

Modification of Polypropylene by UV-Radiation

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Polypropylene (PP) is a commodity plastic that can be used for various applications. Conventional methods for synthesizing PP result in a broad molecular weight distribution (MWD) with high molecular weight averages. In order to accommodate processing requirements in various applications, the molecular weight distribution of PP needs to be adjusted. For this reason, long chains of PP may be degraded. After degradation, PP has lower viscosity and is referred to as “controlled rheology PP” (CRPP)[1,2].

Furthermore, in spite of the large market of polypropylene, poor rheological properties such as lack of melt strength limit its processing in certain applications. The melt strength of PP can be modified by introducing long chain branching (LCB) to its backbone [4,5].

In order to modify melt strength or decreasing its MWD benzophenone (BPH) is used as photo-initiator for generating the radicals in the PP backbone. UV radiation is conducted in solid state. Effect of radiation duration on the degree of degradation and LCB is studied in this work.

Experimental procedure and characterization

PP homopolymer (Pro-fax PH 382M) from Lyondell Basell Ind. with \bar{M}_n and \bar{M}_w of 66,900 and 314,900 was used along with Benzophenone (99% purity).

In order to come up with a homogeneous distribution of BPH with PP pellets, 0.5 wt-% of benzophenone was dissolved in acetone and mixed with the pellets at room temperature. After evaporation of the acetone, the pellets were impregnated with benzophenone [3].

Impregnated pellets were mixed inside the batch mixer at 200 °C and 100 rpm for 7 minutes. The samples were ground and compression moulded into discs with 25 mm diameter and 1 mm thickness at 200 °C under applied force of 10000 lb_f for five minutes.

The discs were irradiated using a Mercury UV lamp (Versa Cure). Radiation was set at 47 % of the lamp intensity.

Irradiation steps were conducted in one minute intervals. Samples were irradiated for 60, 120, 240 and 360 seconds in 60 seconds intervals. Before each irradiation intervals the lamp was turned on for three minutes so that a constant level of radiation intensity was achieved. After three minutes, samples were irradiated for a minute and then the lamp was turned off to cool down. During irradiation, pressurized air was used to cool down the area beneath the lamp and keep temperature below 50 °C.

Table 1 shows the sample number and duration of irradiation for each sample. In all runs except one (run 2 in Table 1) samples were irradiated on both sides, which means that half of the irradiation time was spent irradiating one side and the other half was spent irradiating the other side. The labels in Table 1 are used to identify different samples on the graphs/plots that follow. These labels show the run number along with the number of 60 s intervals that each side of the disc was irradiated. For example, 2-1s1 means run 2, one side irradiated, for one time interval (60 s). As another example, 4-2s2 means run 4, two sides irradiated, for two 60 seconds time intervals.

Table 1: Experiment runs for studying the effect of UV exposure duration

Run number	Conc. ¹ (wt-%)	Radiation (%)	Label	Total duration(s)
1	0.5	0	1	0
2	0.5	47	2-1s1	60
3	0.5	47	3-2s1	120
4	0.5	47	4-2s2	240
5	0.5	47	5-2s3	360

1. Concentration

Parallel plate rheometer at constant stress was used to measure rheological properties of the irradiated mixtures. The actual tests were subsequently performed within the frequency range of 0.01-100 HZ at constant strain of 4 %.

Results and discussions

Cole-Cole plots are also constructed (Figure1) to compare the virgin PP with the irradiated samples. It can be seen that at the low frequency range runs 4 and 5, which are irradiated for longer times, show more elastic behaviour (greater G') than virgin PP (run 1). The initial part of the graph has blown up again in order to visualize this trend better. Figure1 also indicate that in runs 2 and 3 the PP chains are mostly degraded and thus appear below runs 1, 4 and 5.

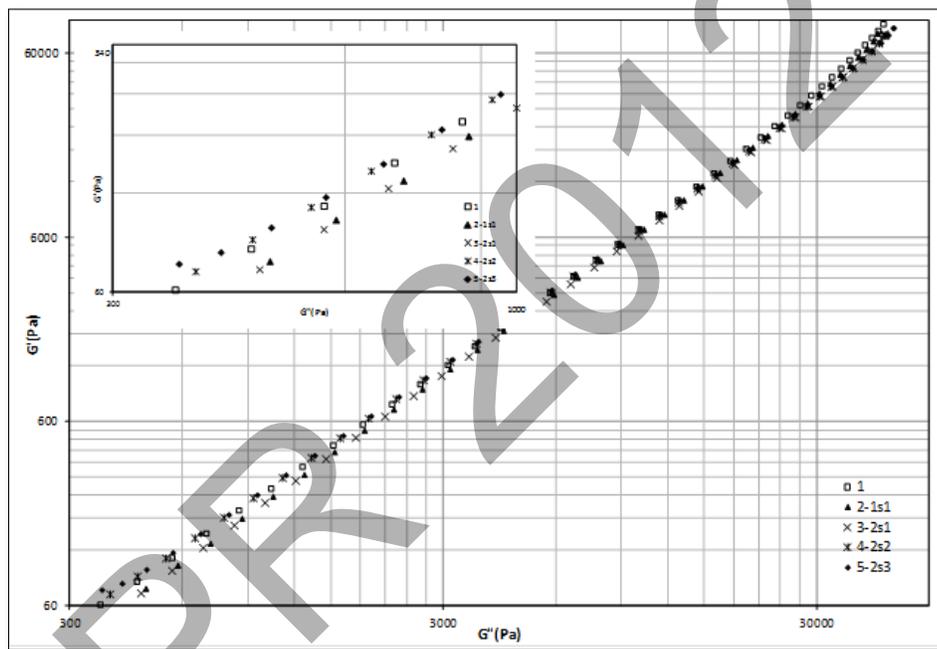


Figure 1: Cole-Cole plots for runs with different irradiation time, the small graph is zoomed at low frequencies

Figure 2 shows complex viscosity (η^*) versus frequency and it indicates that more irradiation time results in higher viscosities and more shear thinning behaviour. It has been reported that long chain branched PP has greater complex viscosity values, smaller flow index and smaller Newtonian plateau region compare to linear PP [4]. In Figure 2 it can be seen that runs 4 and 5 show higher viscosities compare to runs 2 and 3 due to formation of long chain branches or any other network. In run 5 this increase at the terminal region results in complex viscosity that is as high as virgin PP viscosity. Furthermore, it can be

seen that Newtonian region is eliminated in run 4 and 5 and it becomes shorter as the irradiation duration increases. Moreover, run 4 and 5 show more shear thinning behaviour compare to the virgin PP (run 1) and runs that have been gone through degradation (runs 2 and 3). These behaviours are also in agreement with the behaviour reported for long chain branched PP in the literature [4-8].

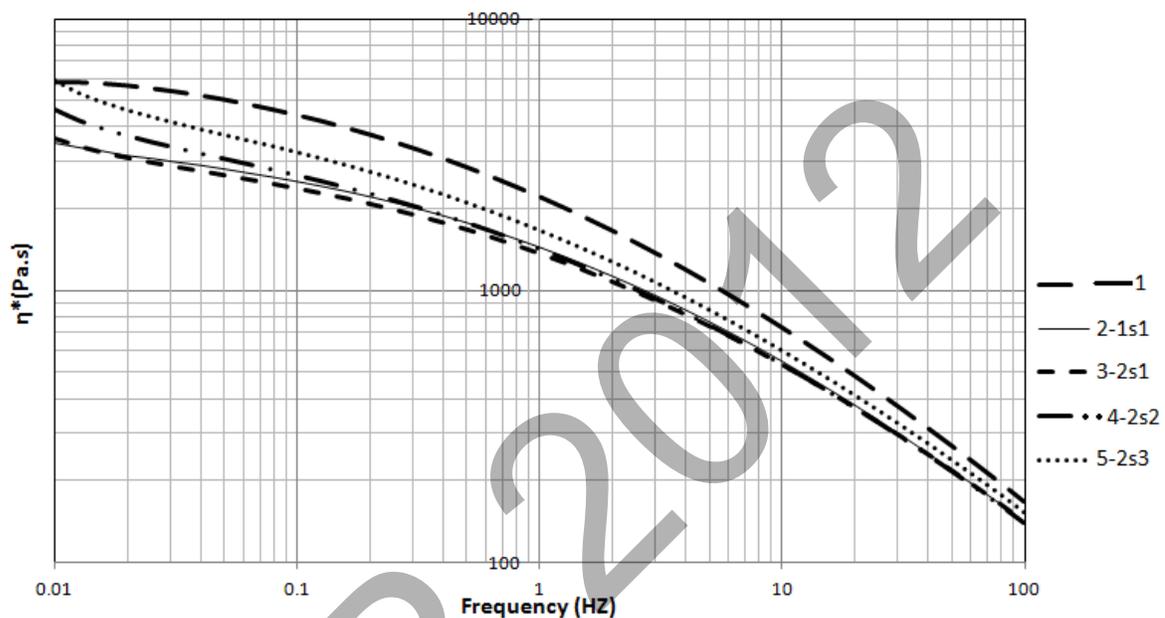


Figure 2: Changes in complex viscosity (η^*) vs. frequency plots for runs with different irradiation time

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Problems with Commercial Polypropylene (PP)

High molecular weight (MW) averages

- Low melt flow rate (MFR)
- Difficulty in processing

Broad molecular weight distribution (MWD)

- High elasticity
- Need for low elasticity in some processing applications

Low melt strength

- Foaming, thermoforming, film blowing, blow moulding; not possible

Solutions

Controlled degradation

Long chain branching (LCB)

Refs [1-5] 2

Controlled Rheology PP (CRPP)

Break long PP chains
Increasing MFR

Reduce MW

Chemical modification

- Utilizing peroxide initiators
- Techniques: Ampoule, Extruder

Narrow the MWD

Radiation techniques

- Gamma
- Electron beam
- Ultraviolet (UV)

Ref[2,6-12] 3

UV-Initiation kinetics

$$R^* + P_r \xrightarrow{k_2} RH + P_r^*$$

Initiation

- BPH absorbs UV light and generates an electronically excited state.
- This excited state can be either a singlet or a triplet.

S + hv $\xrightarrow{\text{Absorption}}$ $^1S \rightarrow ^3S$

- Triplet state can abstract tertiary H from PP backbone.

$^3S + P \xrightarrow{K_a} S^* + P^*$

Refs [12,14-16] 4

Modification: UV Radiation

Ref[12] 5

Methods for Production of Long Chain Branched PP (LCB PP)

- Addition of co-agents:
 - Multi functional chemical compounds
 - Reaction with radical center on PP backbone \rightarrow stabilizes the radical center
- Electron beam radiation
- Utilizing supercritical fluid (SCF)
- Utilizing photo-initiator

Multi functional acrylic

TAM

Macroradical

Multi functional allylic

TMPTA

Multi functional acrylic

TAP

Styrene monomer

Refs [8-10,17,19] 6

Steps/Objectives of the Project

Modifying rheology of PP by photo-initiator

- Investigating effect of radiation duration and cooling

Increasing the melt strength of polypropylene by LCBs

- Modification in solid state
- Temperature around 53 °C or lower

Characterizing modified PP

- Rheometry
- GPC

Experiments: Materials and Methods

Pre-impregnation of PP granules with BPH
 Melt mixing in the batch mixer
 Grinding
 Hot pressing
 Irradiation (1 to 8 minutes)
 Characterization

Refs [12,24,25]

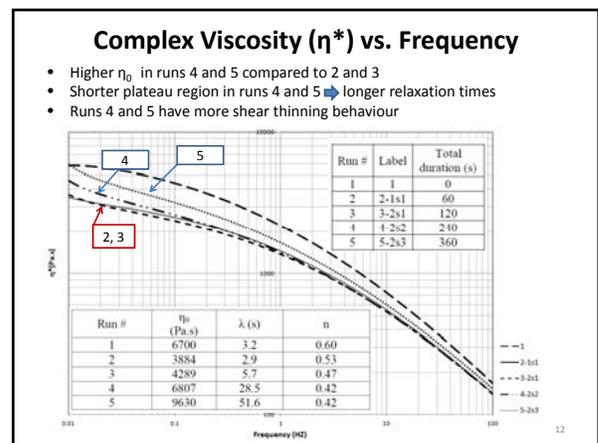
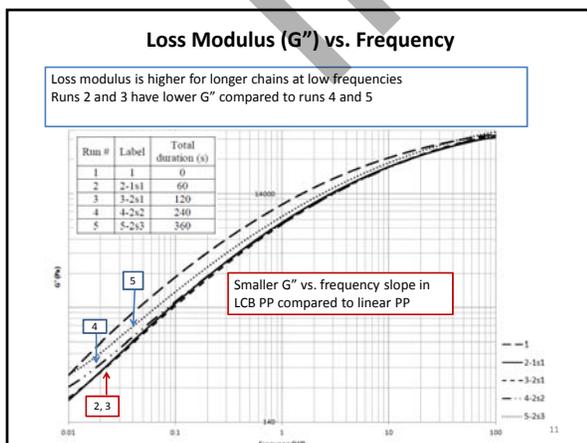
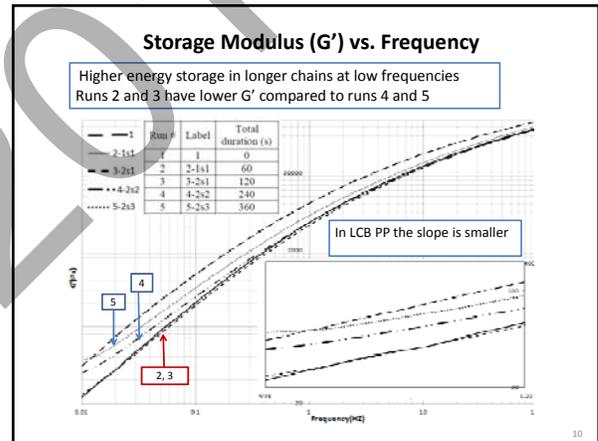
Characterization: Rheometry

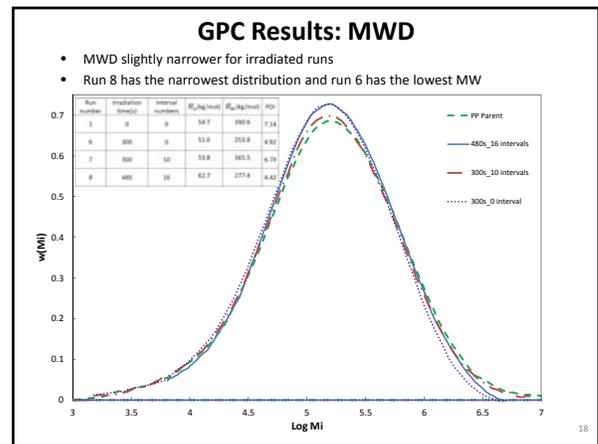
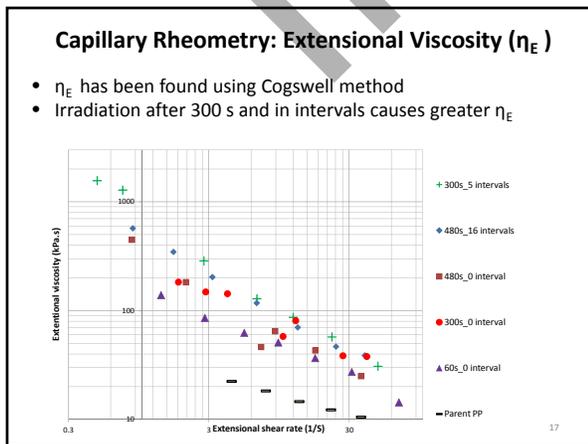
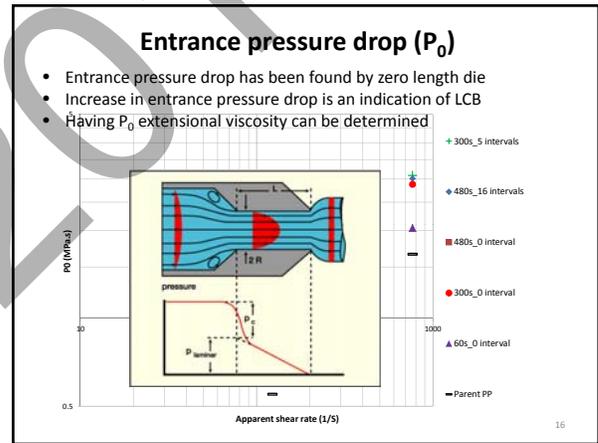
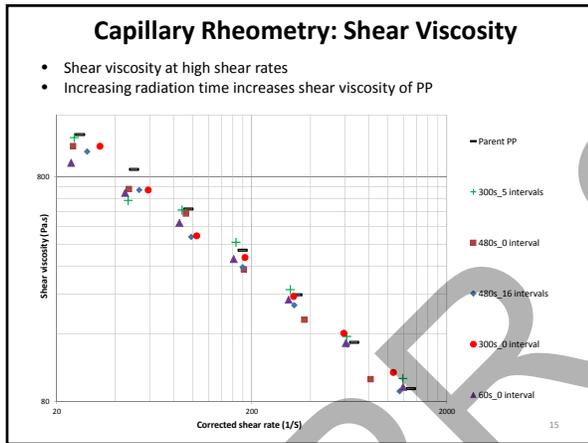
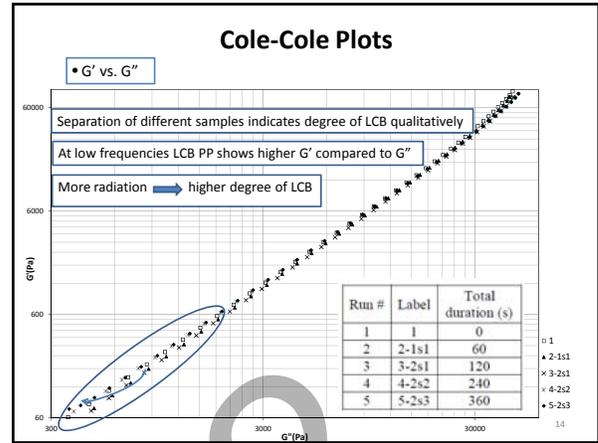
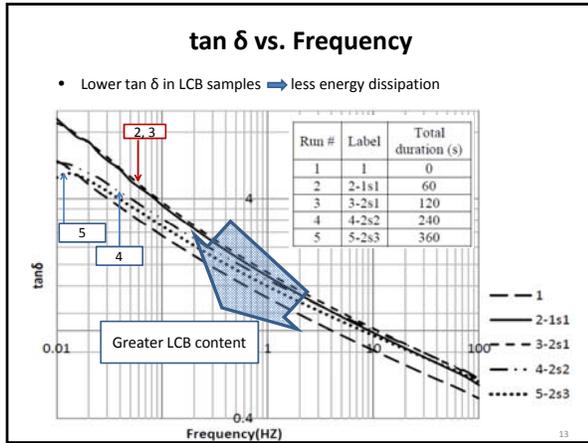
Degradation → linear polymer with shorter chains and narrower MWD than parent polymer
 Reference for comparisons: Linear PP with broad MWD

G' : Storage modulus G'' : Loss modulus $\tan\delta$: Loss angle η^* : Complex viscosity

Rheological properties	Degradation	LCB	Comment
G' at low frequencies	↓	↑	Higher G' → more elastic
G' - ω slope at low frequency	No change	↓	
G'' at low frequency	↓	↑	Higher G'' → more energy dissipation
G'' - ω slope	No change	↓	
$\tan\delta$ - ω	↑	↓	More viscous behaviour
η^* at low frequencies	↑	↓	
η_0	↓	↑	
Shear thinning index (n)	↑	↓	Lower n → more shear thinning
Relaxation time (λ)	↓	↑	Shorter plateau region for LCB

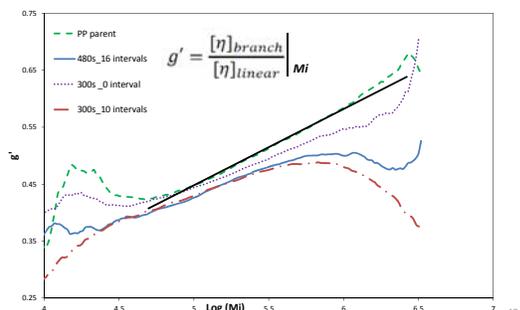
Refs [20,23]





LCB Content

- Increasing irradiation time from 300 to 480 s decreases the degree of branching
- Irradiating in intervals increases degree of branching



Concluding Remarks

BPH can act as an initiator for PP modification reactions

Radiation in solid state ($T < 53^\circ\text{C}$) leads to LCB

Increasing radiation time to 5-6 min leads to greater degree of LCB

Irradiation at temperatures greater than 53°C leads to β -scission and narrowing MWD

Larger G' , η_0 and more shear thinning behaviour confirm formation of LCBs

Higher η_e and P_0 are indications of formation of LCB

Thank You

Questions?

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Kinetics of PP Degradation and LCB

- The following reactions are considered for PP modification:

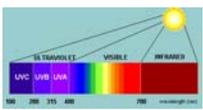
$S \xrightarrow{K_1} 2R^*$	Initiation
$R^* + P_r \xrightarrow{K_2} RH + P_r^*$	
$R^* + P_r \rightarrow P_i + P_r^* + R$	β -scission
$P_r^* + P_r \xrightarrow{K_4} P_r - P_r$	Termination (Combination)
$P_r^* + P_r \xrightarrow{K_5} P_r + P_i$	Termination (Disproportionation)
$P_r^* + Q \xrightarrow{K_6} P_r - Q^*$	Grafting to small molecule
$P_r - Q_n^* + P_r \xrightarrow{K_7} P_r - Q_{n+1}^*$	Small molecule addition
$P_r - Q_n^* + P_s \xrightarrow{K_8} P_r - Q_n - P_s$	Long chain branching
$P_r - Q_n^* + P_s - Q_m^* \xrightarrow{K_9} P_r - Q_{m+1} - P_s$	Cross-linking

Ref[7] 26

BPH UV-initiation Kinetics

- Absorption of UV light

$$S + h\nu \xrightarrow{\text{Absorption}} {}^1S \rightarrow {}^3S$$

$$I_a = -\frac{d[S]}{dt} = \frac{d[{}^1S]}{dt}$$


Beer-Lambert law:

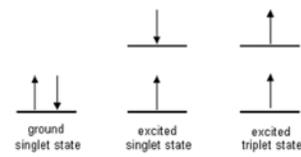
$$\frac{I_t}{I_0} = 10^{-\epsilon l [S]}$$

$$I_a = I_0 - I_t = I_0(1 - 10^{-\epsilon l [S]})$$

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Excited State Generation

- UV absorption electron transition from ground state to a higher orbital (internal conversion IC) spin favoured transition formation of Singlet state (S_1)
- Radiationless transition from unpaired spin favoured state (S_1) to spin forbidden state (T_1) (inter system crossing ISC)



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Other Probable Reactions

${}^3S + P \xrightarrow{K_q} S + P$ Physical quenching

${}^3S \xrightarrow{K_d} S$ Deactivation

${}^3S + P \xrightarrow{K_a} S^* + P^*$ Hydrogen abstraction

Rate of initiation $\frac{d[S]}{dt} = K_a [P][{}^3S]$

Rate of Triplet state consumption:

$$\frac{d[{}^3S]}{dt} = I_a - (K_0 + K_q[P] + K_a[P]) [{}^3S]$$

With SS assumption:

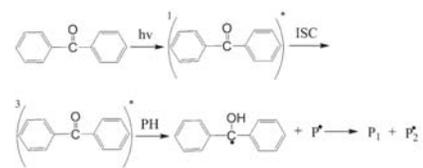
$$\frac{d[{}^1S]}{dt} = 0 \quad \frac{d[S]}{dt} = \frac{K_a [P] I_0 (1 - 10^{-\epsilon l [S]})}{(K_0 + K_q[P] + K_a[P])}$$

$$\frac{d[{}^3S]}{dt} = 0 = I_a - (K_0 + K_q[P] + K_a[P]) [{}^3S]$$

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BPH Radical Formation

- UV absorption
- Formation of (S_1)
- Formation (T_1)
- Hydrogen abstraction from H donor (PP)



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Kinetics of PP Peroxide Degradation

- Moments model: Predicts \bar{M}_n, \bar{M}_w and PDI of PP after degradation
- The following reactions are considered for PP modification using peroxides

$S \xrightarrow{K_1} 2R^*$	Initiation
$R^* + P_r \xrightarrow{K_3} P_r + P_{r-1}^* + R$	β-scission
$P_r^* + P_r \xrightarrow{K_5} P_r + P_r$	Termination (Disproportionation)
$P_r + P_r \xrightarrow{K_{tr}} P_r + P_{r-s}^*$	Transfer to polymer
$P_r \xrightarrow{K_{deg}} P_r^* + P_{r-s}^*$	Thermal degradation

By solving four differential equations Q_1, Q_2, Q_3 and initiator conc. vs. time will be found

S	Initiator	Initiator conc.	Initiator efficiency factor	time	[S]	[R*]	[P _r]	[P _r]	[P _r]	[P _r]
R*	Initiator radical									
P _r	Initiator conc.									
Q ₁	1 st moment of MWD									
K ₁	f									
K ₃										

By solving four differential equations Q_1, Q_2, Q_3 and initiator conc. vs. time will be found

$\frac{d[S]}{dt} = -K_1[S]$	$\frac{dQ_0}{dt} = -Q_1 - 3Q_2$	$\frac{dQ_1}{dt} = -Q_1 - Q_2$
$\frac{dQ_2}{dt} = -\frac{1}{3}Q_3 + \frac{1}{3}Q_1 - 2Q_2$	$Q_3 = \frac{2Q_2}{Q_1 Q_0} (2Q_2 Q_0 - Q_1^2)$	$\theta = 2fK_1[S]$

Step model

This model predicts the whole MWD
Initiation, β-scission and termination are reactions considered for modeling the MWD

$S \xrightarrow{K_1} 2R^*$	Initiation
$R^* + P_r \xrightarrow{K_3} P_r + P_{r-1}^* + R$	β-scission
$P_r^* + P_r \xrightarrow{K_5} P_r + P_r$	Termination (Disproportionation)

Writing the rate of these reactions and assuming S.S for intermediates the following reactions will be obtained:

$$[P_r] = \frac{\lambda_3 + \lambda_2(P_r)}{\lambda_2} \exp[\lambda_2 \lambda_1 (t_2 - t_1)]$$

$$\lambda_1 = \frac{2fk_1 m_0 [S]_0 \exp(-k_1 t)}{\rho} \quad \lambda_2 = (1-n) \quad \lambda_3 = 2 \sum_{r=n+1}^{\infty} [P_r]$$

Concentration of a chain with length "r" at time "t" from initiation of reaction

Concentration of a chain with length "r" at time "t-1" from initiation of reaction

Having the parent PP MWD $[P_r]_{t=0}$, molecular mass of monomer unit m_0 , MWD of PP after passing time "t" from reaction initiation

n - Number of repeating units in the chain

Rate of UV-initiation

- Moments and step model can be used for predicting MW of PP after UV degradation
- The initiation rate should be modified for UV-initiation reaction

S + hv -> [S] -> [S] -> [S] + ISC -> [S] + ISC
[S] + P -> S + P*

$$\frac{d[S]}{dt} = 2300 \Phi \epsilon I_0 [S]_0 \text{ intensity} [K_1] - 2300 \Phi \epsilon I_0$$

Quantum yield of BPH in initiation
K₁ compare to the rate constant of other possible reactions, i.e. initiator quenching or deactivation

Initiator concentration
Molar absorption coefficient
Initiation rate constant
amount of radiation photo-initiator absorbs

Moments model predicts faster kinetics

Both models deviate from experimental results

Polypropylene	\bar{M}_n (kg/mol)	\bar{M}_w (kg/mol)	PDI
Parent	66.6	242.2	3.6
After UV radiation	51.0	159.3	3.1
Moments model (t=100)	62.98	195.54	3.1
Step model (t=100)	59.11	182.47	3.1

Results: step model predictions

Scission of long chains
Decrease in PDI

Reasons for deviation

- Φ and I₀ amounts are not accurate
- Degradation due to UV radiation without initiator is not taken into account
- Residence time in the profile is not known.
- Chain transfer reactions/thermal degradations are not taken into account.

Scission of short chains is not predicted in the model