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CHALLENGES IN POLYPROPYLENE BY CHEMICAL MODIFICATION

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Abstract: Radical reactions of i-PP are a well known technical process for the chemical degradation to increase the flowability of the i-PP melt. By decreasing the temperature and increasing the life time of the PP-radicals, a process to synthesize long chain branched i-PP, was developed. The long chain branched-i-PP allows to introduce the i-PP in processing technologies as blow moulding film technology or foaming technology. The mechanism will be discussed.

The radical grafting of Polypropylene (PP) becomes more important for the developing of PP-alloys with extended properties. Methylmethacrylate and styrene were polymerized and grafted in PP at low temperatures in solid state. Grafting and polymerizing in solid state means solving the monomers in the PP-powder dircetly from the reactor without contacting with oxygen (air). The reaction is started by the thermal decomposition of a peroxide. The reactivity of the primary radicals from the peroxide and the transfer reactions of the polymer radical of the PMMA or PS influences the amount of the grafted polymer. The solubility of the monomers and the peroxide in the amorphous i-PP-phase was measured. The grafting yield and the dispersity of the second polymer depends on the solubility and dispersity of peroxide and monomers in the PP-powder particles.

INTRODUCTION

The topic presented in the lecture is the radical modifying of i-PP in two directions. One is the developing of a high melt strength i-PP that means a long chain branched (lcb-i-PP) for widening the processing window. The second direction is the polymerization and grafting of styrene (S) and methylmethacrylate (MMA) on i-PP to form special PP-alloys. Therefore, we compare the polymerization kinetics of the two monomers as well as the morphologies and properties of both PP-alloys.

The radical modification of PP in the melt disturbes the original molecular structure by polymer degradation. The polymer degradation of i-PP, in an extruder is a commercial practised process to reduce the molecular weight of i-PP which was first developed by PCD. The degradation proceeds as a β-scission reaction which is

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enormously influenced by the temperature. At temperatures below 100°C the β-scission can be neglected. In presence of monomers the β-scission is further reduced so that radical reactions up to 150°C are possible without a degradation of the PP chain, influencing the properties importantly.

Radical modification, polymerization and grafting of monomers onto PP below 150°C means chemical reactions in the solid PP. In practice the radical initiator and the monomer are absorbed in the solid PP-grains from the polymerization reactor.

THEORETICAL BACKGROUND

Basis for understanding the process are the fundamentals of diffusion and sorption of the monomers and the initiator in the PP-powder grains. The REM-image of spherical powder particles (grains) directly from the polymerization reactor (Montell Spheripol Process) is shown in FIGURE 1.

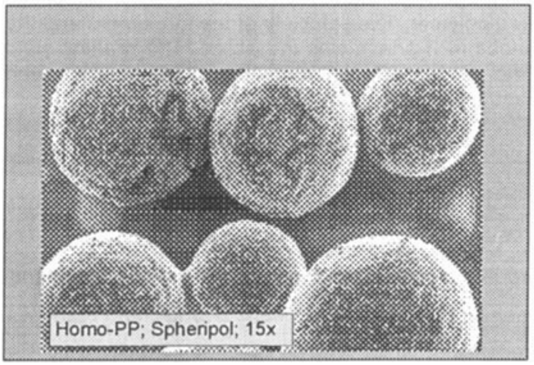


FIGURE 1: Raster electron microscope image of spheripol PP, magnification 15x

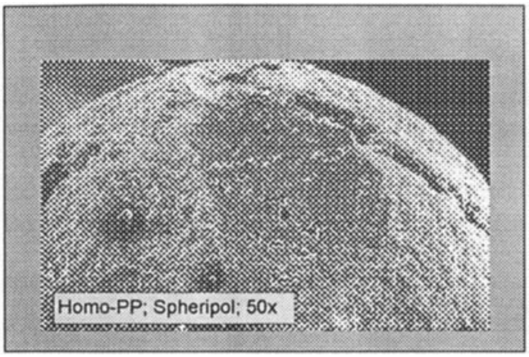


FIGURE 2: Raster electron microscope image of spheripol PP, magnification 50x

The inner porous structure can be detected in FIGURE 2 as surface of a radial cut through the particle. The particle substructure is the basis of the inner porous structure and the solved monomer and initiator in the amorphous phase are schematically demonstrated in FIGURE 3.

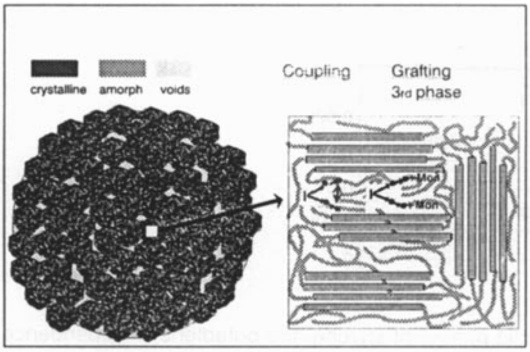


FIGURE 3: Daploy RM - the process

Diffusion rates and sorption measurements in comparison to theoretical calculations for styrene and butadiene have been presented in previous papers /Ref. 1,2/. The results demonstrate that the diffusion coefficient is reverse proportional to the

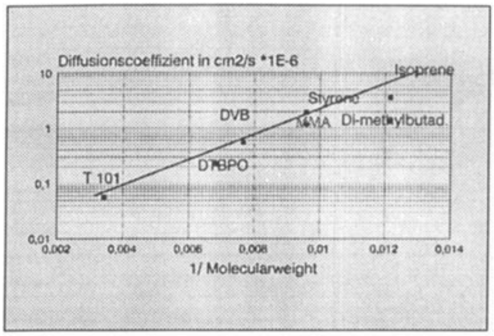


FIGURE 4: Relation between diffusion coefficient and molecular weight (temperature = 100 °C)

molecular weight of the absorbent. FIGURE 4 shows that the diffusion coefficient of MMA is comparable with Styrene (they nearly have the same molecular weight). The absorbed weight content of styrene and butadiene in dependence on time at 100 °C, (absorption isotherms) are presented in FIGURE 5.

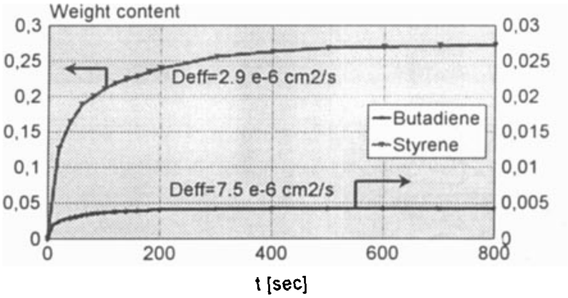


FIGURE 5: Weight content (in solid phase) of styrene and butadiene in dependence on time (temperature = 100°C)

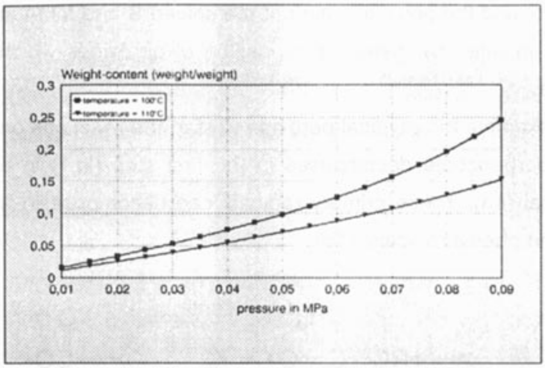


FIGURE 6: Weight content of MMA (weight/weight/) in solid phase in dependence on pressure

FIGURE 6 shows the weight content of MMA in PP at 100 and 110 °C in dependence on pressure. The intake of both monomers, (styrene and MMA) absorbed at 100 °C and 0,1 MPa in PP is more than 25 %. The crystallinity of the i-PP influences the absorption enormously (FIGURE 7) whereby the absorbed styrene is reduced with increased crystallinity. We assume that the monomer is only solved in the amorphous phase of the i-PP and in the pores and holes between the subgrains.

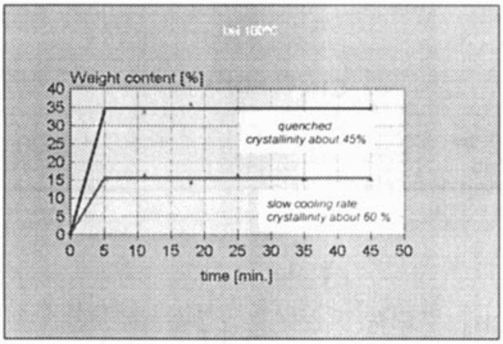
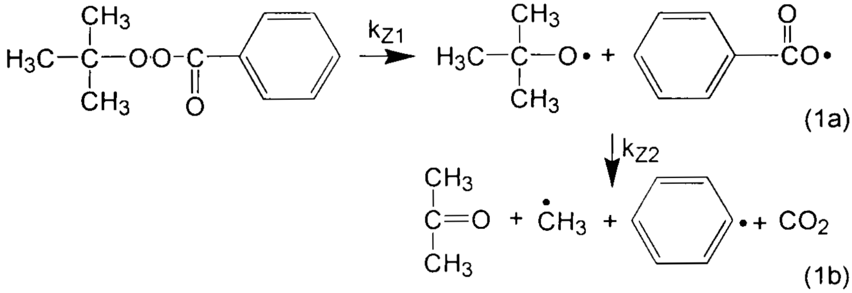


FIGURE 7: Weight content of styrene in dependence on time (in films with different crystallinity), temperature = 100°C

The radical reactions of the i-PP and the polymerization of the solved S and MMA in the i-PP-powder particles was initiated by thermal composition of peroxides which are absorbed in the i-PP-phase.

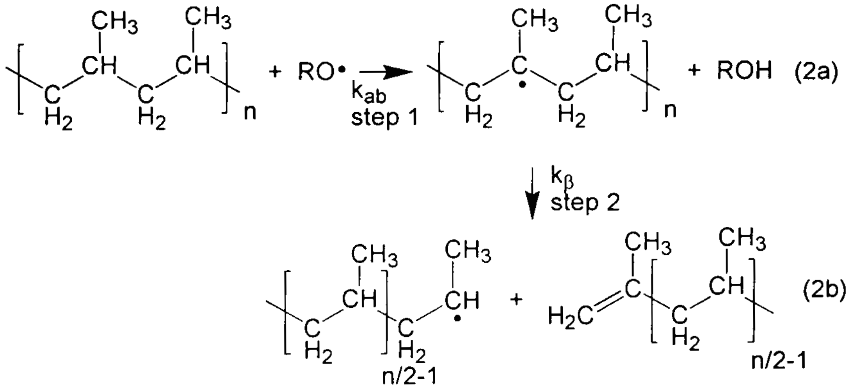
Tert. butylperbenzoate is one example for a typical peroxide to start the reactions on the PP-mainchain. Tert. butylperbenzoate decomposes in the first step (kz1) in a tertbutoxy- and a carboxyradical (1a). These primary radicals can decompose in a second step (kz2) in methyl- and phenyl radicals: (1b)



(1a)

(1b)

The alkyloxy-, phenyl or methylradicals have a high proton acceptor activity. These radicals abstract hydrogen atoms from the i-PP-mainchain, the first step of the reaction (k_{ab}):



(2a)

(2b)

The PP-mainchain radical after step 1 (2a) is a secondary or tertiary carbon radical (depending on the temperature). The second step (2b), is the so-called β-scission reaction. The β-scission is a decomposition reaction of the PP-mainchain radical into two shorter macromolecules. One of the products is a chain-end radical and the other one has a double bound on the end-group.

We have measured the intensity of PP degradation by radical reactions in dependence on temperature using the method of melt flow index (MFI) in FIGURE 8.

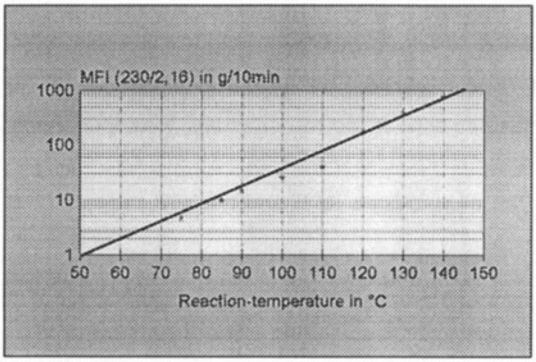
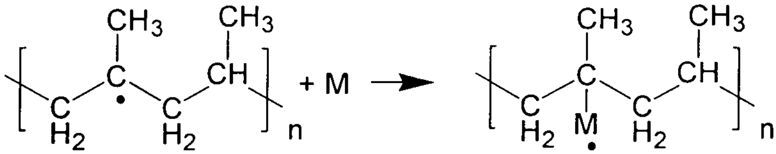


FIGURE 8: PP-Degradation in dependence on temperature

The original i-PP had a melt index of 0,3. The experiments at different temperatures revealed two opposite effects. At temperatures below 60°C the melt index was decreased in presence of radicals. This means an increasing of the molecular weight or a crosslinking reaction occured. By increasing the reaction temperature above 60°C the MFI was increased as a logarithmical function of temperature.

In presence of monomers as S or MMA below 140 °C it was found that the PP-degradation can be excluded. The reason is that by adding a monomer (M) to the mainchain-radical the β-scission reaction (2b) is enormously reduced (3):

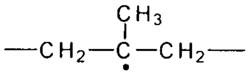


(3)

Thus, radical reactions on i-PP in presence of monomers can be carried out until 140°C without changes of MFI. That means the original properties of the PP will not be influenced negatively.

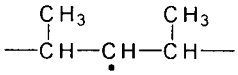
In the case of the initiation of radical reactions of i-PP with electron-beam or γ-irradiation reliable analytical mesurements of radical structures were performed. /Ref. 3-11/

By means of EPR-spectroscopy the alkyl-radicals A, B and the allyl radicals C, D were identified.



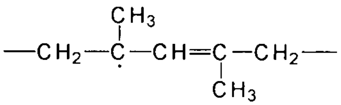
$$-CH_2-\underset{\bullet}{\overset{CH_3}{\overset{|}{C}}}-CH_2-$$

(A)



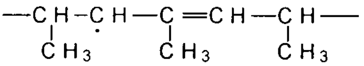
$$-\overset{CH_3}{\overset{|}{C}H}-\underset{\bullet}{C}H-\overset{CH_3}{\overset{|}{C}H}-$$

(B)



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

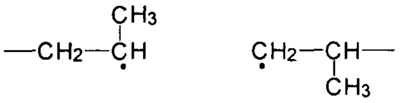
(C)



$$-\underset{CH_3}{\underset{|}{C}H}-\underset{\bullet}{C}H-\underset{CH_3}{\underset{|}{C}}=CH-\underset{CH_3}{\underset{|}{C}H}-$$

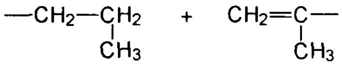
(D)

Irradiation of PP leads to H-abstraction and chain scission (analogous to polyethylen /Ref. 12,13/). Due to chain scission of PP by γ-irradiation secondary and primary alkyl radicals occure (E).



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

Via H-transfer is the conversion of radicals (E) to the saturated fragments (F) possible:



$$-CH_2-\underset{\underset{CH_3}{|}}{C}H_2 \quad + \quad CH_2=\underset{\underset{CH_3}{|}}{C}- \qquad (F)$$

For the reaction of PP with peroxide we predict that only the radical A was certainly built because the low double bound content of i-PP from the reactor. Radicals C and D are subordinated and the radical B can be converted by H-transfer reactions to the more stable radical A. To confirm these theoretical assumptions the reaction products by the conversion of peroxide between 140 and 150 °C were measured by Tüdös et. al /Ref. 14/. 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. The error in determining the relative radical concentration according to reproduced experiments is about +/- 7 %. TABLE 1 demonstrates one example of the relativ radical A-concentration at 150 and 170 °C by the reaction of i-PP with the peroxide tert.butyl-perbenzoat. (Time units correspond with the scans of the ESR-spectra.)

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

TABLE 1: The relative concentration of „A" radicals in PP according ESR measurements

With these measurements only the radical A could be identified so that our prediction was confirmed.

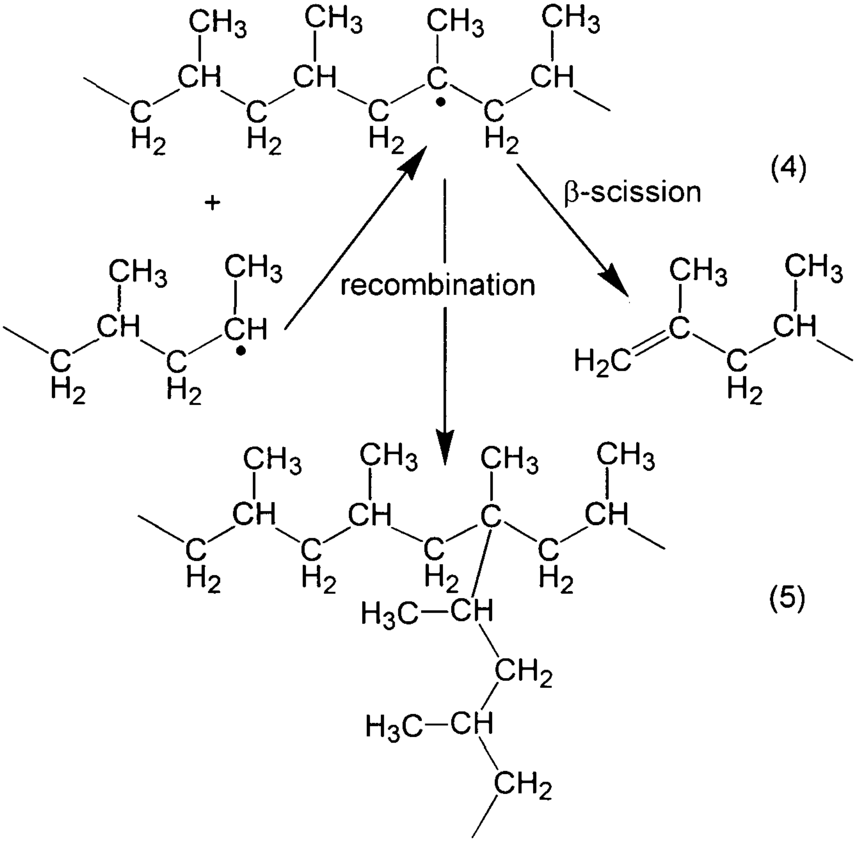
EXPERIMENTAL PART

The experimental investigations were carried out in a laborautoclave at 333 to 383 K. The PP-powder with a melt index of 0,3 g/10min directly from the reactor without contacting by air was mixed with the initiator and the monomer at 298 K and stirred over a time of 2-3h. 3,7x 10^{-3} mol/10g. Tert.-butylperbenzoate (TBPB) was used as initiator. The reactions were started by rising the temperature with an oil bath during mixing. The conversion and the grafting yield of the monomers were measured by sampling with a specially prepared sampler under inert conditions. The reactions of the samples were stopped by introducing the powder into methanolic solutions of 0,1g/100 ml hydrochinon. The grafted amounts of PS and PMMA were determined using consecutive extraction-precipitation procedures with xylene and aceton. The crude product was dissolved, samples were separated by filtering and drying in vacuum at 60 °C for 24 hours. The conversion degree and the grafting yield were gravimetrically determined.

DISCUSSION OF THE RESULTS

1) lcb-PP:

Montell is using a technically intelligent process in commercial state for production of long chain branched PP (lcb-PP). By using an electron-beam-irradiation of i-PP in an inert atmosphere at temperatures below 100 °C, which means in solid state, a long chain branched PP is received. The 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 radicals under the reaction conditions < 100 °C is so long that the radical combination to long-chain branches (lcb) can occur (4) and (5).



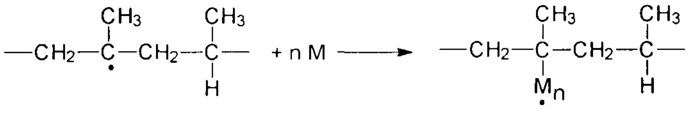
(4)

(5)

The found dependency of melt viscosity from shear rate and the bimodal distribution molecular weight combined with the increased melt strength confirm the assumed reaction course.

Another way to introduce long chain branching in i-PP molecules is the radical *grafting with different monomers* (S, MMA) as well as vinyl- or acrylsilanes. The first step of the reaction is a H-abstraction by methyl,- oxy- or phenyl radicals from the PP-backbone (A).

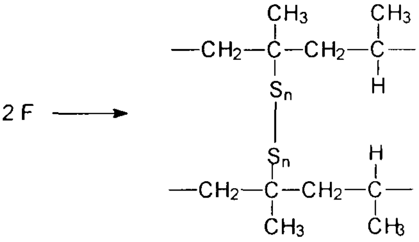
In presence of a monomer radical A can be stabilized against β-scission reaction by adding a monomer to build radical F: (6)



$$-CH_2-\overset{CH_3}{\underset{\bullet}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}- \;+\; n\,M \longrightarrow -CH_2-\overset{CH_3}{\underset{\underset{\bullet}{M_n}}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}- \qquad (6)$$

(A) (F)

The result of the grafting in the solid state below 150 °C is a long PS or PMMA chain grafted PP with interesting properties. With S as monomer and with 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. (7)

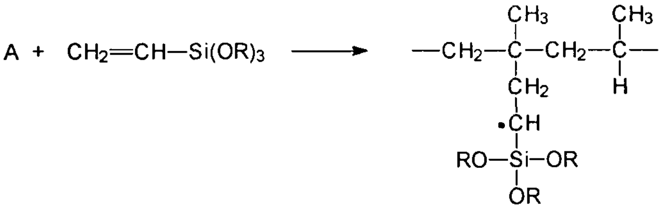


$$2\,F \longrightarrow \begin{array}{l} -CH_2-\overset{CH_3}{\underset{S_n}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}- \\ \quad\quad\quad\;\; | \\ -CH_2-\overset{S_n}{\underset{CH_3}{C}}-CH_2-\overset{H}{\underset{CH_3}{C}}- \end{array} \qquad (7)$$

To reduce the β*-scission reaction of PP the monomers have to fullfill the following* conditions:

1. Quick addition on the PP-chain A-radical, this needs a good solubility of the monomers and a quick diffusion inside the amorphous PP-phase.
2. Low radical transfer rate from the monomer radical to the PP-chain.
3. Preferred termination mechanism by the recombination reaction.

Another mechanism to a lcb-PP follows from the reaction of radical A with vinyltrimethoxysilan (8). Vinlysilanes do not homopolymerise under grafting conditions on PP-radicals in the solid state. The reaction product of radical A with the vinylsiloxane is:



$$\mathrm{A} + \mathrm{CH_2{=}CH{-}Si(OR)_3} \longrightarrow \mathrm{{-}CH_2{-}\overset{CH_3}{\underset{CH_2{-}\bullet CH{-}Si(OR)_3}{C}}{-}CH_2{-}\overset{CH_3}{\underset{H}{C}}{-}} \qquad (8)$$

The siloxanegroups (-SiOR) are easy to hydrolyse with water to Si-OH-groups and able to react in presence of a catalyst with the Si-OR-groups of the neighbour 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 reaction of i-PP macromolecules.

In the viscosity curve (η^*(a)) as well as the frequency depence of the dynamic moduli (G', G" (w)) the influence of lcb is seen as an increased shear thinning and higher melt elasticity at lower frequencies (FIGURE 9).

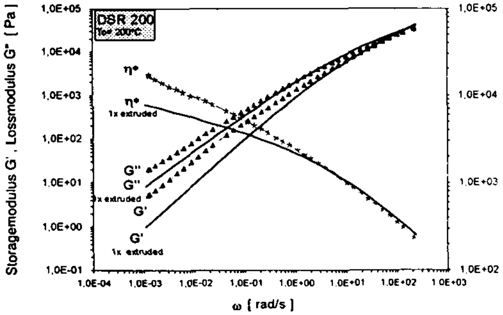


FIGURE 9: Dynamical rheology of HMS-PP

The influence of the lcb on PP processing behaviour can be characterised better by the so-called rheotens-method. The experimental set-up used for the laboratory evaluation of the melt strength consistes 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 polypropylene melt is stretched in uniaxial extension. The required tensile force is recorded as a function of take-up speed of wheels of the Rheotens apparatus. 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 10.

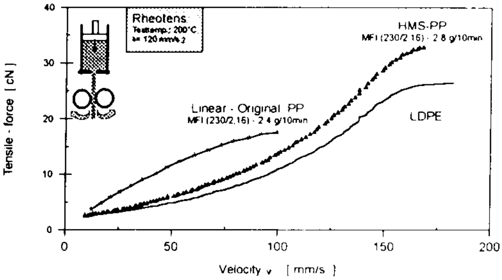
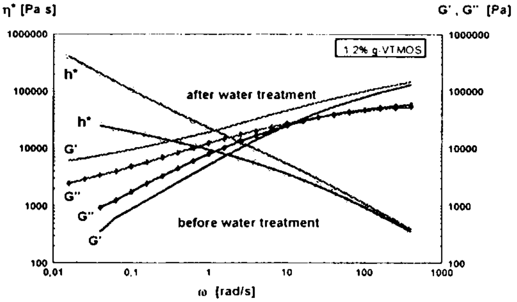


FIGURE 10: Melt strength of HMS-PP

The melt strength comparison of three different polyolefins is depicted in FIGURE 10. The standard PP-material with a melt index of 2,4 has a low melt strength and low drawabilities of the melt. The LDPE melt shows increased melt strength and enhanced drawability. It is well known that from all commerical polyolefins only LDPE is long chain-branched. Our modified PP shows the same melt strength and drawability like LDPE. For that reason we are sure that the discussed long chain-branching mechanism has taken place.

The increase of the melt strength up to partial crosslinking is also possible with i-PP´s, grafted with silanes, by hydrolytic coupling.



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

FIGURE 11: Daploy-RM (Cone-plate rheology of modified PP)

FIGURE 11 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 hydrolytic crosslinked i-PP.

2) PP-PS and PMMA-alloys:

FIGURE 12 shows the dependence of styrene conversion and grafting on the i-PP powder with 20% initial S concentration at 90 °C.

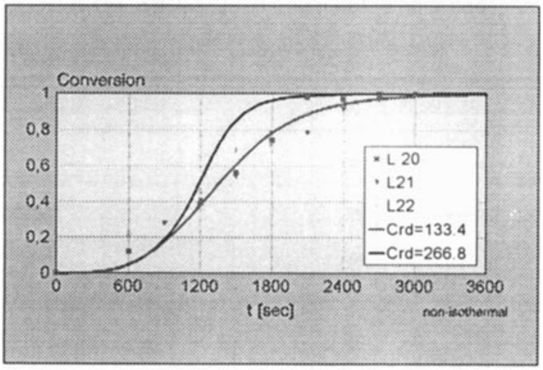


FIGURE 12: Comparison of observed with calculated results of conversion

The grafting yield can be varied from 30 to 80 % in dependence of the reaction temperature at 20 wt% of styrene (FIGURE 13).

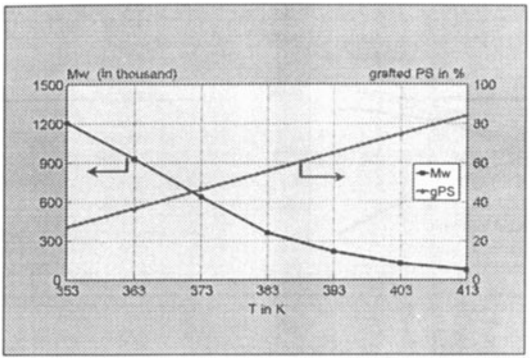


FIGURE 13: Dependence of styrene grafted onto PP powder and its molecular weight (Mw) on temperature (20 wt.% styrene)

The increasing of reaction temperature results in a reduction of the molecular weight of the grafted polystyrene from 1,2 million to nearly 100.000 g/mol. We have investigated for monomer MMA the dependence of the yield and molecular weights Mw of grafted MMA on the initial concentration of MMA at 268,5 K (95,5 °C). We found a molecular weight of ~ 500.000 g/mol for PMMA at 268,5 K (95,5 °C) and a weak dependence on the initial concentration of the monomer (FIGURE 14).

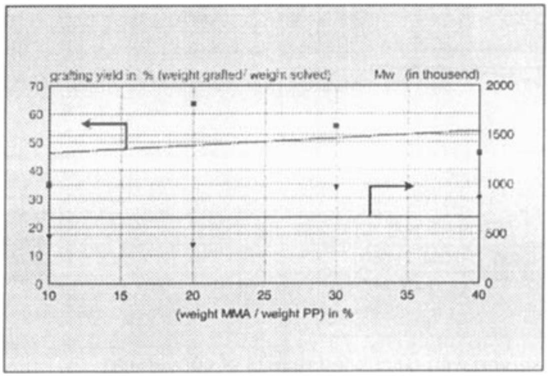


FIGURE 14: Dependence of MMA-grafted and of Mw on initial concentration (temperature = 95.5°C)

In comparison with styrene at the same temperature a molecular weight of ~ 700.000 for polystyrene was found. The molecular weights of the two polymers are comparable within the tolerance of all of the analytical methods. We were surprised from these results and will discuss them lateron.

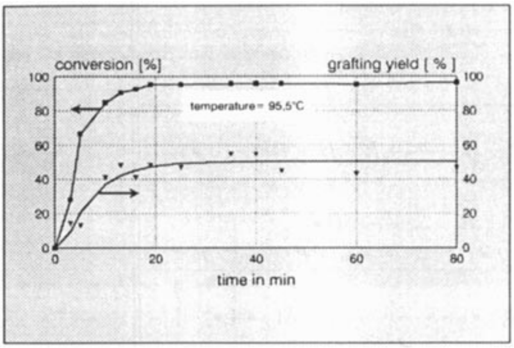


FIGURE 15: Dependence of MMA-conversion and grafted MMA onto PP-powder on time

The dependence of MMA-conversion and the yield grafted MMA on time at 368,5 K (95,5 °C) is shown in FIGURE 15. We have compared the grafting yield of the two monomers with the initial concentration of 20 % at 363 K (90 °C) on reaction time and found a higher grafting yield for MMA (FIGURE 16). The grafting of MMA is almost finished after a short reaction time of 4 to 5 minutes. The grafting of styrene onto PP is much slower under same conditions. This correlates with the higher polymerisation rates of MMA in comparison of S.

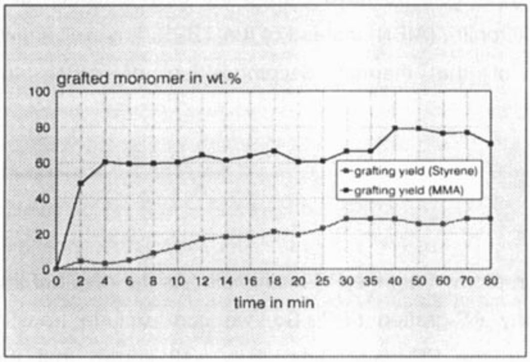


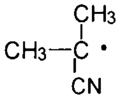
FIGURE 16: Grafting yield in dependence on time (temperature 90°C, initial concentration = 20 wt%)

The mechanism of the radical grafting of S on i-PP is described in TABLE 2.

decomposition of peroxide	$I_1 \xrightarrow{k_d} 2 * R^\bullet$
hydrogen abstraction	$R^\bullet + PP - H \xrightarrow{k_{tr}} R - H + PP - (0,\bullet)$
start	$R^\bullet + S \xrightarrow{k_s} S(1,\bullet)$ $PP - (0,\bullet) + S \xrightarrow{ks} PP - S(1,\bullet)$
propagation	$PP - S(j,\bullet) + S \xrightarrow{k_p} PP - S(j+1,\bullet)$ $S(j,\bullet) + S \xrightarrow{k_p} S(j+1,\bullet)$
termination (termination by disproportionation in range of 90°C to 110°C can be neglect)	$PP - S(j,\bullet) + PP - S(j1,\bullet) \xrightarrow{k_t}$ $PP - S(j + j1,\circ)S - PP$ $PP - S(j,\bullet) + S(j1,\bullet) \xrightarrow{k_t} PP - S(j + j1,\circ)S$ $S(j,\bullet) + S(j1,\bullet) \xrightarrow{k_t} S(j + j1,\circ)S$

TABLE 2: Mechanism of radical grafting reaction of styrene onto PP

We suppose no or only a minor transfer reaction of the styrene radicals onto the i-PP-mainchain. To prove this hypothesis we have started the polymerization of S solved in i-PP with Azobisisobutyronitril (AIBN) instead of the TBPB. It is well known that the reaction products of the thermal decomposition of AIBN, the isobutyronitrilradicals



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}\,\bullet$$

are not able to split off hydrogen atoms from the PP-mainchain. As the result of this experiment we did not find any PS-grafted i-PP. So, we can exclude transfer reactions of styrene radicals to the PP-mainchains. It is well known that the termination reaction of styrene-radicals is a recombination to a high degree.

When we compare the reaction mechanism of the radical grafting of S with MMA we assume a transfer reaction of the MMA-radicals on to the PP-mainchain and a preferred disproportionation recombination mechanism of the PMMA-radicals in contrast to S (TABLE 3).

decomposition of peroxide	$I_1 \xrightarrow{k_d} 2 * R^\bullet$
hydrogen abstraction	$R^\bullet + PP - H \xrightarrow{k_{ü}} R - H + PP - (0,\bullet)$
start	$R^\bullet + MMA \xrightarrow{k_s} MMA(1,\bullet)$ $PP - (0,\bullet) + MMA \xrightarrow{k_s} PP - MMA(1,\bullet)$
propagation	$PP - MMA(j,\bullet) + MMA \xrightarrow{k_p} PP - MMA(j+1,\bullet)$ $MMA(j,\bullet) + MMA \xrightarrow{k_p} MMA(j+1,\bullet)$
chain transfer	$PP - MMA(j.\bullet) + PP - H \xrightarrow{k_{ü}} PP(0.\bullet) + PP - MMA(j,0)$ $MMA(j.\bullet) + PP - H \xrightarrow{k_{ü}} PP(0.\bullet) + PP - MMA(j,0)$
termination (termination by combination in range of 90°C to 110°C can be neglect)	$PP - MMA(j,\bullet) + PP - MMA(j1,\bullet) \xrightarrow{k_t}$ $PP - MMA(j,\circ) + PP - MMA(j1,\circ)$ $PP - MMA(j,\bullet) + MMA(j1,\bullet) \xrightarrow{k_t} PP - MMA(j,\circ) + MMA(j1,\circ)$ $MMA(j,\bullet) + MMA(j1,\bullet) \xrightarrow{k_t} MMA(j,\circ) + MMA(j1,\circ)$

TABLE 3: Mechanism of radical grafting reaction of MMA onto PP

We do not have experiments with the initiator AIBN for the transfer reaction of acrylate radicals to PP. We follow the general opinions from the literature. But, we conclude that we have two different reaction mechanisms.

The similarity of the molecular weights of the two monomers with the different termination reactions can be explained by the higher propagation rate of the MMA-polymerization in comparison to the S-polymerization. In TABLE 4 are the first and second column the frequence factors and the activation energy of the propagation and termination rate constants of S and MMA from the literature /Ref. 15,16/ listed.

Rate constants						
Reaction	frequency factor [l/(mol*min)]		activation energy [kJ/(kmol*grd)		C_{RD}	
	MMA /15/	Styrene /16/	MMA	Styrene	MMA	Styrene
propagation k_p [l/(mol*min)]	2,95 e+7	1,26 e+7	18200	29000	90 /18/	800 /18/ ⇓ 133 (exp.) /2/
termination k_t [l/(mol*min)]	5,88 e+9	1,7 e+9	2900	9000		

TABLE 4: Frequency factors and activation energy of MMA, S

The answer to our questions to the comparable molecular weights of the PS and PMMA in the i-PP can also be the high viscosity of the reaction medium. The medium of reaction is the amorphous phase of the solid i-PP swollen with the monomer. Furtheron, the reaction temperatures are below the glass transition temperatures Tg of both polymers.

From investigations of the polymerization of S and MMA at high conversions G.V. Schulz /Ref. 17/ gives an equation for describing the termination rate constants. The physicochemical background of this formula is based on the idea that the termination reaction proceeds by radical propagation which become nearer and meet by chain growth. The chain growth depends moreover on a so-called CRD-factor, a value for the reaction capture radius of the chain end radicals. Buback and Huckstein /Ref. 18/ have further developed the basic idea of Schulz. In column 3, TABLE 4, the CRD-values of Buback and Huckstein are listed. The results are from investigations of the polymerization in solution at high conversions. That means in high viscosities of the solved monomers in their polymer. The result shows a tenfold difference between S and MMA.

From these theoretical considerations and the fact that termination reactions of radicals proceed with very high rate they conclude that the termination reaction in the case of hindered mobility of reaction partners can be described by the equation:

$$k_t = k_{trans} + \frac{CRD}{M^0} * k_p * M$$

k_{trans} = translation rate constant

$\frac{CRD}{M^0} * k_p * M$ = reaction diffusion

The term k_{trans} stands for the chain termination reaction via movement of the polymerchains that means for the „translation diffusion" and the term: $\frac{CRD}{Mo} * kp * M$ for the chain termination reaction which grow together because of the movements of the chain ends, the so-called „reaction diffusion" described by Schulz.

In experiments with Ivantchev /Ref. 19/ we measured the decrease of the radical concentration in i-PP after γ-irradiation on time at 70 °C, 90 °C and 117 °C. FIGURE 17 shows a fast drop of the radical concentration in rad/g x 1 x e-18 in a time scale up to 7.200 seconds.

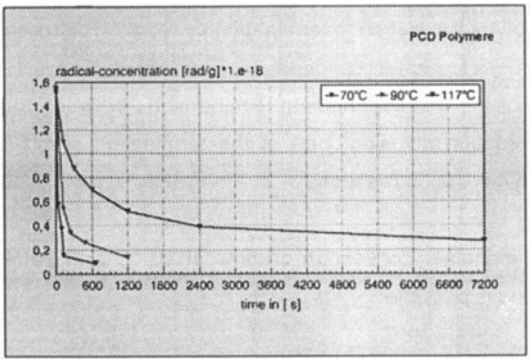


FIGURE 17: Dependence of radical-concentration in PP on time and temperature

These values correlate with the „translation diffusion" rates of the whole termination rates. By acception this correlation the „translation diffusion". rate constants k_{trans} result to

70 °C k_{trans} = 1,3 l/mol s

90 °C k_{trans} = 8,5 l/mol s

117 °C k_{trans} = 37,5 l/mol s

and an activation energy of E_A = 75,9 KJ/mol.

In comparison to the „reaction diffusion" values at the same termpatures in dependence of the concentration of MMA in mol/l it can be seen in FIGURE 18 that up from 01, mol/l MMA solved in i-PP-powder grains the „translation diffusion" reactions can be neglected.

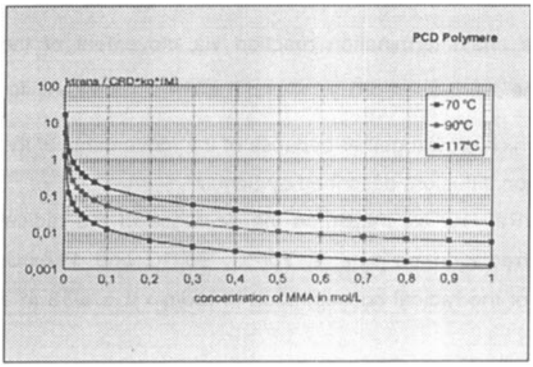


FIGURE 18: Ratio from termination by translation to termination by reaction diffusion

So far we know that this is one of the first experimental comparisons between the „translation diffusion" and the „reaction diffusion" part of the termination reaction constant in diffusion hindered polymerization reactions.

The mathematical calculation of monomer conversion on time at 90 °C and 20 % with the material-balance equations is possible:

$$\frac{\partial[I]}{\partial t} = -k_I * [I]$$

$$\frac{\partial[R^\bullet]}{\partial t} = 2 * RAF * k_I * [I] - k_{R^\bullet,tr} * [R^\bullet] * [PP] - k_s * [R^\bullet] * [M]$$

$$\frac{\partial[M]}{\partial t} = -k_p * ([PP(j,\bullet)] + [M(j,\bullet)]) * [M]$$

$$\frac{\partial[M(j,\bullet)]}{\partial t} = k_s * [R^\bullet] * [M] - k_t * [M(j,\bullet)]^2 - k_{M^\bullet,tr} * [M(j,\bullet)] * [PP]$$

$$\frac{\partial[PP(j,\bullet)]}{\partial t} = k_{R^\bullet tr} * PP * [R^\bullet] - k_t * [P(j,\bullet)]^2 + k_{M^\bullet,tr} * [M(j,\bullet)] * [PP]$$

The termination rate constants calculated with the CRD-values and the propagation constants from Buback in TABLE 4 demonstrates in FIGURE 19 a good conformity between the calculated and the experimental values for MMA, but not for S.

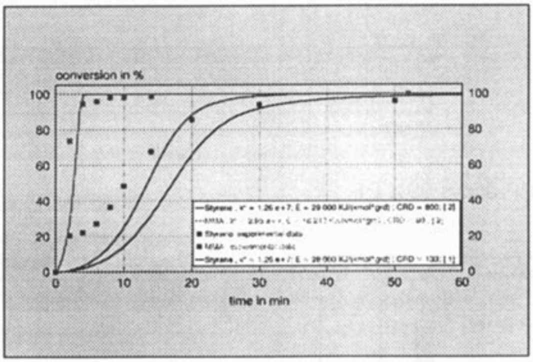


FIGURE 19: Calculation of conversion in dependence on time

The high difference in the CRD-values of S (800) and MMA (84) is not easy to understand because the reaction proceeds in the same reaction media and under the same conditions. In comparison to the polymerization of the monomers in a high viscous medium where the reaction medium are the concentrated PS-solution or the PMMA-solution we have at our conditions an amorphous solid i-PP-phase as medium for both monomers.

After correction the CRD-constant of S from 80 to 133 we get a good correlation also for the S-conversion-time relation. The difference from 84 (MMA) and 133 (S) under the same reaction conditions now is easy to understand.

PROPERTIES OF THE PP-ALLOYS

In FIGURE 20 and 21 the relativ change of the flexural modulus and flexural stress, the impact resistence, the heat deflection temperature and the hardness of alloys and chemical modified (CM) alloys compared with the original i-PP are listed. We found, as expected, a decrease of the impact resistance because the alloy partner PS and PMMA are brittle-polymers. This can be corrected by adding elastomers as EPR or and SEBS to the alloy.

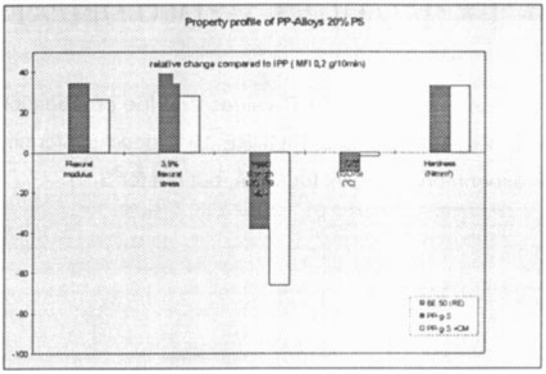


FIGURE 20: Property profile of PP-alloys 20% PS

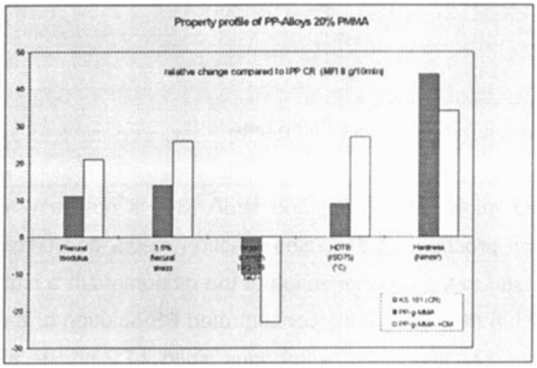


FIGURE 21: Property profile of PP-alloys 20% PMMA

All the other properties (modulus, hardness, HDTB) are increased.

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