

ON THE MOLECULAR MASS OF PYROLYSIS OILS FROM POLYOLEFINS

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Abstract

Pyrolysis of polyethylene (PE), polypropylene (PP) and polystyrene (PS) was performed at 420, 380 and 360 °C respectively and the obtained oils were analysed by GC-MSD and Q-TOF MS. The GC-MSD analysis showed typical chromatograms and distribution of major compounds in pyrolysis oils, with homologies series of olefins and paraffins up to *n*-C₃₀ for PE and oligomer series for PP (up to P7) and PS (up to S3). However the Q-TOF MS analysis showed that the pyrolysis oils of studied polyolefins also contain much heavier compounds with molecular mass up to around 1 000. This rises the question of the origin of high molecular mass compounds and a possible explanation could be the heterogeneous chain-end scissions occurring at liquid – gas interface inside pyrolysis reactor.

Keywords: PE, PP, PS, Q-TOF MS, chain-end scission mechanism

1. Introduction

Pyrolysis of polymers have been extensively studied and the identification of the thermal degradation mechanism was among the most important subject of interest envisaged by researchers. K. Murata proposed a macroscopic mechanism for thermal degradation of polyolefins, consisting on two main reactions.[1,2] Random scissions occur in condensed phase (polymer melt) strongly decreasing the length of initial macromolecular backbone while chain-end scissions liberate volatile fragments that are collected as condensable products. It was suggested that the chain-end scissions occur at the gas-liquid interface since the steady state degradation of polyolefins was affected not only by the liquid phase condition but also by the gas phase condition inside reactor. This proposed idea was sustained by thermodynamic and kinetic data as well as by global characterisation of degradation products by gas chromatography and by gel permeation chromatography. Here we report our preliminary results on the characterisation of pyrolysis oils from polyolefin by GC-MSD and by Q-TOF MS, the latter technique opening new insights on the molecular mass of the produced compounds

2. Materials and Methods

Pyrolysis of about 0.5g commercial polyethylene (PE), polypropylene (PP) and polystyrene (PS) was performed at 360, 380 and 420 °C respectively in a semi-batch process using a tubular glass reactor of 15 cm length and 1 cm internal diameter. The upper 5 cm part of the reactor was not heated, being kept outside the electric furnace. The volatile degradation products were condensed and the collected oils were analysed by GC-MSD and by Q-TOF MS

3. Results and Discussion

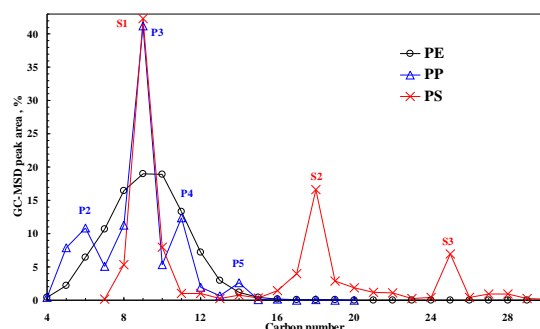


Fig. 1. C-NP gram of pyrolysis oils of PE, PP and PS.

The GC-MSD analysis of pyrolysis oils showed typical composition for studied polyolefins, with homologues series of paraffins and olefins (C₄ – C₃₀) for PE, propylene oligomers (P₂ – P₇) for PP and styrene oligomer structures (S₁ – S₃) for PS. The GC analysis is limited to mixtures of volatile compounds, the instrument operating at maximum 300 °C, which corresponds to the boiling point of *n*-C₁₇ hydrocarbons. On the other hand the pyrolysis temperatures utilised in this study correspond to the boiling points of *n*-C₂₂ – *n*-C₂₅ hydrocarbons. However the GC analysis was able to identified compounds up to *n*-C₃₀. This rise the question of the nature and origin of the compounds with higher molecular masses in the pyrolysis oils.

Direct analysis of pyrolysis oils by injecting them in the electrospray ion source of Q-TOF MS offer double advantage compared to GC-MSD analysis, namely *i*) volatilisation is not needed therefore compounds with high molecular mass can be analysed and *ii*) low ionisation energy is involved therefore molecular mass of compounds can be determined.

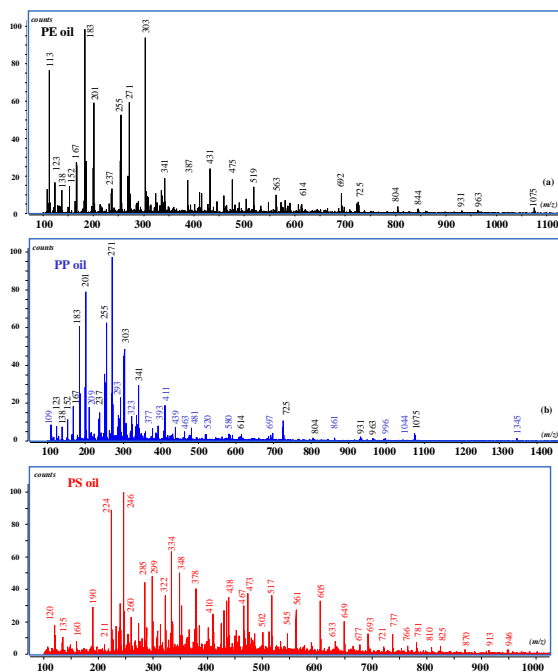


Fig. 2. Q-TOF MS spectra of polyolefins pyrolysis oils.

The strongest signals from the Q-TOF MS analysis of the PE oil (Fig. 2.a) were in the range of m/z 183 – 303 (with the exception of the signal at m/z 113 which belongs to octene) that corresponds to n -C₁₃ – n -C₂₀ hydrocarbons, which are actually at the tail of the large PE peak of the NP-gram in Fig. 1. However signals at high m/z values up to 1 075 were found, suggesting that the PE pyrolysis oil also contains heavier hydrocarbons up to C₇₅.

PP oil gave more Q-TOF MS signals compared to PE oil, due to its more complex composition, expected from the numerous tertiary carbon atoms in polypropylene. For PP pyrolysis oil the highest m/z signal was found at 1 345, which corresponds to a C₉₆ unsaturated structure while for PS pyrolysis oil the highest signal was found at m/z 946 which corresponds to a P₉C₁₇ nonamer structure (P stands for phenyl units and C for aliphatic units in the structure of the degradation product).

Identification of compounds with molecular mass around 1 000 in pyrolysis oils from polyolefins is of great interest since their volatility is too high for them to pass from the reactor content to the condensed oils through the vapour phase by volatilisation and condensation process.

A possible explanation for the presence of compounds with such high molecular mass in pyrolysis oils could be the heterogeneous chain-end scissions of the primary degradation products, occurring at the liquid – gas interface inside the reactor, as proposed by Murata mechanism.

The chain-end scission at gas-liquid interface could produce long-chain molecules directly in the gas phase. However as soon as they are formed, they condense as liquid droplets (very fine particle like a fog) due to a temperature drop from the liquid to the vapour phase in reactor [2]. Very small droplets are transported out of reactor by the upward stream of volatile products. This effect explains the presence of compounds with high

boiling points in liquid products that normally should not leave the reactor.

4. Conclusions

The Q-TOF MS analysis of pyrolysis oils obtained at 360, 380 and 420 °C from polystyrene, polypropylene and polyethylene respectively showed the presence of heavy compounds with molecular mass up to about 1 000 for PE and PS and up to 1 350 for PP. These stand for C₇₅ structures in PE oil, C₉₆ structures in PP oil and styrene nonamer structures (P₉C₁₇) in PS pyrolysis oil. The presence of such heavy compounds in pyrolysis oils might be explained by the macroscopic degradation mechanism proposed by Murata, which consider that the chain-end scission responsible with formation of volatile compounds occur at gas-liquid interface inside reactor. However more studies are to be performed to confirm the presence of heavy compounds in pyrolysis oils from other polymers too.

References

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