Advanced Polyolefin Analysis

Author: Dr. Peter Montag
PSS Polymer Standards Service GmbH
E-Mail: PMontag@polymer.de

Polyolefins and their copolymers are insoluble in typical GPC/SEC eluents at room temperature. Common solvents for these products are e.g. 1,2,4-trichlorobenzene, 1,2-dichlorobenzene and decaline. The analysis has to be performed at temperatures between 130 °C and 160 °C. This is a typical high temperature (HT) GPC experiment. For faster and better results for polyolefin analysis PSS hat invested in a new high temperature GPC system.

This system has the following advantages:

Sample preparation

Older autosamplers heat up the samples for hours before injection. This can lead to uncontrolled degradation and therefore to a bad reproducibility. The new system allows to program an individual temperature program for every sample with automated solvent delivery and gentle preparation. Filled samples (e.g. with fiber glass, carbon black, talcum) can be used directly without elaborate preparation, due to the automated filtering system with backflush cleaning. This saves time and costs.

Detection systems

Polyolefins have a very low dn/dc value, so the RI signal can be very noisy due to low signal intensity. For reliable measurements the analysis has to be interrupted for hours or days to achieve good baseline stability through purging.

IR detection is a powerful alternative for polyolefins. Detection of the CH-valence vibration with the IR4-detector gives a linear concentration signal with a good signal/noise ratio, without consuming too much eluent and time during the process of purging.

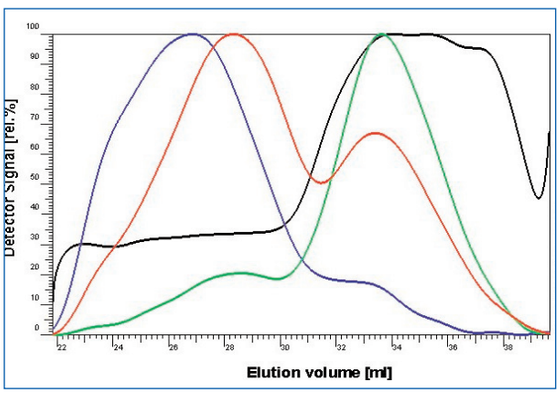

Fig 1: elugram with multi detection of an ethylene-vinyl acetate copolymer
blue: Viscosity signal; red: CH_2 signal; green: C=O signal; black: relative amount of vinyl acetate
The vinyl acetate content in the oligomeric part is around 40% and in the high molar mass area around 5%.
GPC conditions: Temperature: 140 °C, Flow rate: 1 ml/min, Eluent: 1,2-dichlorobenzene, Injection volume: 200 µl, columns: PSS POLEFIN 10 µm 100 Å + 1 000 Å + 100 000 Å + 1 000 000 Å (each 8x300mm) and precolumn

Molar mass determination

Molar masses are commonly determined based on a Poly(styrene) calibration. Light scattering detectors can be used, but the dn/dc value of polyolefins are often unknown and therefore the advantage of light scattering detection is lost. Alternatively a viscosity detector can be used, providing good data from oligomers up to ultrahigh molar masses. True molar masses can be obtained by universal calibration, if a proper GPC/SEC method can be established.

Structure analysis

By using intelligent detector combinations, structural information is monitored in addition to the molar mass distribution.

Fig 1 shows a typical elugram for a bimodal ethylene vinyl acetate (EVA) copolymer. The combination of the molar mass sensitive viscosity signal and the concentration signal of the CH_2 vibration gives a true molar mass distribution. In addition two different types of structure information are available:

Chain branching

Long chain branching influences e.g. the rigidity of a material. By creating a Mark-Houwink-plot long chain branching can be monitored. A Mark-Houwink-plot is created by plotting the measured intrinsic viscosity vs. the measured molar mass. The slope of this plot gives information about the chain branching. α decreases when the number of branches increases.

Copolymer content

The ratio of IR-vibrations gives information about the comonomer content. For α-olefin copolymers the content of CH_3 groups is detectable. By switching to a carbonyl-sensitive chip, copolymers with C=O groups can be analyzed. This means that the vinyl acetate content can be directly measured with excellent correlation.

Summary

- Higher reproducibility through gentle sample preparation
- Simple analysis of filled samples through integrated hot filtration
- More precise and faster determination of the molar masses through sensitive IR detection
- True molar masses and long chain branching through combination with viscosity detection
- Determination of copolymer content through dual detection with different IR-vibrations

PSS Polymer Standards Service-USA,Inc
43 Jefferson Blvd. Ste 3
Warwick, RI 02888 • USA
Tel.: +1-401-780-8884
Fax: +1-401-780-8824
E-Mail: pssusa@pssGPCshop.com
Web: pssGPCshop.com