

TGA/IST/GC/MS coupling : an advanced technique for LLDPE structure interpretation.

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The polyethylenes (LDPE, LLDPE, HDPE) are the most industrially produced synthetic polymers in volume with a production of around 75 MT a year. The LLDPE which is produced by coordination catalysis is a copolymer of ethylene with a alpha-olefin (typically hexene or octene).^{1,2} One of its main advantage is that its structure and consequently its properties are easily adjustable by variation of the co-monomer content (short chain branching). It is thus of high interest to determine the structure of LLDPE.

A range of crystalline copolymers of ethylene with alpha-olefins (propene, hexene, octene, octadecene and norbornene) were prepared using the complexes *rac*-Et(Ind)₂ZrCl₂ and (nBuCp)₂ZrCl₂ activated with MAO. The average composition of the copolymers was measured using ¹H, ¹³C NMR and TREF. In the present paper, these copolymers were investigated by coupling of the TGA with the GC-MS technique to get information about the structure of LLDPE.

For a clearer understanding of certain reactions, the TGA technique is often coupled to mass spectrometry (MS) and infrared spectroscopy (IR) for identifying the gaseous compounds emitted during thermal decomposition of the sample. When it comes to complex materials such as LLDPE, then gas mixtures are produced but the majority of components cannot be identified precisely with MS or IR. In this case, coupling of the TGA with the GC-MS technique offers interesting advantages. The emitted compounds are first separated by gas chromatography (GC) then identified and quantified by MS. An innovative TGA/IST/GC/MS coupling is presented that significantly increase the number of data collected and thus provides an efficient way to take advantage of the GC/MS technique. The configuration uses a fractions collector inserted between the TGA and the GC.³

This coupling is a powerful and versatile tool for interpretation of structure of LLDPE. The characterization of several polyethylene samples is presented.

References:

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2. M. P. McDaniel, *Adv. Catal.* 2010, 53, 123.
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