

## Polypropylene degradation: Theoretical and experimental investigations

Denis Bertin, Marie Leblanc, Sylvain R.A. Marque\*, Didier Siri

UMR 6517, Université de Provence, case 521, 13397 Marseille Cedex 20, France

### ARTICLE INFO

#### Article history:

Received 17 September 2009

Received in revised form

1 February 2010

Accepted 3 February 2010

Available online 10 February 2010

#### Keywords:

Polypropylene degradation

DFT calculations

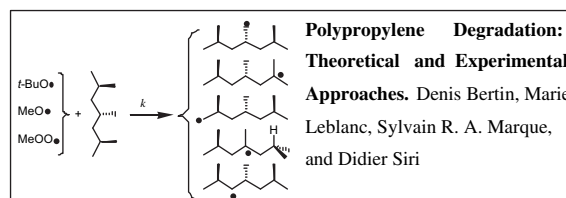
Radical chemistry

Peroxides activities

### ABSTRACT

The controlled-rheology peroxide degradation of polypropylene is a major issue for the industry. Combining DFT calculations – about H-abstraction onto model 2,4,6-trimethylheptane by model radicals such as *t*-butoxyl, methoxy, and methylperoxy – with degradation studies of short chain polypropylene, we showed that the degradation depended a lot on the amount of oxygen, on the temperature, on the concentrations of both polypropylene and peroxide, and on the radicals generated from the thermal decomposition of peroxide. Besides the expected enthalpic control on the H-abstraction reaction, the bulkiness of both the oxyl radical and the reactive centre modified dramatically the regioselectivity, i.e., preferred H-abstraction from the terminal primary carbon atom by the *tert*-butoxyl radical vs the H-abstraction from the terminal tertiary carbon atom by methoxy and methylperoxy radicals.

*Graphical abstract:*



© 2010 Elsevier Ltd. All rights reserved.

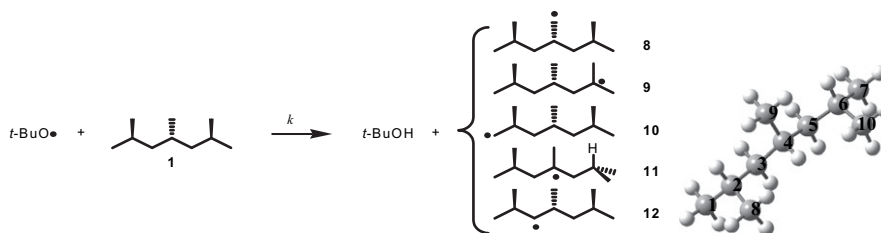
### 1. Introduction

Polyolefin modification reactions [1] (degradation [2], grafting [3] or cross-linking [4]) are widely used in the conversion of low cost polymers. One of the most polymers used is the isotactic polypropylene PP, because it is easy to handle, stable towards aqueous solutions and organic solvents, and thermally stable [5]. Its interesting properties, used in many applications, depend a lot on its averaged molar mass  $M_n$ , its averaged weight mass  $M_w$ , and its polydispersity index PDI [6,7].  $M_n$ ,  $M_w$ , and PDI can often be modified through oxidative degradation of the polypropylene [8]. That is, the first step is always the abstraction by free radicals of a hydrogen atom from the polymer backbone (H-abstraction). In factories, the degradation of PP occurs at high temperatures (>200 °C, melted polymer) in a screw, and sometimes in the presence of peroxides as radical initiators [9,10]. Therefore, several models describing the degradation of PP in a screw were developed taking into account several aspects: the chain cleavage and

self-termination reactions [11], the homolysis of peroxides [6,12], the fragmentation/self-termination/chain transfer reactions of the polymeric radicals [13], all the reactions occurring during the degradation of PP [14], the kinetics of the degradation reactions [15]. However, the characteristics of the polymer depend largely on the industrial set-up, making the development of general models very difficult.

There are several potential sites of abstraction on the polymer backbone. Therefore, polypropylene (PP) degradation [16] depends a lot on the relative rates of H-abstraction from various C–H bonds by alkoxy radicals (peroxide degradation [peroxide degradation [10,17]]) or by  $O_2$  (oxidative degradation [18,19]). Over the last 50 years, several experimental studies have been carried out on model structures of PP to understand the processes of peroxide [20–24] and oxidative [25,26] degradation. These model structures are generally 3-methylpentane, 2,4-dimethylpentane (DMP) and 2,4,6-trimethylheptane **1** (Scheme 1). On the other hand, the study of PP degradation in solution aroused little interest although the experimental conditions – such as the homogeneity of the solution, the concentration of peroxide, the amount of oxygen, the temperature and pressure, the experimental time – were better controlled

\* Corresponding author. Tel.: +33 (0) 491288046; fax: +33 (0) 491288758.  
E-mail address: [sylvain.marque@univ-provence.fr](mailto:sylvain.marque@univ-provence.fr) (S.R.A. Marque).



**Scheme 1.** Radicals generated by H-abstraction with  $t\text{BuO}(\cdot)$  on **1** the molecule model of PP.

and more reproducible than those for industrial set-ups [27–31]. These studies showed that the degradation processes depended on the length of the polymer chain, on the peroxides and the subsequently generated radicals, the solvents, the temperatures, the concentrations of both PP and the peroxides. However, they did not discuss the potential role of the oxygen on the processes of degradation. In this paper, we present a study of the efficiency of various peroxides (Fig. 1) such as ditert-butylperoxide **2** ( $t\text{-BuOO}t\text{-Bu}$ ), 2,2,5,5,8,8,11,11-octamethyl-3,9-diperoxidodecane **3**, 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxinonane **4**, dicumylperoxide **5**, and also of the *tert*-butyl hydroperoxide **6** ( $t\text{-BuOOH}$ ), and of the *tert*-butylperoxyl *iso*-propyl carbonate **7** ( $i\text{-PrOCOO}t\text{-Bu}$ ) on the degradation of low molar weight ( $M_w \approx 12\,000\text{ g mol}^{-1}$ ) polypropylene in 1,2,4-trichlorobenzene as solvent. The efficiency of these oxidants was estimated by measuring the diffusion coefficient  $D$  of the polymer solution by Diffusion Ordered Spectroscopy (DOSY) [32,33], since the value of  $D$  is directly related to the molar weight  $M_w$ . Then, DFT calculations [34] on the hydrogen atom abstraction reaction from 2,4,6-trimethylheptane – model of syndiotactic polypropylene – by several radicals mimicking the most active primary radical species were performed, aiming to get a deep insight into the initial molecular processes involved in degradation of the polypropylene (PP).

## 2. Experimental section

Polypropylene ( $M_w \approx 12\,000\text{ g mol}^{-1}$ ,  $\text{PDI} = 2.4$ ) as pellets [35] and 1,2,4-trichlorobenzene were purchased from Aldrich and used as received. Ditert-butylperoxide **2** (95%), 2,2,5,5,8,8,11,11-octamethyl-3,9-diperoxidodecane **3** (95%), dicumylperoxide **5** (95%), *tert*-butyl hydroperoxide **6** (70%w in water), *tert*-butylperoxyl *iso*-propyl carbonate **7** (75%w in isodecane) were kindly provided by Arkema and used as received. 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxinonane **4** (41%w in isopar M) was purchased from Acros and used without further purification.  $^1\text{H}$  NMR was performed in tetrachloroethane- $d_2$  as solvent on an Advance 400 MHz Bruker spectrometer at the Spectropole Marseille.

### 2.1. Degradation of PP under nitrogen atmosphere

In a 100 ml three-neck round bottom flask, PP (10 g) was solved in 15 g of 1,2,4-trichlorobenzene at  $85\text{ }^\circ\text{C}$  for 30 min. Then, the peroxide solved in 5 g of 1,2,4-trichlorobenzene was added dropwise, and the solution was again degassed for 30 min with nitrogen bubbling at  $85\text{ }^\circ\text{C}$ . Then, the solution was heated to  $140\text{ }^\circ\text{C}$  or  $165\text{ }^\circ\text{C}$  for five times half-life time of the peroxide under magnetic stirring. Then, the solution was cooled down to room temperature and the solvent removed under vacuum.

### 2.2. Degradation of PP under oxygen atmosphere

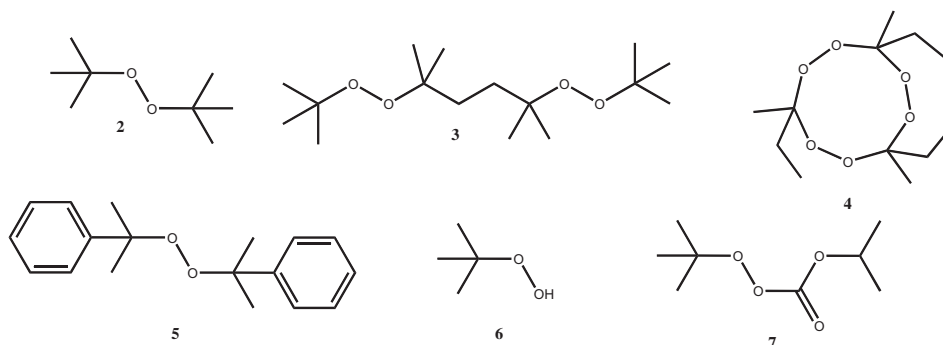
In a 100 ml three-neck round bottom flask, PP (10 g) and peroxide when required were solved in 15 g of 1,2,4-trichlorobenzene. Then, the solution was bubbled with oxygen for 20 min at room temperature. The solution was heated to  $140\text{ }^\circ\text{C}$  or  $165\text{ }^\circ\text{C}$  for five times the half-life time of the peroxide or 75 min under magnetic stirring. Then, the solution was cooled down to room temperature and the solvent removed under vacuum.

### 2.3. Degradation of PP under oxygen bubbling

In a 100 ml three-neck round bottom flask, PP (10 g) and peroxide when required were solved in 15 g of 1,2,4-trichlorobenzene. Then, the flask was sunk into a  $215\text{ }^\circ\text{C}$  pre-heated oil bath for 75 min under magnetic stirring and oxygen bubbling. The solution was cooled down to room temperature and the solvent removed under vacuum.

### 2.4. DOSY NMR experiment

The diffusion coefficient  $D$  was measured as described in the literature [36,37]. The crude material (1 mg) issued from the degradation procedure was solved in 0.7 ml of tetrachloroethane- $d_2$ .



**Fig. 1.** Peroxides investigated for the degradation of PP under controlled conditions.

Download English Version:

<https://daneshyari.com/en/article/5203551>

Download Persian Version:

<https://daneshyari.com/article/5203551>

[Daneshyari.com](https://daneshyari.com)