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Unravelling the contribution of chain microstructure in the mechanism of the syndiotactic polypropylene pyrolysis

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ABSTRACT

The pyrolysis of a highly syndiotactic and high-molecular weight polypropylene (sPP) has been thoroughly studied through preparative TGA experiments, which were performed up to final temperatures between 262 °C and 427 °C. The ^{13}C NMR characterization of the samples shows a two-stage process clearly evidenced by changes in the chain microstructure. In a first period, up to a 22% weight loss, the molecular weight collapses and only vinylidene end-capped chains are produced. In a second stage, over 22% weight loss, a wider variety of groups, including both terminal vinylen and isobutenyl functions as well as n-propyl tails, are also detected. Regardless the type, all these new species are formed at the expense of propylene units belonging to rrrr pentads.

The evolution of the E_{act} predicted by means of analytical TGA allows us to associate the lowest E_{act} value found with the changes taking place during the very beginning of the process (up to a 3% weight loss), i.e. the molecular weight collapse and a some evidence of configurational stereo-specificity. As regards the further E_{act} build-up, it can be rationalized in terms of the ability of chains to be rolled in the most stable GGTT conformation, as it is supported by complementary FTIR and DSC characterization of the samples.

1. Introduction

One of the topics in current polymer research to which it is worth dedicating a big effort is pyrolysis. This thermally induced degradation process provides a way to recover valuable chemicals, as well as to contribute to sustainability of the increasingly growing use of plastics in society. Additionally, the interest in pyrolysis is also large from a basic point of view, since the understanding of the mechanism involved is essential in the searching for both polymer-based materials showing improved fire resistance and special oligomers.

Concerning the first topic, the remarkable contribution of pyrolysis to the polyolefin degradation mechanism has been revealed. Actually, this process has been found to play in the ignition of PP at high heating rates, i.e. when the material is exposed to large heat fluxes, and is particularly influencing in the case of PP nano and micro-composites, where the combustion of the outer layer yields a silicate-rich surface through which the oxygen diffusion is hindered [1]. Similar results had been already reported for the LLDPE/montmorillonite composites [2]. In this case, the typical hydroperoxide-induced mechanism of the LLDPE degradation was found to change to an anaerobic one, when the degradation exceeds a conversion degree of 0.6. Such a change has been set out on the basis of the rate-limiting effect imposed by the inorganic layer to the oxygen diffusion into the material. As for the production of special polyolefin oligomers, the preparation of telechelics has been long pursued, as an example, for the purpose of rendering functional groups able to copolymerize polar monomers. On this matter, the viability of pyrolysis has been explored in some works [3,4].

Due to the fact that pyrolysis is a process taking place in an ever-changing material, it is of fundamental importance to know the evolution of the polymer intra-chain microstructure all along the process, so as to account for the nature of volatiles evolved and their releasing kinetics. In the case of PP, molecular weight, configuration and chemical nature of the defects produced are the main chain features which are expected to drive the E_{act} required. In the particular case of the configuration influence, Pen et al. [5] reported that the E_{act} of the PP pyrolysis depends whether on it is syndio or isotactic. Moreover, the FTIR monitoring of changes in the sPP chain conformation during the process, made evident that it requires the previous unrolling of the GGTT helix so as to yield the TTTT arrangement, which exhibits a lower E_{act} for chain scission.

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On this matter, some previous work carried out recently by us has indeed confirmed that, even though the nature and relative content of the volatiles are the same, the E_{act} of the sPP pyrolysis is linked to the syndiotacticity degree [6]. Actually, the pyrolysis E_{act} of a highly syndiotactic sPP was found to vary from 200 to 260 kJ/mol in the 10 wt% to 95 wt% weight loss range, which is clearly larger than the 110 kJ/mol shown by a low syndiotactic one in the same conversion range. This finding led us to propose that there could be a configurational specificity linked to the length of syndiotactic sequences and, consequently, a variation of the tacticity distribution could be expected as long as the pyrolysis progresses. To the best of our knowledge, no study in the literature has been carried out on the configurational evolution of PP in the course of pyrolysis. Only Sawaguchi et al. [4] have marginally reported no changes in the configurational microstructure in iPP pyrolysis at the triad level.

In an attempt to look for some evidences on the stereospecificity in the sPP pyrolysis, we present a study on the chain microstructure evolution of a high-molecular weight and highly syndiotactic sPP. The purpose is to monitor thoroughly the nature of chemical defects, appearing in the course of the pyrolysis up to a high conversion degree, and to know whether they are related to potential configuration changes or not. The study includes an analysis of the evolution of chain features by means of the FTIR and NMR techniques as well as an analysis of the changes in the DSC thermal properties, which are expected to vary accordingly.

2. Experimental part

2.1. Materials

Toluene (Merck) has been previously refluxed and distilled over metallic sodium and stored under N_2 to avoid the presence of traces of water and oxygen. Both propylene (Praxair 2.5) and nitrogen (Praxair 3X) were purified by flowing through oxygen-trap columns and molecular sieves before use. Diphenylmethylidene-cyclopentadienyl-(9-fluorenyl)-Zirconium-dichloride (*$Ph_2C(Cp)(9\text{-}Flu)ZrCl_2$*) (*Boulder Scientific*) and Methylaluminoxane (MAO) (10 wt% solution in toluene from Aldrich) were used as catalyst and co-catalyst respectively. The activated catalyst was prepared by dissolving 15 mg of the metallocene in 3 mL of MAO solution in a dry box. Ethanol (Acros, 96%) and HCl (VWR, 37%) were used for the precipitation of the polymers. Xylene (Panreac, 98%, mixture of isomers) was used as received for the purification of pyrolyzed samples. Tetraline (Aldrich, 99%) was stabilized with Irganox 1010 (1 g/L) prior to its use as a solvent for viscosimetry.

2.2. Polymerization procedure and preparation of the material

The syndiotactic polypropylene sample (sPP) was synthesized in a $^{1/4}$L stainless steel autoclave through the following steps. The reactor was firstly fit out by performing several N_2/vacuum cycles at 70 °C. Then the temperature was lowered to 20 °C and 90 mL of dry toluene were introduced. The feeding of propylene was on from this moment and maintained until a constant pressure of 2 bars at −5 °C was reached. Finally, 3 mL of the MAO solution and 0.250 mL of the catalyst/MAO complex in toluene were injected. The reaction was run at the initial pressure value and at −5 °C for 24 h. The polymerization was stopped by adding 5 mL of ethanol and enabling the unreacted propylene out from the reactor. The polymer was obtained in a powder state by pouring the reaction batch on an Ethanol/HCl (30:1) mixture. The precipitated was stirred thoroughly overnight, filtrated, washed again with ethanol and dried under vacuum at room temperature.

The so-obtained powder was processed as a film by compression-molding in a Collin 200×200 press. The processing conditions used were melting at 180 °C and 20 bar during 3 min and, finally, quickly cooling at room temperature by placing the mold between water-refrigerated plaques at the same pressure. The films obtained have a thickness of 175 μm.

2.3. Pyrolysis

The pyrolysis of the polymer in the film state was carried out by running dynamic TGA analysis [6] and also in an ad-hoc pyrolysis set-up so as to obtain quantities of dynamically pyrolyzed samples, large enough to perform a complete characterization of the polymer all along the process.

The analytical TGA measurements were carried out from 40 °C up to 750 °C in a Thermal Analysis TGA-Q-500 device. The samples were 4 mm discs of approximately 5 mg cut from the film with a calibrated die. Constant heating rates of 2, 5, 10 and 20 °C/min under a 50 mL/min flow of Helium were used. The reproducibility of the weight loss curves was checked by running every heating rate twice.

As far as the preparative dynamic pyrolysis runs are concerned, they were implemented in necked Pyrex glass tubes set in the furnace of a TA instruments DMA983 equipment, whose software facilities allows completing heating ramps in the low-temperature pyrolysis range, up to 500 °C. A scheme of the pyrolysis set-up is shown in Fig. 1. The actual pyrolysis heating ramp inside the tube was known by performing a calibration with an internal thermocouple and a commercial sPP as a standard. After an initial period, during which the heating rate increases, a constant 2 °C/min is achieved from 130 °C. The calculated error at the different final temperatures of pyrolysis is shown in Table 1.

Initial weights of 0.6 g of the polymer were put into the glass tube and purged with a N_2 stream (250 mL/min) for 10 min. Under these conditions, the system was heated at 2 °C/min from 28 °C up to a final temperature (Tpyr) ranging from 262 °C to 427 °C. Then, the sample was cooled under N_2 at room temperature. Although some tar residues were collected in the pre-cell at the highest pyrolysis temperatures, they were easily removed by wiping with pentane and further drying at 60 °C under vacuum. The weight loss could be then estimated by difference weighing (Table 1). Only a negligible content of impurities, i.e. volatile oligomers, could stay in, but the purification assures that any trapped hydrocarbon species into the solid sample are completely extracted.

The purification of the samples was carried out by dissolving the samples in xylene at 110 °C under N_2 bubbling and final precipitation in ethanol. After washing with ethanol and drying at room temperature under vacuum, a white polymer residue was obtained in all cases.

2.4. NMR characterization

The chain microstructure of samples, i.e. tacticity and anomalous groups associated to the pyrolysis process, has been analyzed

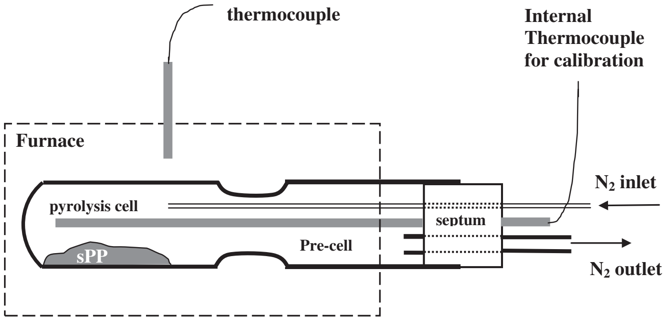

Fig. 1. Scheme of the pyrolysis set-up.