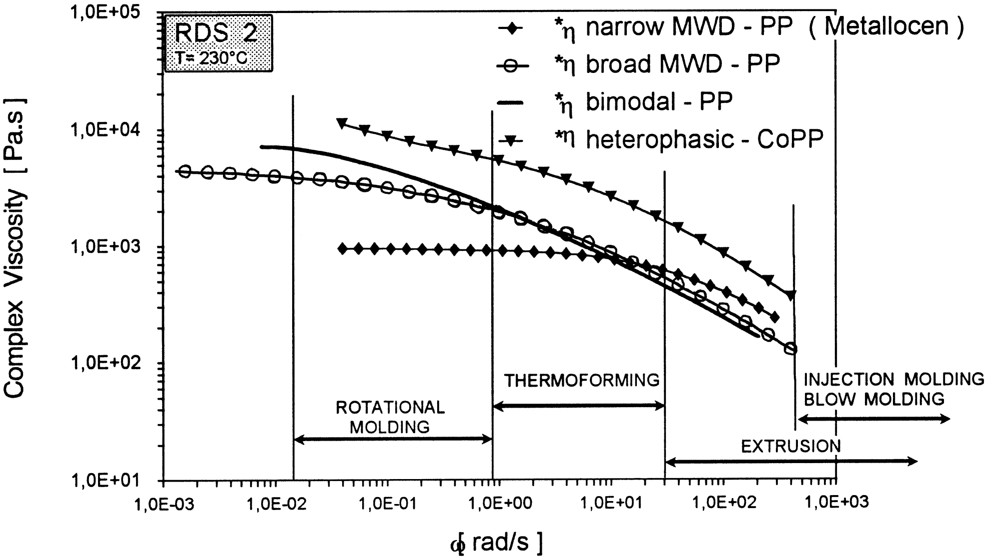


Figure 1. Melt viscosity of different PP.

atactic-isotactic super-soft properties for new market segments could be developed.

The excellent flow behavior of the melt for different processing technologies is a particular advantage of i-PP. This is being reflected in the viscosity-shear rate course (Figure 1). However, also the disadvantages of PP for special applications are documented in this course. The so-called "processing window", that means the required viscosities of the melt are in a tight field and are not sufficient for some special applications. This is especially relevant for the processing applications deep drawing, extrusion coating, fiber spinning, film blowing, and foam processing.

Basis

From experiences of the structure property relations of low density polyethylene, it can be derived that long-chain branches lead to an increase of the stiffness and extensibility of the melt. Hence, it follows the target to produce long-chain branched i-PP which means high melt strength (HMS-i-PP) as shown in Figure 2. From the various possibilities for the production, we have chosen the radical chemical modification of i-PP.

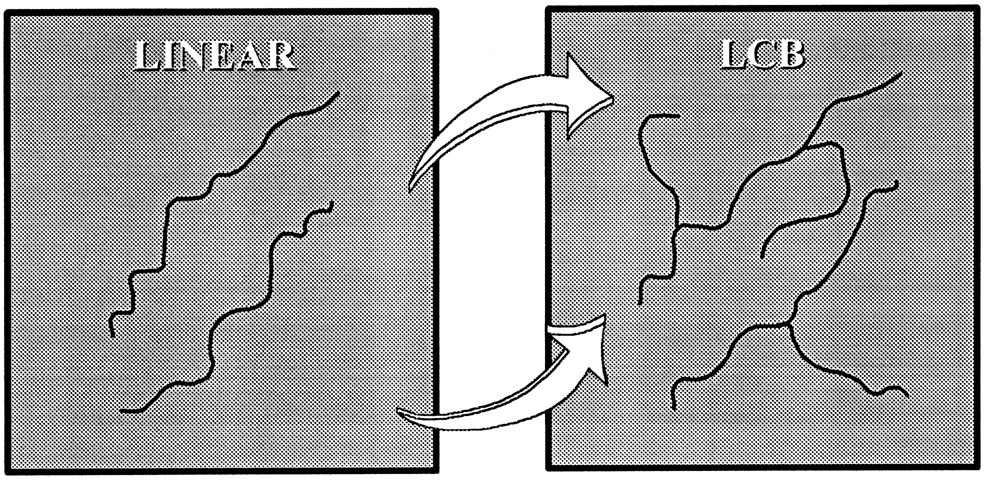
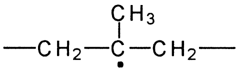
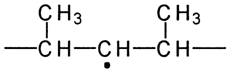


Figure 2. Creating long-chain branched PP.

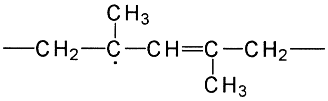
Reliable analytical measurements of radical structures are known from γ- respectively, e-irradiation of polypropylene [1-9].

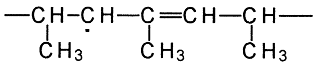
By means of EPR-spectroscopy, the alkyl-radicals


$$-CH_2-\overset{CH_3}{\underset{\bullet}{C}}-CH_2-$$
(A)


$$-\overset{CH_3}{CH}-\underset{\bullet}{CH}-\overset{CH_3}{CH}-$$
(B)

and the allyl radicals

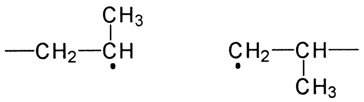

$$-CH_2-\overset{CH_3}{\underset{\bullet}{C}}-CH=\underset{CH_3}{C}-CH_2-$$
(C)



$$-\underset{CH_3}{C}H-\underset{\bullet}{C}H-\underset{CH_3}{C}=CH-\underset{CH_3}{C}H- \qquad (D)$$

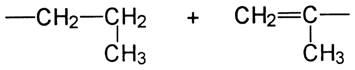
were identified.

Via γ-irradiation, also the chain scission to the chain end radicals (analogous to polyethylene [10, 11].



$$-CH_2-\overset{CH_3}{\underset{\bullet}{C}}H \qquad \underset{\bullet}{C}H_2-\underset{CH_3}{C}H- \qquad (E)$$

and via H-transfer their conversion to the saturated fragments:



$$-CH_2-\underset{CH_3}{C}H_2 \quad + \quad CH_2=\underset{CH_3}{C}-$$

are possible.

If the radical structure is caused by peroxides. it is important to choose such peroxides whose radicals are very reactive so that a H-abstraction of the PP-chain occurs. Such radicals are oxyradicals, methylradicals and phenylradicals. At the reaction of peroxides with i-PP, basically the radicals A-D can be built. A primary radical structure E can be excluded. Radical E can be identified by the β-scission reaction of the radical A.

Because of the low double bound content of the i-PP from the reactor, the radicals C and D are subordinated. Their higher content at high energy irradiations results from following reactions of H-abstractions of neighboring C-atoms. The radicals A and B differ by the level of energy, whereas radical A can also be built by H-transfer from radical B.

This is the most important cause for the fact that in kinetic analysis for the polymer radical formation of the polypropylene only the radical A could certainly be identified. These measurements were carried out at the conversion with peroxides at temperatures between 140 and 150°C by Tüdös *et al.* [12] with the help of EPR.

The kinetic measurements were carried out using Mn^{2+} standard in the cavity in order to determine the change in relative radical concentrations. The simulation of the super imposed spectra of signals of radical and Mn^{2+} standard directly gives the ratio of these signals. Thus, we can evaluate the radical concentration in arbitrary units.

TABLE 1. The Relative Concentration of "A" Radicals

Time unit	Relative radical concentration	Initiator concentration m %	Temperature °C
1	21.90	1	150
2	22.20	1	150
3	16.80	1	150
4	14.98	1	150
5	8.97	1	150
6	7.48	1	150
1	17.96	1	170
2	7.28	1	170
3	3.33	1	170

The error in determining the relative radical concentration according to reproduced experiments is about +/- 7%.

Table 1 demonstrates one example of the relative radical A-concentration at 150 and 170°C by the reaction of i-PP with the peroxide tert.butyl-perbenzoat. Time units correspond the scans of the ESR-spectra.

The mechanism of the formation of lcb is formulated in Figure 3. Basis is the β-scission of the polymer chain which follows a H-abstraction (respectively chain fracture at high energy irradiation).

The dependence of the β-scission on temperature is shown in Figure 4 [13, 14]. To build long-chain branches the chain end radical, built at the β-scission, has to be brought to a recombination at the PP-chain with the primarily built ter.-C-radical. Moreover, a bimodal distribution of the PP is the result of this reaction.

EXPERIMENTAL

Montell used a technically intelligent solution in commercial state. By meaning of an electron-beam-irradiation of i-PP in an inert atmosphere at tem-

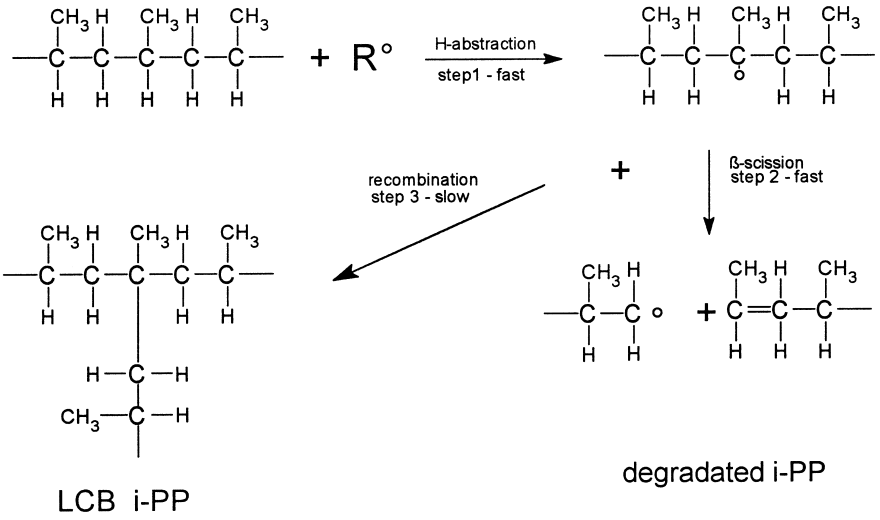


Figure 3. LCB - i-PP by radical reactions on i-PP below 80°C.

peratures below 100°C, which means in solid state, a long chain branch could be the result. An electron-beam-irradiation leads to a H-abstraction and to a fracture of the PP-chain (directly or via β-scission). The duration of life of the built radicals under the reaction conditions < 100°C is so long that the radical combination to long-chain branches (lcb) occurs, like above defined. The found lcb and

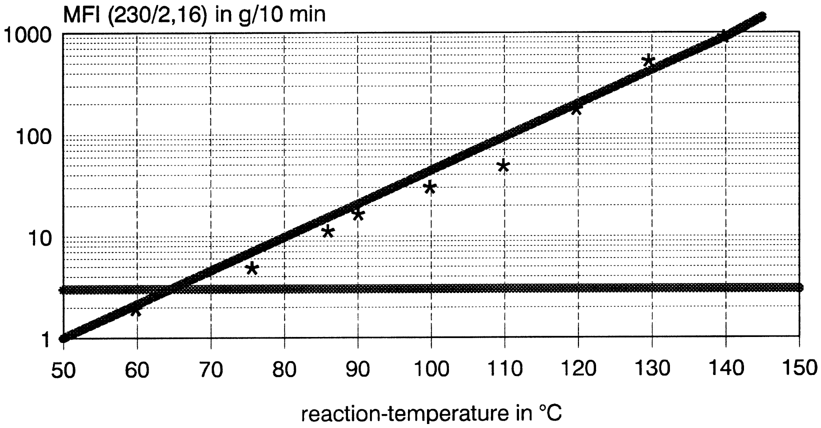
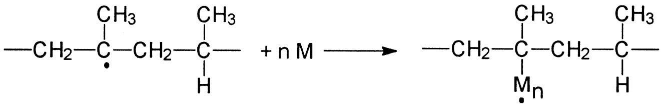


Figure 4. PP-degradation in dependence on temperature.

bimodal distribution, as well as the increased melt strength confirm the assumed reaction course.

Another way to introduce long chain branching in the i-PP molecule is the radical grafting with different monomers as well as vinyl or acrylsilanes as styrene and methylmethacrylate (MMA). The first reaction step of the reaction of a methyl,- oxy- or phenyl radical from the thermal decomposition of the peroxide-initiator.

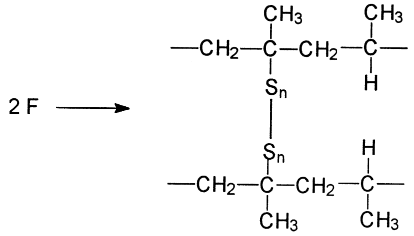
In the presence of a monomer the radical A can be stabilised against the β-scission reaction by adding a monomer to build radical F:



$$-CH_2-\overset{CH_3}{\underset{\bullet}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}- + n\,M \longrightarrow -CH_2-\overset{CH_3}{\underset{\overset{|}{\underset{\bullet}{M_n}}}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-$$

(A) (F)

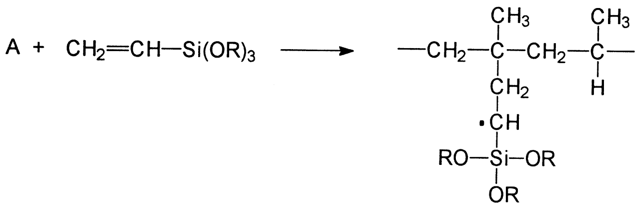
The result of the grafting of the monomers S or MMA on i-PP in the solid state that means below 150°C is a long PS or PMMA chain grafted PP with interesting properties. With S as monomer and one graft per i-PP chain the recombination termination reaction leads to a H-formed structure with styrene bounding elements between two i-PP chains.



To reduce the β-scission reaction, the monomers have to fulfilL the following conditions:

- Quick addition on the PP-chain A-radical. This supposes a good solubility of the monomers and a quick diffusion in the amorphous PP-phase.
- Low radical transfer from the monomer radical to the PP-chain.
- Preferred termination mechanism by the recombination reaction.

Another mechanism to a lcb-PP follows from the reaction of radical A with vinyl-trimethoxysilan. Vinlysilanes do not homopolymerize under the grafting conditions on PP-radicals in the solid state. The reaction product of radical A with the vinylsiloxane is:



The siloxanegroups (-SiOR) are easy to hydrolyze with water to Si-OH-groups and they react in the presence of a catalyst with the Si-OH-groups of the neighbor i-PP molecule to -Si-O-Si-bridges. The consequence of the reaction is at low siloxan- concentrations a long chain branching and at high siloxan concentrations a crosslinking of the i-PP macromolecules.

RESULTS AND DISCUSSION

In the course of the viscosity. as well as G' and G" via shear rate, the increase of the lcb in an important increase of the viscosity together with a decreasing shear rate is shown in Figure 5. After extrusion, we found a dramatic

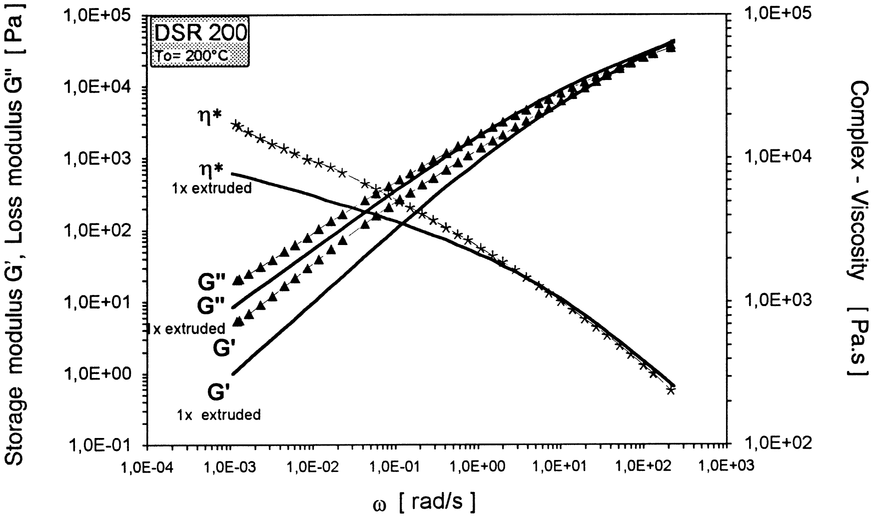


Figure 5. Dynamical rheology of HMS-PP.

decrease of complex viscosity, as well as G' and G". The reason for that is the solution of the entanglements during the processing technology by the shearing energy of the melt. This has been proved by solution of the sheared material and later on of the precipitation. Thus, we can get back the high melt strength of the material. That means the macro molecules are able to entangle again in the solution and we can get the structure of the original HMS-material.

The influence of the lcb can be proved more essentially by means of the so-called rheotens-method. The experimental set-up used for the laboratory evaluation of the melt strength consisted of a Göttfert single-screw laboratory extruder equipped with a capillary die and a Rheotens apparatus as take-up device. With this set-up the polypropylenes are stretched in uniaxial extension. The required tensile force is recorded as a function of the take-up speed of the wheels of the Rheotens. The maximum tensile force attained during the test is defined as the melt strength.

The scheme of the capillary and a Rheotens-apparatus are shown in Figure 6. The results of measurements of our standard PP-materials with a melt index of 2,4. We found low force and low drawabilities. In comparison to that LDPE demonstrates an increasing of the strength with the drawability. It is well known that, from all polyolefins, only LDPE is long chain-branched. In compar-

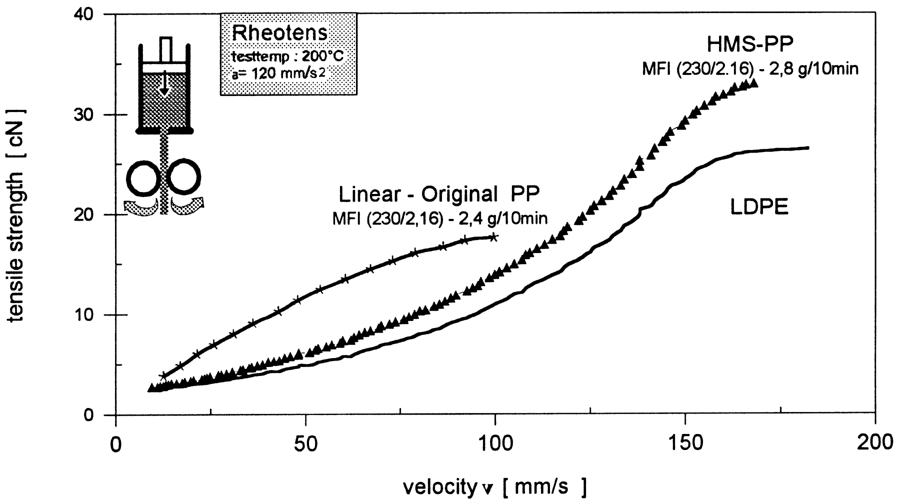
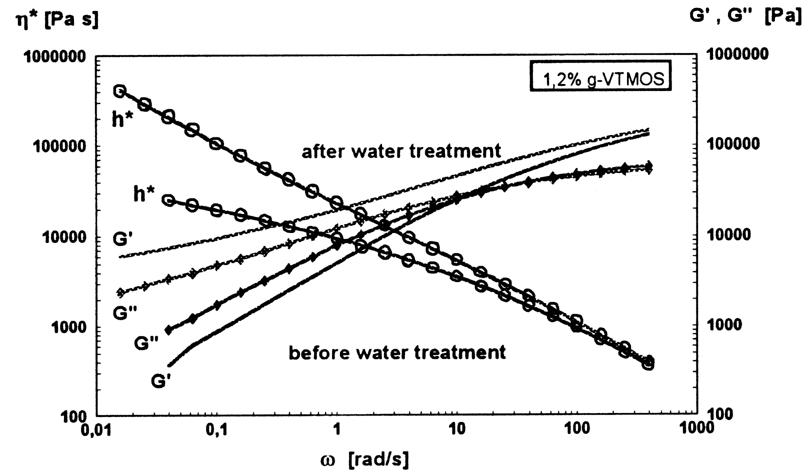


Figure 6. Melt Strength of HMS-PP.



RDS II, 230 °C, frequ. sweep, 5% strain, nitrogen, G306, G306A

Figure 7. Daploy RM - Cone-plate rheology of modified PP.

ison to LDPE we found in our modified PP the same melt strength as in LDPE so that we are sure that the discussed long chain-branching mechanism has taken place.

The increase of the melt strength up to partial branches is also possible with i-PP´s, grafted with silanes, by hydrolitic coupling. Figure 7 shows the extreme course of the viscosity and of G' as well as G" with a decreasing shear rate at a with 1,2% vinyltrimethoxysilan grafted and following in the melt hydrolytic crosslinked i-PP.

CONCLUSION

The experimental analysis of the radically initiated degradation of PP has shown that in dependence of the temperature an equilibrium arises between the β-scission and the recombination of the built radicals. At low temperatures (60-80°C) long-chain branched (lcb), melt strength products are being built which show a great technical interest. This explains the reactions which are going on at the Montell-process including the electron beams. Under these conditions long-chain branched PP can be produced. By means of own examinations it could be shown that by using special monomers as styrene, the β-scission could be prevented also by higher temperatures (up to 180°C). As mechanism, the recombination of the styrene radicals could be proved.

The terms for the course of this reaction are discussed. Also by using vinylsiloxanes and a following hydrolysis long-chain branched PP can be produced.

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