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Recent Developments in Polyolefin Characterization

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SUMMARY: The synthesis and characterization of polyolefins continues to be one of the most important areas for academic and industrial research. One consequence of the development of new "tailor-made" polyolefins is the need for new and improved analytical techniques for the analysis of polyolefins with respect to molar mass and chemical composition distribution. The present article briefly reviews different new and relevant techniques for polyolefin analysis. The analysis of copolymers by combining high-temperature GPC and FTIR spectroscopy yields information on chemical composition as a function of molar mass. Crystallization analysis fractionation is a powerful new technique for the analysis of short-chain branching in LLDPE and the analysis of polyolefin blends. Additives in polyolefins can be determined efficiently by pyrolysis-gas chromatography-mass spectrometry.

Introduction

The polymerization of olefins to polymers with different microstructures and properties continues to be one of the most investigated areas for both industrial and academic laboratories in polymer science. The use of polyolefins as polymeric materials is rapidly growing due to the fact that polyolefins are made from simple and easily available monomers. In addition, they contain only carbon and hydrogen, and can be reused or degraded by thermal processes to oil and monomers1). New or improved properties are achieved by combining new monomers in a copolymer system, or by using new catalysts. Forty years after the discovery of the metallorganic catalyzed polymerization of olefins by Ziegler and the stereospecific polymerization of propene and α-olefins by Natta, the use of metallocene catalysts shows the way to expand the possibilities of olefin polymerization and the properties of the resulting polyolefin materials.

One consequence of the development of new "tailor-made" polyolefins is the need for new and improved analytical techniques. In addition to monitoring the polymerization process, the molecular heterogeneity of the resulting products must be described by suitable methods. Irrespective whether a Ziegler-Natta or a metallocene catalyst is used, information on molar

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mass distribution, chemical composition, tacticity, and branching is required to properly evaluate a polymeric material. Very frequently, polyolefins exhibit multiple distributions, e.g. long chain branching and molar mass distribution in low-density polyethylene (LDPE) or chemical composition distribution and molar mass distribution in linear low-density polyethylene (LLDPE), copolymers and polymer blends.

The present article briefly reviews different relevant techniques for polyolefin analysis. Attention is paid to the analysis of the polyolefin itself, and to the analysis of additives in polyolefins.

Coupling of High-Temperature GPC and FTIR Spectroscopy

The molar mass distribution of polyolefins is frequently determined by high-temperature gel permeation chromatography (HT-GPC). Due to the high crystallinity of the polyolefins temperatures of 140 °C or higher must be used to dissolve the polyolefin sample in the mobile phase, which in most cases is trichloro benzene (TCB) or dichloro benzene (DCB). Conventional HT-GPC is equipped with a refractive index (RI) detector for monitoring the concentration of the sample in the eluate. In exceptional cases, HT-GPC is coupled to viscosity or light scattering detectors, which give additional information on long-chain branching.

For a detailed analysis of olefin copolymers or polyolefin blends it is important to determine the chemical composition distribution. The gross chemical composition of polyolefins can be determined quantitatively by FTIR spectroscopy. A standard technique for the determination of the chemical composition as a function of molar mass is, however, not available. Such dual information can be obtained when HT-GPC is directly coupled to FTIR spectroscopy. Recently, Lab Connections Inc. introduced the LC-Transform™, a direct GPC-FTIR interface[2-4)]. The design concept of the interface is shown in Fig. 1. The system is composed of two independent modules, the sample collection module and the optics module. The effluent from the liquid chromatography column is split, with a fraction going into an ultrasonic nebulizer nozzle located above a rotating sample collection disc. The nozzle rapidly evaporates the mobile phase while depositing a tightly focused track of the solute. When a chromatogram has been collected on the sample collector disc, the disc is transferred to the optics module in the FTIR for analysis of the deposited sample track. A control module defines the sample collection disc position and rotation rate in order to be compatible with the run time and peak resolution of the chromatographic separation. The sample collection disc is made from germanium which is optically transparent in the range 6000-450 cm^{-1}. The lower surface of the disc is covered with a reflecting aluminum layer.

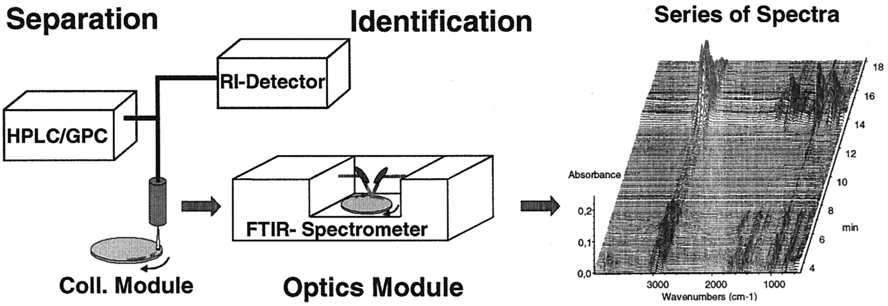

Fig. 1: Schematic representation of the universal GPC-FTIR coupling using the LC Transform Interface.

As a result of the investigation a complete FTIR spectrum for each position on the disc and, hence, for each sample fraction is obtained. This spectrum bears information on the chemical composition of each sample fraction. The set of all spectra can be arranged along the elution time axis and yields a three-dimensional plot in the coordinates elution time-FTIR frequency-absorbance. Another way of representation is a diagram, where the content of one component in the copolymer is plotted across the molar mass axis.

As an example, the analysis of a blend of two EPDM copolymers with different molar masses and chemical compositions is presented in Fig. 2. The FTIR spectrum of an EPDM copolymer is given in Fig. 2A. The propylene percentage is determined from the absorption peak at 1378 cm^{-1}, while the ethylidene norbornene is determined from the peak at 1690 cm^{-1}. The percentage of the two monomers across the molar mass axis is given in Fig. 2B. As can be seen clearly, the propylene content of the higher molar mass copolymer is lower$^{5)}$.

Using this experimental set-up, a multitude of different materials can be analyzed, including α-olefin copolymers, and polyolefin blends. In addition to the analysis of macromolecular components, the technique can be used for the detection and quantification of additives.

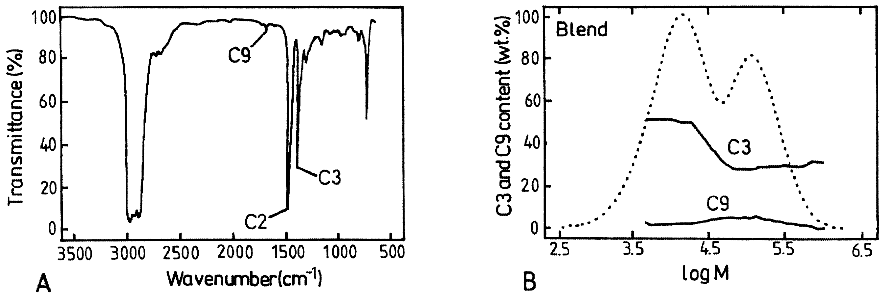

Fig. 2: FTIR spectrum of an EPDM copolymer (A) and HT-GPC/FTIR analysis of the blend of two EPDM copolymers (B).

Crystallization Fractionation

The principles of polymer fractionation by solubility or crystallization are based on the Flory-Huggins statistical thermodynamic treatment that accounts for melting-point depression by the presence of a diluent, and can be expressed as follows[6,7]:

$$1/T_m - 1/T_m^o = -(R/\Delta H_u) \ln N_A \qquad (1)$$

where T_m^o is the melting temperature of the pure polymer, T_m is the equilibrium melting temperature of the "diluted" polymer, ΔH_u is the heat of fusion per polymer repeating unit, and N_A is the mole fraction of the diluent. A solvent or a comonomer can act as the diluent. In both cases, the crystallization temperature decreases with increasing diluent concentration. Therefore, for copolymers the separation by crystallizability can be regarded as a separation by chemical composition.

There are two experimental techniques, which separate polyolefins by crystallizability: **T**emperature **R**ising **E**lution **F**ractionation (TREF) and **Cryst**allization **A**nalysis **F**ractionation (CRYSTAF). TREF is regarded as the most common technique for anlysis of the chemical composition of olefin copolymers and short-chain branching distribution (SCBD) of LLDPE. It has been established as an analytical technique through the work of Wild et al. in the late 1970s[8,9]. A TREF experiment includes dissolution of the sample, loading of the TREF column with hot solution and the crystallization of the sample by slow temperature-programmed cooling. After crystallizing the sample, the elution of the sample fractions is conducted by slow temperature-programmed heating of the TREF column. The total analysis time per sample is in the magnitude of days, hence TREF can be used only in selected cases.

Compared to TREF, CRYSTAF is a much more feasible technique for the analysis of large numbers of samples. This powerful method, which has been developed only recently by Monrabal[10-12], is based on the monitoring of the concentration of a polyolefin solution during the crystallization. A schematic presentation of the experimental set-up is given in Fig. 3A. The analysis of a mixture of atactic, syndiotactic and isotactic polypropylenes is shown in Fig. 3B.

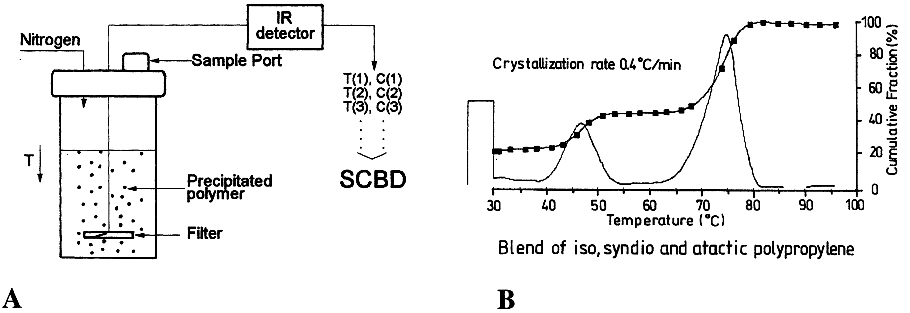

Fig. 3: Schematic represenation of a CRYSTAF experiment (A) and analysis of a mixture of atactic, syndiotactic and isotactic polypropylenes (B) [from Ref. 11].

In brief, crystallization is conducted in stainless steel containers where dissolution and filtration takes place automatically. In total, five containers are placed in the CRYSTAF apparatus making it possible to run five samples simultaneously. The sample is introduced into the container, and dissolved in TCB at 160 °C. When the sample is fully dissolved, the temperature is decreased and aliquots of the solution are taken, filtered and analyzed by a concentration detector. As the result, a concentration profile of the solution vs. temperature is obtained, which can be related directly to the amount of crystallizing fractions. As is shown in Fig. 3B, CRYSTAF readily separates a polypropylene mixture into the highly crystalline i-PP, the lower crystalline s-PP and the amorphous a-PP. The advantage of CRYSTAF over TREF is that the analysis time per sample is significantly lower. A set of five samples can be analyzed within 6 to 10 hours.

The versatility of CRYSTAF shall be demonstrated for one further application. Using traditional methods it is rather difficult to separate HDPE and LDPE in corresponding blends. In particular, DSC gives overlapping crystallization and melting curves for the components, making it impossible to determine a quantitative blend composition. The separation of HDPE-LDPE blends of different compositions by CRYSTAF is shown in Fig. 4. It is obvious from the curves, that even extreme compositions can be analyzed without problems.

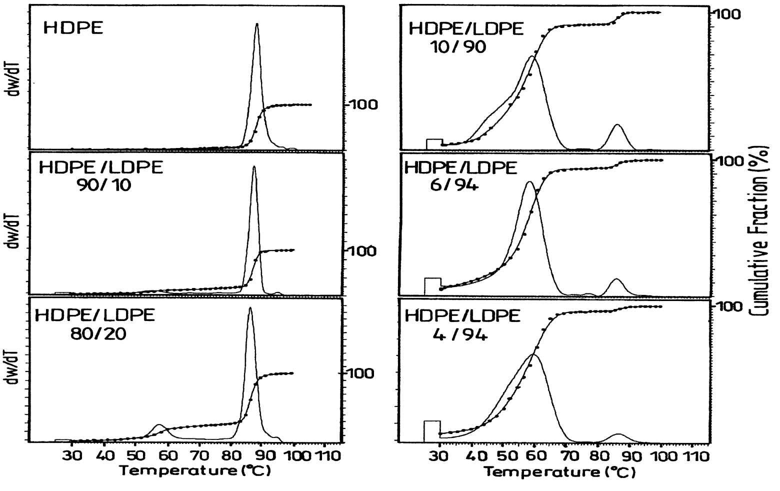

Fig. 4: CRYSTAF analysis of HDPE-LDPE blends of different compositions.

Analysis of Additives in Polyolefins

Polyolefins are sensitive towards oxidative degradation, they must be processed and their properties must be tailored for a specific application. To this end a variety of different additives are used, including stabilizers, antioxidants, processing aids. The analysis of an additive in a polymer matrix is a demanding task due to the fact that (a) universal methods for additive analysis do not exist, and (b) the concentration is generally very low. Typical problems encountered in additive analysis are the analysis of an unknown (competitors) sample, the determination of additive concentrations as a means of quality control, the evaluation of additive stability during processing and materials lifetime, and the investigation of the cause of a materials failure. In addition to reliability, sensitivity and accuracy, short analysis times and little or no sample preparation are desirable.

Out of the multitude of different methods, Pyrolysis-Gas Chromatography-Mass Spectrometry (Pyr-GC-MS) shall be briefly reviewed as a new and powerful technique for additive analysis[13]. Pyr-GC-MS combines a fast sample introduction device (pyrolyzer) with high separation efficiency (GC) and excellent identification (MS) of the sample components. Without sample preparation, about 50-100 µg of the sample are pyrolyzed at 550 °C, the pyrolysis products are introduced into the GC column using a stream of carrier gas and separated into the polymer matrix and additive components. A quadrupole mass spectrometer (mass range 45-700 m/z) is used as the detector and identification of the additives is carried out using an additive data base. The construction of a Pyr-GC-MS is schematically presented in Fig. 5.

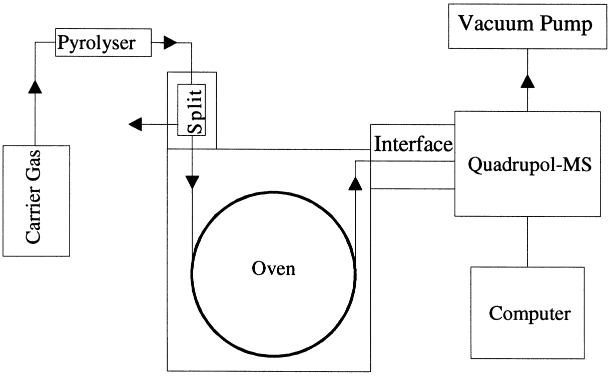

Fig. 5: Schematic presentation of Pyr-GC-MS.

The analysis of two antioxidants in polypropylene is shown in Fig. 6. For each chromatographic peak an automated peak search is carried out in the additive data base. The measured mass spectrum is compared with the mass spectrum of the data base, and the difference spectrum indicates the fit. The sensitivity of the method is very high, even concentrations of 0.05 % by weight of a particular additive can be determined.

The advanges of Pyr-GC-MS over other analytical techniques for additives are as follows: no sample preparation is required, sample introduction and measurement is fast, additives can readily be identified by their characteristic mass spectra, different additives (phenols, benzotriazols, hindered amines) can be identified by one procedure, a wide variety of different polymers can be analyzed, and high sensitivity. One of the major disadvantages of the technique is that the quality of quantification significantly depends on the skills and experience of the operator.

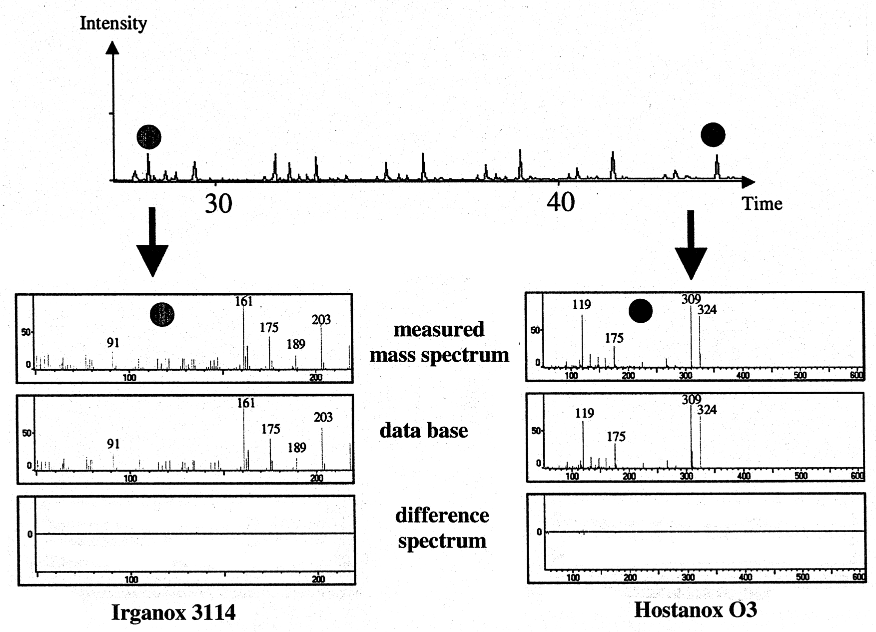

Fig. 6: Determination of two additives in polypropylene by Pyr-GC-MS.

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