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Solid-State Polypropylene Grafting as an Effective Chemical Method of Modification

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Summary: The role of vinylidene groups, formed by the action of organic peroxides, on crosslinking reactions in isotactic polypropylene (iPP), is discussed. Grafting of polymerizable monomers on powdered iPP, performed below its melting temperature, occurs with high efficiency, depending on the structure of peroxide used.

Introduction

Generally, grafting of polypropylene by polymerizable monomers has long been studied for its possibility to influence the properties of the original materials. The main goal of isotactic polypropylene (iPP) grafting is to increase the polarity of iPP and so to obtain a material suitable for preparation of polymer blends and composites which exhibit improvements of some physical or mechanical properties over the original polymer(1-11).

In principle, the methods of polypropylene grafting can be carried out by three procedures: in melt, in solution (in slurry) and in the solid state. In this paper, the grafting of iPP in the solid state, which has been a method developed over the last two decades, will be described. The first patent was applied in 1983 by Borsig et al.(3) but the first paper in open literature was published by R. Rengarajan et al. in 1988(12). Solid state grafting of iPP has already found at least one commercial application. In this short contribution will be discussed the effect of

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peroxide on iPP and the efficiency of iPP grafting with maleic anhydride (MAN), methyl methacrylate (MMA) and styrene (S).

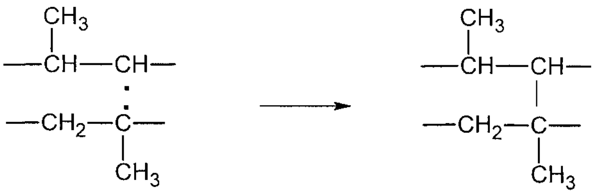
Results and Discussion

A: The Effect of tert-Butyl Perbenzoate on Thermally Annealed iPP

In the investigation of the course of degradation and build-up reactions during the decomposition of tert-butyl perbenzoate (TBPB) in iPP, it was found that at all investigated peroxide concentrations from 4.62 – 200 mmol/kg iPP, the degradation reactions of iPP prevailed. Molecular weight changes in iPP, as determined by melt flow index (MFI), were examined during early periods of the reactions. Changes in molecular weight as a function of time were due to the generation of free radicals arising from the thermal degradation of TBPB. Polymer degradation, as well as branching and crosslinking reactions, have also been examined in treated PP at 230 °C using MFI measurements[13].

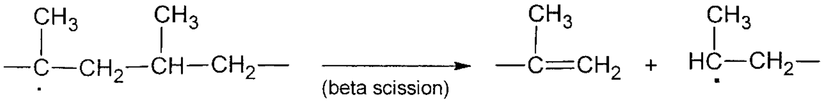
Using TBPB-impregnated iPP at peroxide concentrations not higher than 37 mmol/kg iPP, only an increase of the MFI was observed during the annealing process working of seven different half-life time of the peroxide in the range 160 to 320 min (Fig. 1). This indicates that fragmentation of polymer chains is taking place under these conditions. At higher starting concentrations of TBPB, changes in the MFI were much more complicated. At first, MFI increased, and only after a particular amount of peroxide decomposition the competitive crosslinking process became dominant, resulting in decreased MFI. This fact contradicts the simple kinetic idea according to which at high concentration of macroradicals the bimolecular recombination (crosslinking) (1) prevails over monomolecular fragmentation reactions. The fragmentation of PP is believed to take place by a beta scission reaction (2).

The crosslinking reaction by combination of PP free radicals e. g.:



(1)

The monomolecular reaction of fragmentation of one PP free radical is given in (2).



$$-\overset{CH_3}{\underset{\cdot}{C}}-CH_2-\overset{CH_3}{CH}-CH_2- \xrightarrow[\text{(beta scission)}]{} -\overset{CH_3}{C}=CH_2 + H\overset{CH_3}{\underset{\cdot}{C}}-CH_2- \quad (2)$$

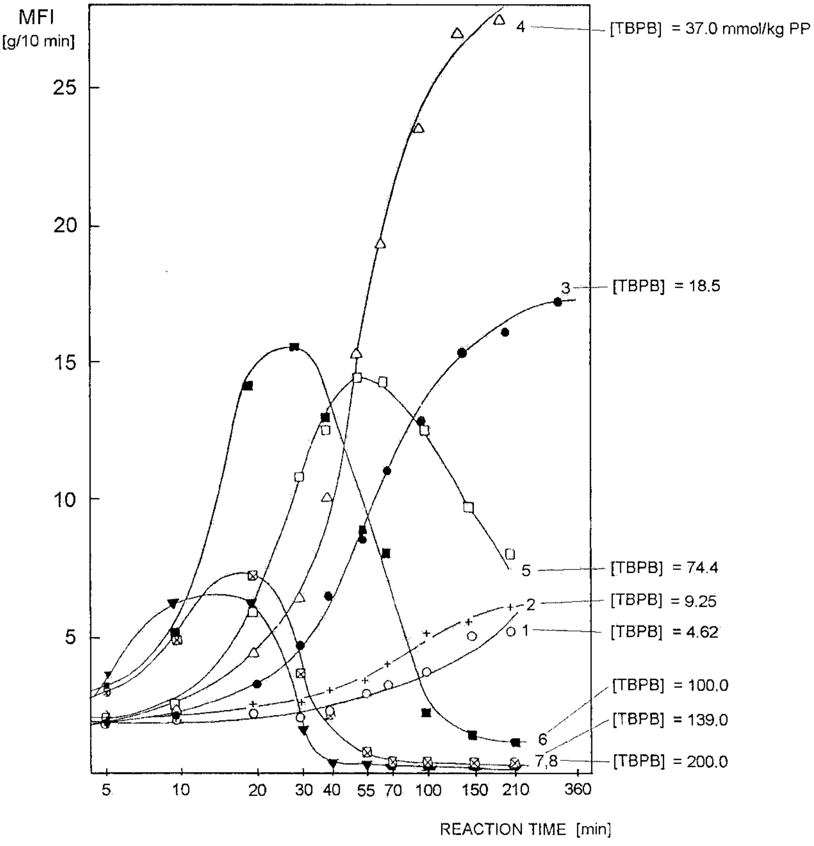
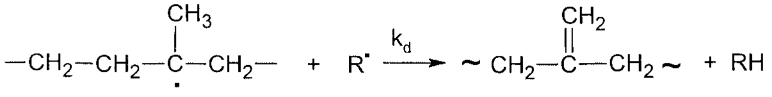


Fig. 1: The effect of tert. butyl perbenzoate (TBPB) on polypropylene at 129 °C.

From quantitative measurements of double bonds in iPP during the decomposition of TBPB by the IR method[13], it was found that vinylidene bonds are formed (Fig. 2). The most important are those which are formed from the disproportionation of PP macroradicals[13]:



$$-CH_2-CH_2-\underset{\bullet}{\overset{CH_3}{\overset{|}{C}}}-CH_2- + R^{\bullet} \xrightarrow{k_d} \sim CH_2-\overset{CH_2}{\overset{\|}{C}}-CH_2\sim + RH \qquad (3)$$

because the vinylidene bonds formed are most effective at the molecular weight increase (4).

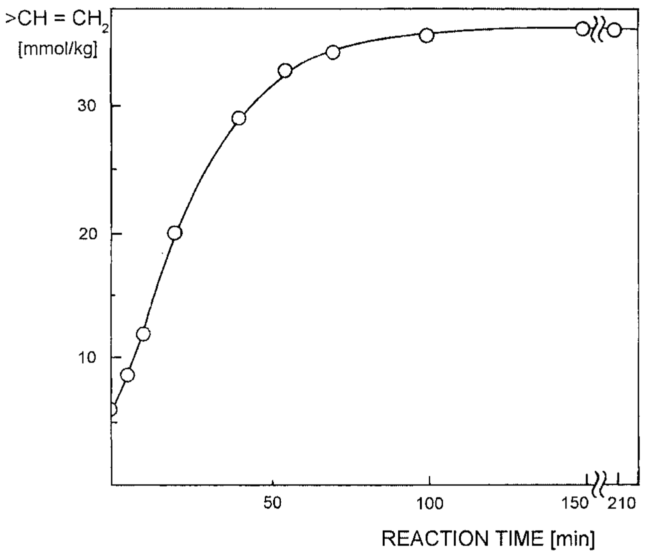
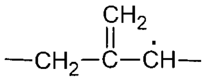


Fig. 2: Vinylidene bond formation in iPP at decomposition of TBPB = 139 mmol/kg PP at 129 °C

The formation of double bonds within the macromolecules is caused by both disproportionation (3) and by fragmentation (2) to give rise to the accumulation of vinylidene bonds in the PP during peroxide decomposition. It is worth mentioning that the ratio of rate constants for disproportion k_d and combination k_c of tert-alkyl radicals k_d/k_c is higher than 2.5.

The most significant consequence of the increased concentration of double bonds is however the subsequent increase of the concentration of allyl type radicals which will be formed by transfer reactions of radicals with the polymer chains containing double bonds:



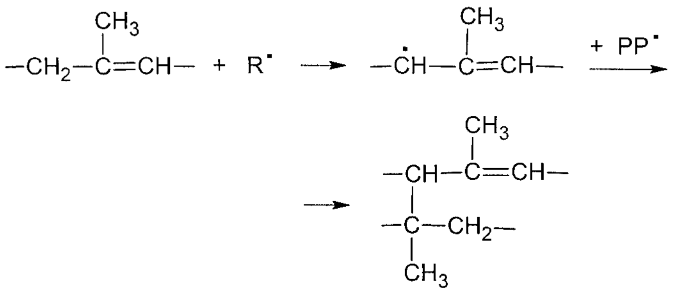
$$-CH_2-\overset{\overset{\displaystyle CH_2}{\|}}{C}-\dot{C}H-$$

1

The combination rate constant of allyl radicals like **1** is about 100 times higher than that for disproportionation[13)].

From this we can expect that the increase of the concentration of allyl radicals will substantially enhance the portion of reactions leading to the molecular mass increase of modified PP.

From this observation, we believe that combination reactions of primary formed macroradicals on iPP chains created by the action of peroxide, leading to crosslinking or branching and so to an increase in the molecular weight of iPP, cannot alone prevail over fragmentation reactions taking place during the beginning of the reaction. The crosslinking can prevail over fragmentation only at the point when also a "critical" concentration of double bonds in the iPP chain are present at the given reaction conditions. This "critical" point should be reached at the maximal values of MFI of the curves on the plot of MFI of iPP versus time of TBPB decomposition at initial concentration of peroxides higher than 37.0 mmol/kg iPP (Fig. 1). On the other hand, for achievement of the "critical" point, both reactions are necessary i.e. the combination of primary macro-radicals e. g. $-C^{\bullet}(CH_3)-CH_2-$ which are created by the effect of peroxide on PP chain and crosslinking reactions of double bonds in iPP chain $-CH_2-C(CH_3)=CH-$ e.g.:



(4)

B: Grafting of Vinyl Monomers to iPP

The procedure of solid state grafting is based on radically-initiated grafting reactions in iPP powder or granules in the presence of a monomer. The morphology of iPP powder particles allows the absorption of a monomer and initiator in a very short time. For example, after about 200 seconds an equilibrium state between absorbed styrene and its vapor pressure can be attained14). The weight content of a monomer in iPP depends on the crystallinity of the iPP, indicating that the monomer and initiator are only dissolved in the amorphous phase of iPP. The solubility of the monomer (initiator) depends on the temperature. For example absorption of styrene on iPP powder is about 27 % at 100 °C14). So it is assumed that grafting reactions on iPP proceed in the amorphous phase only.

In the studies reported here on the solid-state grafting of iPP, maleic anhydride (MAN), styrene (S), and methyl methacrylate (MMA) were used.

Because of its poor ability to propagate, MAN undoubtedly does not lead to long chain branching, but rather only to monomeric or oligomeric side chains. Nevertheless, the attached MAN units serve to increase polarity of the iPP chains1, 15-17). The type of initiator used has been found to greatly influence the efficiency of grafting by MAN. For example, dilauroyl peroxide (DLP) is almost two times more effective at iPP grafting with MAN than tert-butyl perbenzoate (TBPB) at the same concentration (0.15 mol/kg) at 100 °C (Tab. 1). Curiously, it is known that TBPB is generally considered a more effective radical initiator of polymerization than is DLP. Also, iPP grafting with other monomers e.g. methyl methacrylate, in the presence of TBPB, the attained grafting efficiency was higher than in the

Table 1. Calculated grafting efficiency of maleic anhydride onto poly(propylene) at 100 °C for equal concentrations of different peroxides (peroxides at 0.15 mol/kg and maleic anhydride at 0.4 mol/kg)15).

Peroxide	Efficiency	Maximal observed efficiency/ °C
Dilauroyl peroxide	1.09	1.35/70
Dibenzoyl peroxide	0.77	0.95/90
tert-Butyl perbenzoate	0.59	0.77/150
Dicumyl peroxide	0.19	0.21/110

presence of DLP[15]. This means that in solid state grafting, also other parameters, e.g. solubility of the peroxide and monomer in PP or decomposition of primary radical from the peroxide (and so the change of the radical reactivity), can play an important rôle[15].

On the other hand, the low efficiency of dicumyl peroxide (DCP) as an initiator for iPP crosslinking reactions is considered as a surprising result (Tab. 1). One of the reasons can be the influence of polar maleic anhydride resulting in the limited decomposition of dicumyl peroxide.

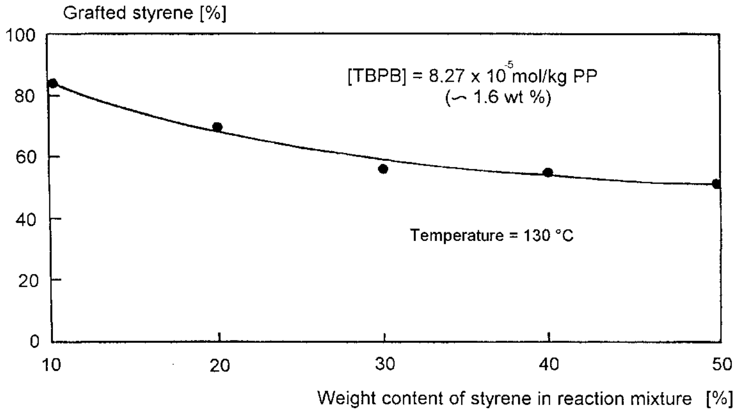
The grafting mechanism of styrene onto iPP is expected to take place according to the general scheme:

$$\begin{array}{ll} R^{\bullet} + PP\text{-}H \longrightarrow R\text{-}H + PP^{\bullet} & \\ PP^{\bullet} + n\,M \longrightarrow PP\text{-}(M)_{n-1}\text{-}M^{\bullet} & (5) \\ PP\text{-}(M)_{n-1}\text{-}M^{\bullet} + R^{\bullet}\ (PP\text{-}(M)_n\text{-}M^{\bullet}) \xrightarrow[\text{combination}]{\text{disproportionation}} \text{grafted PP} & \end{array}$$

Besides homopolymerization, a grafting reaction of styrene onto PP-backbone occurs. The grafting efficiency depends on the styrene content and on the polymerization temperature.

Fig. 3 shows the grafting efficiency of styrene onto iPP at 130 °C for a monomer content ranging from 10 % to 50 %. The reaction was initiated by 1.6 wt. % of tert-butyl perbenzoate (TBPB) related to iPP. The grafting efficiency decreases with increased styrene content. In all cases, more than 50 % of styrene was chemically bonded on iPP (Fig. 3). On the other hand, temperature has a positive influence on the level of iPP grafting with styrene. At the same concentration of peroxide in the reaction mixture as above, the amount of grafted styrene from a monomer to PP ratio of 20 : 80, increased from about 25 % at 80 °C up to 83 % of the added styrene at 140 °C[14].

Fig. 3: Dependence of styrene grafted onto PP powder on weight content of styrene in reaction mixture.



In the case of iPP grafting with methyl methacrylate (MMA), the yield of grafting was higher than with styrene (Tab. 2). The type of initiator has also a considerable influence on the level of grafting. From the three types of initiator: tert.-butylperoxy-2-ethylhexanoate (TBPEH), DLP and 1,1-bis(tert. butylperoxy)-3,3,5-trimethyl cyclohexane) (BTBMC) the lowest grafting efficiency was shown by DLP. The type of initiator has also an influence on the degradation of the grafted iPP and so on the required properties of the end product. The TBPEH at the concentrations used, is quite effective in the grafting reaction as is shown in Tab. 2. Furthermore, this peroxide does not influence remarkably the molecular weight of the grafted PP. Different behaviour was shown by DLP and BTBMC. DLP is considerably less effective in the level of grafting of iPP by MMA than is TBPEH (13.6 wt. % and 5.5 wt. % at 4.62 mmol/kg). But on the other hand, the degradation reaction of PP is higher in the case of DLP. The very high degradation reaction accompanying BTBMC was unexpected. One of the reasons for the high degradation effect by BTBMC may be due to the high local concentration of tert-butylperoxy groups, which upon decomposition can produce also a high local concentration of polymer free radicals in iPP. These regions are probably not sufficiently saturated with monomer, which requires some time for diffusion into the amorphous, reactive parts of iPP and therefore fragmentation is much more probable.

Table 2. Grafting of iPP with MMA – Influence of different kind of peroxides at the presence of 15 wt. % of the monomer, melt flow index – MFI of non-grafted iPP was 0.23.

Peroxide		Temperature of grafting	Reaction time	**Grafted MMA**	**MFI * of grafted PP**
Type	Concentration [mmol/kg iPP]	[°C]	[min]	[wt. %]	[g/10 min]
TBPEH	4.62	93	314	13.6	0.11
TBPEH	37.0	93	314	13.3	0.13
DLP	4.62	102	35	5.5	0.52
DLP	37.0	102	35	3.4	0.47
BTBMC	4.62	105	420	13.13	0.38
BTBMC	37.0	105	420	11.54	9.25

* Melt flow index – MFI of reacted iPP was measured at 230 °C.

We believe that this type of iPP grafting with various vinyl monomers can have also practical applications, where grafted iPP can act as a compatibilizer. For example, a comparison of flexural modulus and notched impact strength values on PP/PS alloys with and without a common, grafted compatibilizer, showed the highest increase of flexural modulus (35 %) and the lowest decrease of notched impact strength at 20 °C for the case of the alloy containing the compatibilizer14).

Conclusions

- The degradation prevails over crosslinking reaction in iPP even at all peroxide concentration used (i. e. from 37 mmol/kg PP to 200 mmol/kg PP).
- From the previous point it follows that the simple combination of polymer free radicals in iPP alone can not attain a condition at which crosslinking would prevail over the degradation reaction (beta scission).

- From the observation of the increase of the double bonds in PP by the effect of radicals during peroxide decomposition led to the conclusion that only after formation of a "critical" concentration of double bonds in iPP the crosslinking starts prevail on degradation reaction.
- Optimum conditions for grafting onto iPP can be achieved by the use of a suitable reaction conditions (type of peroxide and temperature) and so that degradation of iPP can be minimized.
- At the solid state grafting of iPP with S or MMA the highest efficiency of about 80 % was attained.

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