Course of Degradation and Build-Up Reactions in Isotactic Polypropylene During Peroxide Decomposition

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ABSTRACT: In the investigation of the course of degradation and build-up reactions during the decomposition of the *tert*-butyl perbenzoate (TBPB) (at eight different concentrations) in isotactic polypropylene (iPP), it was found that, at the beginning of the peroxide decomposition at all investigated peroxide concentrations from 4.62–200 mmol/kg iPP, the degradation reactions of iPP prevailed. At the TBPB concentration of ≤37.0 mmol/kg iPP during the whole period of peroxide decomposition, degradation reactions leading to a lower of molecular mass of PP prevailed. But at higher peroxide concentrations of TBPB ≥74.4 mmol/kg iPP and at the later stage of peroxide decomposition, a predominance of the build-up reactions, that is, an increase the molecular mass, was observed. The degradation and build-up reactions were determined from the measurements of the melting-flow indexes of the peroxide-treated iPP samples. The reaction mechanism of the degradation and build-up reactions in iPP is discussed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 886–893, 2000

Key words: polypropylene; degradation; crosslinking reactions; peroxide radical reactions

INTRODUCTION

Radical reactions such as, for example, grafting, crosslinking, or functionalization on polypropylene (PP) macromolecules are accompanied by simultaneous undesired processes. Some macromolecules increase their mass; others split into smaller fragments.[1,2] These reactions lead to a change of the polymolecularity and a decrease or increase of the average molecular mass of the modified polymer as a function of the ratio of degradation and addition reactions of polymer radicals under given reaction conditions.

The decomposition of various amounts of dibenzoyl peroxide (50–210 mmol DBP/kg PP) in atactic PP (a-PP) at 65–87°C[3] showed that the change in the average molecular mass of the polymer cannot be expressed by a simple dependence on the amount of the decomposed peroxide. After decomposition of very small amounts of peroxide, the limiting viscosity number decreases and increases at higher concentrations, but it does not reach the starting value of the original PP. A similar decrease in the average molecular mass of a-PP as a function of the amount of radicals formed was also measured in dicumyl peroxide decomposition at 145°C.[4] If, however, the initial

molecular mass of a-PP obtained by fractionation of the original polymer is three times higher, crosslinking of the macromolecules is already reached at the same relatively low peroxide concentration (18–150 mmol/kg a-PP) under formation of an insoluble gel.

The efficiency of degradation expressed as a ratio of the number of main-chain scissions of macromolecules (calculated from the decrease in the number-average molecular mass) to the number of decomposed peroxide bonds is very low (0.02–0.15) depending on the temperature used, the type of initiator, its concentration, as well as the starting molecular mass of the degraded polymer. On the other hand, the approximate stoichiometric efficiency of degradation was measured during the decomposition of 2,5-dimethyl-2,5-bis-(*tert*-butylperoxy)hexane (0.4–4 mmol/kg) in i-PP in the presence of the antioxidant 2,6-di-*tert*-butyl-4-methylphenol (4–9 mmol/kg) at the temperature zones of the extruder between 160 and 230°C.[5] At the peroxide concentrations used, the average molecular mass (number and mass) of the degraded polymer constantly decreases with an increasing amount of the peroxide decomposed. As degradation proceeds, polymolecularity of PP is narrowed. A substantially higher efficiency of i-PP degradation is associated mainly with a lower starting peroxide concentration, mechanical stirring of the reactants, and higher temperature of the experiments carried out and probably also with the presence of an antioxidant but probably not with different polymer tacticity.

The recombination reactions of PP macroradicals manifested by the formation of an insoluble fraction of macromolecules evidently predominate when the amount of decomposed peroxide is 200–350 mmol/kg.[6, 7] The results point to the low efficiency of the crosslinked reaction and its dependence on the type of peroxide used, the peroxide decomposition temperature, and/or the rate of the production of free radicals.

The importance of fragmentation and crosslinking of PP within a broader concentration range for different types of peroxides was verified by comparing the flow index of the polymer melt in which a certain amount was earlier thermally decomposed.[8] The measurements show that after peroxide decomposition to 50 mmol/kg PP fragmentation and disproportionation of the macroradicals formed prevail, and when a greater amount of peroxide is decomposed, recombination of macroradicals or another mechanism of a poly-mer crosslinking reaction will be applied to a greater extent.

The increasing crosslinking efficiency with an increasing peroxide concentration can be explained from a kinetic point of view, namely, by a second-order crosslinking and first-order fragmentation reaction of the macroradicals, indicating that the rate of crosslinking should increase with the square of peroxide concentration and fragmentation should be directly proportional to the concentration of the peroxide used. The known results of the effect of peroxides on PP support such an interpretation. The boundaries of the interpretation of the idea used can be verified or doubted by the time dependence of the changes in the average molecular mass of PP at various starting peroxide concentrations, this being the subject of the study.

EXPERIMENTAL

Chemicals

The following chemicals were used: *tert*-butyl perbenzoate (TBPB) 98%, Merck Schuchardt; stabilizer, Ionol (80 g) + B225 (40 g) + 3052 (40 g) per 1 L of acetone; and PP, type Daplen B-Pulver, ÖMV (Linz, Austria), with a melt-flow index (MFL) of 1.2 g/10 min (ASMMD 12138). Pure acetone used for peroxide extraction from PP after partial decomposition of TBPB was used without special purification.

Sample Preparation

A powder PP sample was stirred with TBPB (in a concentration range from 4.62 to 200 mmol/kg) in a nitrogen atmosphere at room temperature for 2 h without using a solvent. The peroxide-impregnated powder was then divided into test tubes and evacuated and sealed in a nitrogen atmosphere. The sealed ampules were annealed for particular times (5, 10, 20, 30, 40, 55, 70, 100, 150, and 210 min) at 129°C in an oil bath. The chosen time of annealing was 2.5 min. The particular temperature of the polymer was reached during 5 min of sample annealing. After the time-limited annealing and cooling, powder PP was extracted for 24 h under stirring at room temperature. After filtering and washing with ethanol and the addition of the thermal stabilizer (Ionol + B225 + 3052) dissolved in acetone, the polymer was dried and the MFI was determined.

Determination of the Concentration of TBPB

The peroxide concentration in powder PP samples which were annealed for different times was determined by titration.[9] The rate constant for TBPB decomposition in PP powder was determined at the starting concentration of 100 mmol/kg. The same method was used to verify the sufficiency of the extraction of nondecomposed peroxide from annealed samples before measuring the MFI.

Measurement of the PP Degradation

The MFI was used to estimate PP molecular weight changes after reaction with TBPB. The MFI was determined at 230°C in an instrument according to ISO 1133. The MFI of the initial polymer annealed in a nitrogen atmosphere in a sealed ampule at 129°C remained unchanged after 210 min (1.2 g/10 min). For a PP sample impregnated by peroxide not annealed (4.62–200 mmol/kg) and then extracted by the method used, the MFI increased from 1.2 to a maximum 1.7 g/10 min.

Determination of the Double Bonds in PP

In the IR-spectroscopical determination of the double bonds formed at fragmentation of PP by the effect of peroxide, the 888-cm^{-1} vinylidene, the 910-cm^{-1} vinyl, and the 967-cm^{-1} *trans*-vinyl stretching absorptions were followed as the analytic bonds. No vinyl and *trans*-vinylene groups were determined in degraded PP.

RESULTS AND DISCUSSION

Fragmentation of Macroradicals

The degradation of PP as a function of the time of the effect of free radicals from the decomposing TBPB is controlled by the initial peroxide concentration. The dependence is graphically presented in a semilogarithmic coordinate system (Fig. 1). As the dependence shows, at TBPB concentrations not higher than 37 mmol/kg PP, only the increase of the MFI during the annealing of the PP impregnated with TBPB throughout seven half-times of the peroxide decomposition[10] was observed. At higher starting concentrations of TBPB, more complicated changes of the MFI are observed: At first, MFI increases, and only after a particular amount of peroxide decomposes does
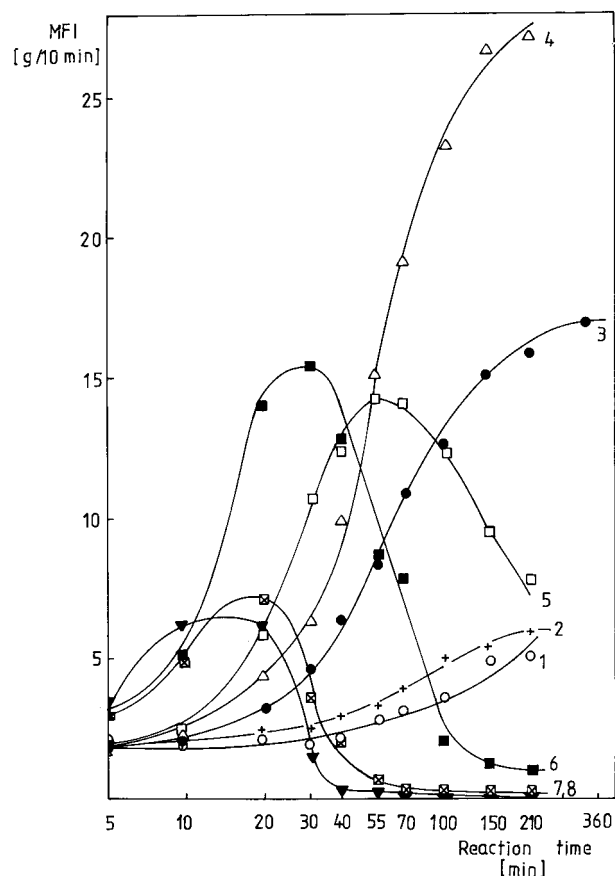

Figure 1   Plot of MFI of PP versus the time of TBPB decomposition at various initial concentrations of peroxides: (1) 4.62, (2) 9.25; (3) 18.5, (4) 37.0, (5) 74.4, (6) 100.0, (7) 139.0, and (8) 200.0 mmol/kg iPP at reaction temperature of 129°C.

the competition crosslinking process start, namely, decrease of the MFI. The figure also shows that the initial rate of degradation is highest at the highest starting TBPB concentration in PP. This fact contradicts the simple kinetic idea according to which the proportion of fragmentation and recombination of PP macroradicals is determined only by the stationary concentration of the macroradicals. If it is valid, the idea that crosslinking results only at the high level of radicals in the system, then at a high peroxide concentration in the first phase of the reaction, the recombination of macroradicals should prevail. On decreasing the rate of the production of free radicals as a result of the lowered peroxide concentration (decomposition of peroxide as a precursor of free radicals), the degradation of crosslinked PP should predominate.

In an effort to evaluate quantitatively the role of radical concentration in degradation and com-

**Table I   Calculated Characteristics of PP Degradation k_s from Relation (1) and k/[TBPB]
in Particular Time Intervals (Δt in Minutes) of the Growth of MFI
for Various Initial TBPB Concentrations**

[TBPB] (mmol/kg)	Δt (min)	n	k_s (10^3 min^{-1})	Cor. c.	k_s/[TBPB] (kg mol^{-1} min^{-1})	k_s'[a] (kg mol^{-1} min^{-1})
4.62	210	10	5.62	0.958	1.217	0.847
9.25	210	10	5.88	0.922	0.636	0.746
18.5	210	10	11.0	0.871	0.595	0.658
37	210	10	12.5	0.819	0.338	0.580
74	55	6	43.6	0.931	0.589	0.512
100	30	4	65.0	0.948	0.650	0.485
139	20	3	53.0	0.976	0.381	0.457
200	10	2	103	1.000	0.515	0.428

n, number of experimental data; cor. c., correlation coefficient in calculation of the k_s value.
[a] Corrected values of the previous column from the statistics of the evaluated dependence of ln[TBPB] versus ln k_s/[TBPB]. The relation can be expressed as $k_s' = 1.12$ [TBPB]$^{-0.181}$ (cor. c. = 0.631).

petitive crosslinking of PP, the changes in MFI were quantified only from that part of time t dependence in which MFI increases. The increase in MFI in time for particular starting concentrations of TBPB was formally evaluated as a first-order reaction and the quantitative value of the quasi-rate constant k_s from the relation

$$\ln \text{MFI} = k_s t + \ln \text{MFI}_0 \qquad (1)$$

was determined by the method of least squares. Our evaluation was based on two acceptable assumptions:

1. TBPB is decomposed monomolecularly also under the conditions of the implemented experiments.
2. The growth of MFI in time t corresponds to the amount of peroxide decomposed in the system.

The measured and evaluated experimental data (Table I) show the expected unequivocal increase in the value of k_s with the increasing initial TBPB concentration. If the k_s values are divided by the particular initial concentration of TBPB, the constant for PP degradation is obtained per unit amount of peroxide decomposed. Although this part of the evaluation shows a rather large experimental error, one can state that by decreasing the TBPB concentration the portion of fragmentation really increases with respect to termination of the PP macroradicals. If the values of calculated and statistically evaluated specific constants are compared at 200 and 4.62 mmol

TBPB/kg PP, then, at 43 times lower peroxide concentration, the degradation efficiency increases approximately twice that at a higher peroxide concentration.

If we assume that the decomposition rate constant for TBPB does not depend on its concentration, then the percentage of the decrease of TBPB in the PP samples should be the same for the particular times of heating. The dependence of MFI on the initial TBPB concentration in various time intervals can indicate the changes in degradation efficiency with the time of peroxide decomposition.

The changes of MFI were evaluated statistically in two ways: The first procedure was based on the experimentally verified direct proportion of MFI versus the amount of peroxide decomposed in PP.[11, 12] In the equation of the straight line,

$$\text{MFI} = \text{MFI}_0 + A[\text{TBPB}]_0 \qquad (2)$$

the constant A expresses the slope of the plot. Such an evaluation led to the fact that with the increasing decomposition time of TBPB A increases in the ascending dependence of the TBPB concentration (Table II). The increasing steepness of the plot with the increasing time of the decomposition of TBPB corresponds to the growth of the degradation efficiency of PP with decreasing peroxide concentration in the polymer medium. A similar situation arises when the results of the measurements are evaluated according to the exponential relation. The value of the exponent x again grows with the reaction time (Table II). The initial very low value of the exponent can be in-

Table II   Values of the Coefficient of Proportion A in the Equation MFI = MFI_0 + A[TBPB] and of Exponent x in the Equation MFI = MFI_0 + k[TBPB]^x at Various Times of the Decomposition of TBPB in PP at 129°C

Time (min)	%[a]	A	Cor. c.	x	Cor. c.	n
5	11	0.011	0.904	0.180	0.756	8
10	21	0.024	0.945	0.327	0.883	8
20	37	0.107	0.920	0.538	0.925	6
30	50	0.135	0.995	0.669	0.993	6
40	60	0.244	0.987	0.628	0.978	4
55	72	0.397	0.993	0.864	0.971	4
70	80	0.519	0.992	0.937	0.975	4
100	90	0.630	0.992	0.952	0.983	4
150	97	0.714	0.985	0.902	0.961	4
210	99	0.721	0.971	0.889	0.958	4

cor. c., correlation coefficient; n, number of measurements in the ascending part of the plot of MFI versus TBPB concentration.

[a] Calculated % of decomposed TBPB the half-time of peroxide decomposition is 30 min.[10]

fluenced by the fact that in the first stages of the reaction the high peroxide concentration is on the surface of the PP powder particles, gradually leading to peroxide diffusion into the volume of the particles. The local high peroxide concentration leads to an increase of mutual deactivation of primary radicals before the possible attack of radicals on the PP macromolecules. The growth of the degradation efficiency of PP with the time of the decomposition of impregnated peroxide in PP also occurs in S-like curves of the MFI increase in the time variation for particular initial TBPB concentrations. The acceleration of the degradation in the first stage of annealing is not necessarily associated only with the diffusion of peroxide from the surface into the PP particles, but it can also reflect the initial narrowing of the polydispersion of the molecular mass of PP.

Competition Reactions in Degradation Process of Macromolecules

By evaluating the changes in MFI during peroxide decomposition, decrease in the degradation efficiency is observed, which, after a certain amount of peroxide is decomposed, leads to significant dominance of crosslinking over degradation. Under particular experimental conditions, it is after the decomposition of 50 mmol TBPB/kg PP (Fig. 2). This result shows that degradation and crosslinking initiated by the free radical proved not only to be a character of competition reactions but also of the processes with an element of succession. In general, during peroxide modification of PP, two processes can take place simultaneously: a decrease of various labile bonds and an increase of the concentration of more reactive crosslinking centers in the macromolecules.

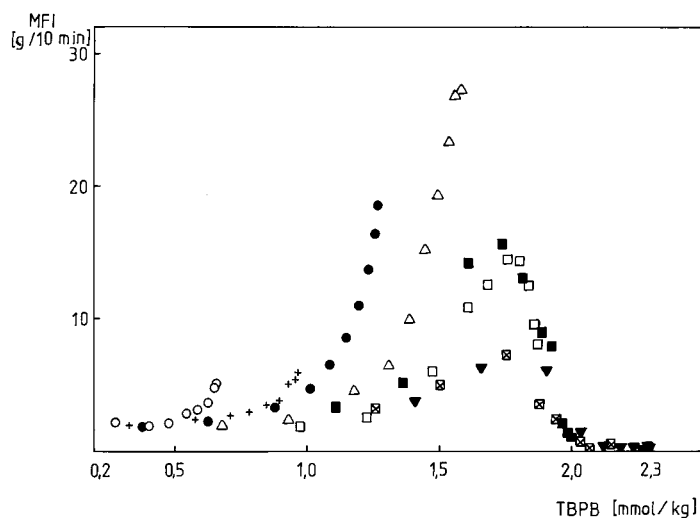An approach similar to that used for characterizing PP degradation was chosen for quantitative

Figure 2   Plot of MFI of PP versus the amount of decomposed TBPB at various initial concentrations: (○) 4.62, (+) 9.25, (●) 18.5, (△) 37.0, (□) 74.0, (■) 100.0, (⊠) 139.0, and (▼) 200.0 mmol/kg iPP at reaction temperature of 129°C.

Table III   Quantitative Data Characterizing the Decrease of MFI of PP with the Time of TBPB Decomposition (in the Region of Higher Initial Concentration 74–200 mmol/kg PP) at 129°C

[TBPB] (mmol/kg)	Δt [min]	n	k_x (10^3 min^{-1})	Cor. c.	k_x/[TBPB] $(\text{kg mol}^{-1} \text{ min}^{-1})$	k_x' [b] $(\text{kg mol}^{-1} \text{ min}^{-1})$
74	55–210	5	4.17	0.994	0.0564	0.0737
100	30–210	7	16.5	0.944	0.165	0.139
139	20–100	6[a]	58.7	0.945	0.422	0.280
200	10–55	5[a]	88.4	0.956	0.442	0.604

The value of k_x was calculated similarly to k_s in Table I, but from the decreasing part of the dependence of MFI on time (after maximum).

[a] Final points of the plot, when MFI decreased below 0.2 g/10 min, were not been included into evaluation in respect to the large absolute error of measurement.

[b] Calculated values of the previous column from the statistically evaluated dependence [TBPB] versus k_x/TBPB. The dependence can be expressed by the relation $k_x' = 0.8 \times 10^{-5} \text{ [TBPB]}^{2.115}$ (cor. c = 0.933).

evaluation of the growth of the molecular mass; however, we used the data of MFI after reaching their maximum value at the time of annealing and decomposition of TBPB. The decrease of MFI with the time of reaction of the TBPB radicals shows (Table III) not only the growth of the crosslinking constant k_x with an increase in peroxide concentration, but, and this is important, also the exponential growth of the constant k_x' recalculated per unit amount of decomposed TBPB. This fact confirms the importance of an instantaneous radical concentration for the resulting effect of the change of MFI during the decomposition of the radical precursor in PP. Simultaneously, the results point to the need of a certain total production of radicals (in the first approximation independently of their instantaneous concentration) to manifest the decrease of the MFI of PP under the effect of the free radicals of the initiator. The dominance of the growth of the molecular mass over the degradation of PP chains is explicable by the change in the structure of the macromolecules due to the effect of radicals formed by the decomposition of TBPB.

Formation of Double Bonds

The process which introduces a significant change into the chemical properties of the PP macromolecules is the fragmentation of the macroradical reaction itself:

The splitting of the macromolecule does not only lead to a decrease in molecular mass but also

to the formation of an unsaturated double bond. The second, yet the more important, source of new vinylidene bonds is disproportionation of PP macroradicals during which radicals

decay by transfer of the hydrogen atom from the beta carbon of one of the pair of radicals to the carbon of the radical center of the second radical. This results in the formation of macromolecules with double bonds, and, therefore, both by disproportionation and by fragmentation, vinylidene bonds will accumulate in the PP during peroxide decomposition (Table IV). From the IR measurements of a series of samples of degraded PP, it follows that at the reaction of radicals arising at the decomposition of TBPB with PP in a decisive proportion vinylidene bonds are formed but vinyl bonds are not accumulated. For the formation of one vinylidene bond in PP, three to five molecules of TBPB have to be decomposed. From the plot of $\angle \text{C}{=}\text{CH}_2$/[TBPB] versus the time (Table IV), it seems that the main reaction mechanism of the formation of the double bonds is the disproportion of the PP$^\bullet$ macroradicals. A small efficiency of this process is probably connected with a high proportion of decay of primary radicals in a cage of the solid or very viscose polymer system but also the radical addition onto the forming double bonds. Addition reactions of macroradicals are a source of branching and crosslinking of PP. The growth of the molecular mass can be realized not only through recombination of nonfragmented radicals but also through the addition of macroradicals to the double bond in PP macromolecules.

Table IV   Plot of Concentration of Vinylidene Bonds Versus the Time of TBPB Decomposition in i-PP and Changes of MFI of PP in Time Dependence

Reaction Time t (min)	$\rangle C{=}CH_2$ (mmol/kg)	MFI (g/10 min)	Decomposed TBPB (mmol/kg PP)	$\dfrac{\rangle C{=}CH_2{}^{a}}{[TBPB]}$
0	6.15	1.7	0	—
5	8.85	3.1	15	0.18
10	11.9	4.8	29	0.20
20	20.0	8.9	51	0.27
40	29.2	2.0	83	0.28
55	32.7	0.6	100	0.27
70	33.9	0.1	111	0.25
100	35.4	0.1	125	0.23
150	36.2	0.2	135	0.22
210	35.8	0.2	138	0.22
40[b]	6.92	2.1	2.8	0.28

The initial concentration of TBPB = 139 mmol/kg PP.

[a] There is the difference between the initial concentration of vinylidene bonds and vinyl bonds in the reaction time t divided by the amount of decomposed TBPB in time t.

[b] Result for an experiment where the initial concentration of the initiator TBPB = 4.62 mmol/kg PP.

The most significant consequence of the increased concentration of the double bonds is, however, the increase of the concentration of the radicals of the allyl type which will be formed by transfer reactions of radicals with the polymer chain containing a double bond:
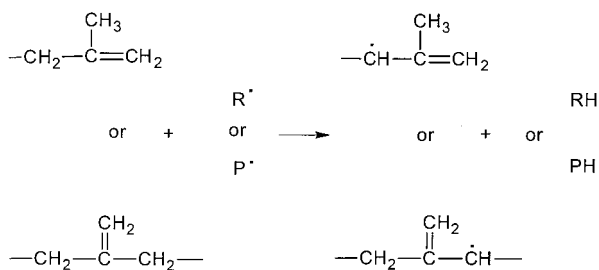
In the initial phase of the decomposition of TBPB in PP, there should prevail alkyl macroradicals,[13] which, during termination, will be preferably disproportionated. As follows from the rate constants for disproportionation k_d and combination k_c, the ratio k_d/k_c is for tert-alkyl radicals higher than 2.5, but for allyl radicals, it is only about 0.01 (ref. 2) and, thus, the increase of the concentration of allyl radicals will substantially increase the portion of reactions leading to the molecular mass increase of modified PP.

Summing up the known facts, the most common idea of peroxide crosslinking of PP, consisting of recombination of tertiary macroradicals,

should be supplemented by the mentioned multistep processes. Such a mechanism is also supported by the results of the effect of ionizing radiation on PP.[14] Other authors[15,16] found that, with small doses, the limiting viscosity number of irradiated PP decreases at first and increases only after the critical dose. These authors and many others proved simultaneous formation and decay of different types of double bonds taking part in crosslinking during PP irradiation. In the presence of multiple bonds between PP macromolecules, crosslinking efficiency increases even when unsaturated low molecular weight monomers are present in the system (e.g., refs. 17 and 18). Another convincing example of the important role of double bonds in a polyalkene macromolecule in the crosslinking process is the fact that the crosslinking of hydrogenated polyethylene, in which anomalous mers containing double bonds are not present, is less efficient.[19, 20, 21]

CONCLUSIONS

Changes in the MFI of PP were examined after partial decomposition of TBPB in the polymer at 129°C and the following extraction of undecomposed peroxide. The degree of destruction and/or crosslinking of PP depends on the amount of peroxide decomposed. Only in the samples with a

high concentration of peroxide as a further effect of the radicals was an increase of molecular mass of PP observed. The molecular mass of PP decreases in the first stages of degradation also in the samples with high peroxide decomposition and a further effect of radicals leads to increase in the molecular mass. This time dependence of the degradation and structuralization effect of peroxide on PP has not been described yet. The importance of the presence of the double bonds formed by chain scission and disproportionation of macroradicals for the efficiency of the formation of side chains and crosslinks between macromolecules was discussed.

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