Polymer Char

A higher standard in Gel Permeation Chromatography analysis for Polyolefins

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Polyolefin (PO) is the largest volume industrial polymer in the world used for making a wide range of commercial products that touch nearly every aspect of our daily lives, such as automobile parts, pipes, packaging films, household bottles, baby diapers and so on.

Polyolefin products derive their wide range of end-use properties from their semi-crystalline structure. The ability of incorporating comonomers in PE and PP makes it possible to control the polymer crystallinity, and thus control the rigidity and flexibility of polyolefin products. The controlling factor also depends to a great extent on the co-monomer variations across the molar mass distribution (MMD). In today's competitive marketplace, products are targeted to specific applications by tailoring both molar mass distribution and comonomer incorporation. This requires a reliable and fast analytical tool for studying comonomer incorporation, or chemical composition, along the MMD in all kinds of polyolefins.

The high temperature GPC-IR by Polymer Char is a compact and fully automated instrument which has set the new standard in gel permeation chromatography for polyolefins, and has increasingly become the preferred choice in the industry.

Optimum Detection Scheme

The IR detector has been shown to be the most appropriate detector for gel permeation chromatography of polyolefins. Flow rate, temperature and pressure variations have little influence on the IR absorbance, and so an outstanding baseline stability is delivered by this detector (Figure 1). In addition, IR shows no injection peaks and the chromatograms are easily integrated resulting in reliable and precise molar mass averages.

Even though its performance as concentration detector is unparalleled, what makes the IR detector unique for this application is the new dimension it provides without any analytical complexity. The sample absorbance at several IR bands is acquired as the polymer traverses the flow-through cell. It is thus possible to investigate chemical composition along molar mass distribution for each material analyzed. When GPC is performed with an IR detector, a wealth of useful information is obtained for catalyst development, product control or technical service support (Figure 2).

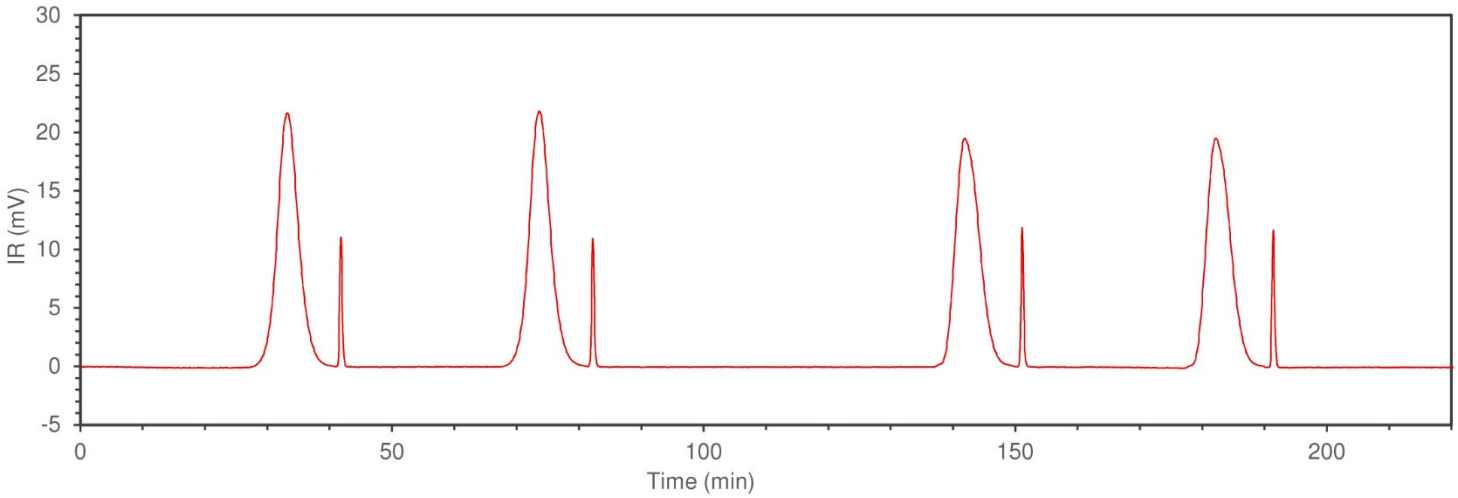

Figure 1. Sequential injections of SRM 1475 linear polyethylene (x2) and SRM 1476 branched polyethylene (x2) at 150ºC in 1,2,4-trichlorobenzene, injection volume 200µL, concentration 0,9mg/mL. A low molar mass hydrocarbon is added to every injection as flow rate marker.

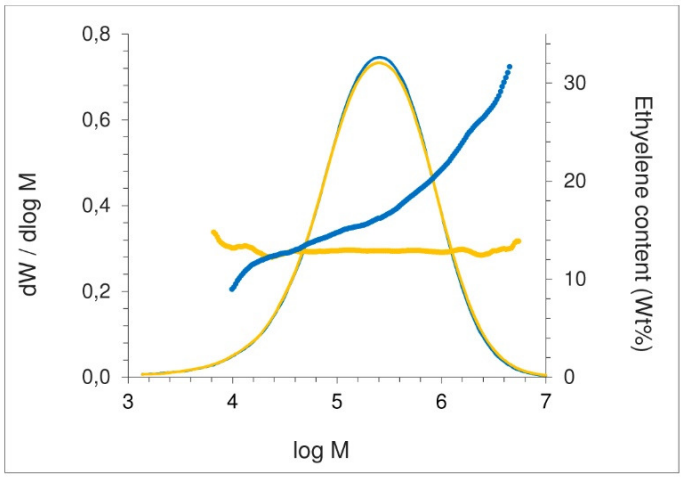

Figure 2. Analysis of two ethylene-propylene copolymers with similar MMD but distinct ethylene distributions, as seen with IR detection.

The simple hardware setup makes IR detectors very rugged, they can withstand high pressures and need no equilibration time. The detector signal is stable even before the samples are ready for injection or the columns are equilibrated.

For high-level triple detector capability, the IR detector complements perfectly the instrument's integrated full bridge viscometer and multiple-angle laser light scattering (Wyatt Heleos II), allowing a deeper insight into molecular architecture and study of short chain branching, long chain branching and absolute molar mass of homopolymers and copolymers.

Sample Care and Safety through Automation

A major innovation that is having a tremendous impact in the laboratories' workflow is given by GPC-IR's full automation of sample preparation, not requiring any external device nor manual work. Once the analysis is started under computer control, the instrument fills the vials by means of an integrated syringe pump. Nitrogen is directed into the vial through an intelligent valve system in order to purge the vial's internal atmosphere, preventing oxidative degradation.

Table 1 shows the benefit of the automated nitrogen purge applied in GPC-IR and the negative effect of excessive heating.

GPC-IR is the only instrument that allows accurate control of the dissolution time for each vial to be analyzed. As soon as it is fully dissolved, the polymer is injected without any additional exposure to high temperature.

A durable filtration system is also incorporated in the instrument. The filter is rinsed in back-flush with clean, hot solvent after every injection. This fact, together with its optimized design, allows for very long continuous operation before replacement.

Conclusions

With the introduction of GPC-IR, a higher standard has been set for analysis of polyolefins. It has been proven that optimum detection is achieved through IR given its stability and sensitivity while providing chemical composition information along the MMD.

References:

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Time @150ºC	Standard procedure		Nitrogen vial purge	
	M_w (g/mol)	Error	M_w (g/mol)	Error
90 min	319,000	6%	337,6	- - -
2 hours	307,400	9%	327,4	3%
4 hours	275,800	18%	325,7	4%
10 hours	236,700	30%	269,6	20%

Table 1. Effect of degradation of higher molar mass chains due to the excessive exposure to high temperature, and benefit of vials nitrogen purge. Polypropylene in 1,2,4-Trichlorobenzene

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