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Molecular weight dependence and stereoselective chain cleavage during the early stages of the isotactic polypropylene pyrolysis



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M.C. Martínez^a, R. Benavente^b, J.M. Gómez-Elvira^{b,*}

^a CTR-REPSOL, Agustín de Betancourt s/n, 28935 Móstoles, Madrid, Spain
^b Instituto de Ciencia y Tecnología de Polímeros, ICTP-CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain

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ABSTRACT

The comparative study on the pyrolysis of two Polypropylene samples, with a similar high isotactic character but quite distinct molecular weights, reveals a significant difference in their thermal performances. The detailed qualitative analysis of the parameters, which are expected to govern the thermal degradation, leads to reasonably assume a main role of the molecular weight in their relative early stabilities. Furthermore, the correlation found between the sharp initial build-up of the E_{act} and the selective cleavage of isotactic stereosequences in both samples, suggests the relevance of the stereoregular length into the energy required for chain scission.

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1. Introduction

Despite the huge effort devoted during decades to the study of thermal stability of polypropylenes, there remains a need of going deeper into the topic, because some aspects are not still well understood. The mechanism of polyolefin pyrolysis, in general and of polypropylene in particular, is accepted to initiate by the homolitic scission of the polymer bonds to produce chain radicals that, in a further step, propagate through a plethora of simultaneous processes [1–5]. This radical activity may eventually finish through recombination or disproportionation events. Notwithstanding this complexity, most of the main steps have been identified, thereby enabling a quite detailed description of the whole process. As a matter of fact, it has been possible to develop kinetic models able to predict the type and relative content of volatiles produced [4,5].

The activation energy (E_{act}) of the process is then an apparent value that mainly reflects the most energy demanding scission step, this one corresponding to random C-C bond cleavages. Such an E_{act} value should be constant with the loss of volatiles and supposedly close to the dissociation energy of C-C bonds, if the mechanism is assumed to be the same all along the conversion

* Corresponding author. E-mail address: elvira@ictp.csic.es (J.M. Gómez-Elvira). range. The real fact is, however, that a quite low value is found at low pyrolysis conversions, and that there is a somewhat expanded range, ca. 10 wt. %, during which the E_{act} builds up towards a roughly constant value.

This dependence of the E_{act} on the conversion has been evidenced by using either iso or non-isoconversional methods and is widely accepted [4,6–10]. In general, it is thought to be the result of the catalytic role of not well defined species, which would play similarly to catalysts used in other well-known low E_{act} pyrolysis processes. For example, Ziegler-Natta (ZN) catalyst residues could trigger a process similar to that one of cracking of polymers in the presence inorganic particles (silica, alumina, zeolites and FCC-catalysts) [11–15], although in a much smaller scale. These are typical catalytic processes where the E_{act} of polyolefin pyrolysis is substantially lowered, due to the fact that the acid character of active centres onto the particle surface promote the hydrogen transfer between radical species [11,16]. This way, polyolefins can be efficiently converted at temperatures under 500 °C into crude oils, suitable to be used as fuels.

The low E_{act} process presented here is apparent at very low temperatures, if it is compared with those ones of the above commented cracking processes. It is associated with the chain scissions found just above 200 °C, when initiation predominates and hydrogen transfer is rather restricted. In fact, the diminution of the molecular weight is remarkable while the loss of volatiles is hardly 1 wt. %. These features have made the researchers to propose

the existence of defects that might be present, either as impurities or as constitutive structures in PP chains, behaving as weak points. Anyway, the controversy arisen around this issue is usually bypassed in related bibliography by resorting to the general concept of labile structures, because of the difficulties encountered, firstly, to identify and quantify such low contents of species and, secondly, to correlate them with thermal stability.

The matter is not entirely solved and is not of little importance since the understanding of the key parameters driving such phenomena has significant technological implications. Similarly to the above commented catalysed polyolefin cracking, low Eact pyrolysis processes, intrinsically associated with the polymer, could be exploited in industry. For instance, in chemical recycling where pyrolysis offers a way of recovering valuable chemicals from polyolefin residues. In fact, the low and medium temperature pyrolysis of polyolefins has a great potential as a process for reducing the molecular weight of polymer waste, up to values that can be thus properly introduced in fluidized bed pyrolysis reactors, where the material undergoes the eventual conversion into chemicals at higher temperatures [12–17]. Of course, another optional utility of the low temperature control of pyrolysis is the production of high added value oligomers, which can be further used as telechelics or lubricants [18–21].

The analysis carried out in a previous work on the pyrolysis of a high molecular weight isotactic PP [9], evidenced the two foregoing facts. First, the very early Eact value of the process is abnormally low. In fact, the initial thermal cleavage of PP chains occurs at an E_{act} as low as the typical value of the oxidation process (about 100 kJ mol⁻¹), and second, the E_{act} depends strongly on the weight loss during the first stages of the process. From that study, the high molecular weight has been proposed as the main factor responsible for the former fact, since a large chain size can produce specific "intra-chain interactions" [22] that would behave as weak points under the severe restrictions imposed to chain dynamics in the molten state. Concerning the initial E_{act} build-up with the pyrolysis conversion, the progressive molecular weight diminution was proposed as the main reason. The hypothesis for this fact is also supported by some theoretical in addition to experimental works on the matter [23].

Notwithstanding the correlation found between the molecular weight and the Eact evolution with the pyrolysis progression, the comparison between the aforementioned thermal response in a high-molecular weight PP, and that exhibited by an isotactic PP with a molecular weight substantially lower would afford an enormous support on the influence of macromolecular character itself, into the labile nature of some regular C-C bonds. On the other hand, this comparative study allows checking the selective involvement of stereo-regular chain segments into the first stages of pyrolysis, whatever the molecular weight of the PP may be. This specific aspect related to the molecular weight reduction was proposed to explain the Eact increase, which takes place from the very beginning of pyrolysis up to intermediate stages. The idea is that, in the particular case of the isotactic configuration, not only the more rigid isotactic sequences are selectively broken at the lowest pyrolysis temperatures, but also that the length of these stereo-regular configuration has an important role in the energy demanded for the cleavage to occur.

This study compiles, therefore, the data already presented before, not only to be compared with the new ones of another isotactic PP but to be reanalysed in more detail, with the purpose of evaluating the general validity of the explanations given and for discussing the relative influence of other parameters, with an impact potentially detrimental on the stability of the PP.

2. Experimental part

2.1. Material and processing

The samples chosen for this study were two ZN highly isotactic PP (PP2472 and PP2477), kindly supplied by Repsol. They were used as obtained from the polymerization reactor, without any additive. Although the synthesis conditions used for both polymers were identical, the high molecular weight specimen (HPP) was obtained in the absence of hydrogen while the low molecular weight sample (LPP) was achieved under 12 bar of hydrogen. The weight average molecular weights, as they have been determined from a GPC/ viscometry relationship, given in section 2.3, are collected in Table 1. Their respective melt index values are also shown in Table 1. The samples as powders were processed by hot pressing at 190 °C and 20 bar for 2 min and further quenched to room temperature to obtain the corresponding films, which were finally used for both analytical and preparative thermo-gravimetric experiments.

2.2. Dynamic pyrolysis

The pyrolysis of the polymer films was carried out by running analytical dynamic TGA as well as in preparative mode, by using a previously described ad-hoc pyrolysis set-up [8,9]. Thus, quantities large enough of dynamically pyrolysed samples could be obtained to perform a complete characterization of the pyrolysed polymer, all along the process. The two series of pyrolysed samples are detailed in Table 2.

The analytical TGA measurements were carried out from 40 °C up to 750 °C in a Thermal Analysis TGA-Q-500 device. The samples used 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.

Experiments were run in the case of preparative dynamic pyrolysis from initial quantities between 1.0 and 1.3 g of the film. The heating ramp inside the pyrolysis cell was checked to correspond to the programmed 2 °C/min rate in the furnace by means of a K type thermocouple/data logger (Lascar Electronics), which tracked the actual temperature value every 10 s. After a 15 min purging stage with nitrogen (250 mL/min), the pyrolysis cell was let equilibrate at 40 °C and, then, the heating ramp was started in the nitrogen stream. Finally, the sample was cooled down under N₂ at room temperature. The weight loss was estimated by difference in weight. All samples were purified by dissolving them in xylene at 110 °C under N₂ 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. The purification step assures the removing of impurities, i.e. volatile oligomers, which can stay into the polymer bulk, especially at the highest pyrolysis temperatures.

2.3. Viscometry

The weight average molecular mass (M_w) of both virgin PP films as well as those ones of samples pyrolysed up to 330 °C and 350 °C, for HPP and LPP respectively, were estimated by means of the intrinsic viscosity in tetralin stabilized with Irganox 1010 (1 g/L), at 135 °C, by using the relationship [η] = 1.66 · 10⁻⁴ · M_W^{0.733} [24].

Viscometry is not suitable for low molecular weights of samples pyrolysed beyond the abovementioned temperatures; hence, the ¹H NMR analysis was employed in these cases to obtain the number average molecular weight (M_n) (section 2.6). In the case of sample HPP pyrolysed at 330 °C and sample LPP pyrolysed at 350 °C, both

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