On-Line Monitoring and Fingerprint Technology: New Tools for the Development of New Catalysts and Polyolefin Materials

*Arno Tuchbreiter, Jürgen Marquardt, Bernd Kappler, Josef Honerkamp, Rolf Mülhaupt**

Freiburger Materialforschungszentrum (FMF) der Albert-Ludwigs Universität Freiburg, Stefan-Meier-Str. 21, D-79104 Freiburg, Germany
E-Mail: rolf.muelhaupt@makro.uni-freiburg.de

Summary: The High-Output Polymer Screening (HOPS) combines process-relevant automated reactor systems and rapid polymer characterization with on-line polymerization monitoring and automated data acquisition ("electronic notebook") in order to make effective use of advanced data mining tools. This has led to the development of fingerprint technology based upon correlations between spectroscopic data and polymerization process conditions, catalyst compositions, as well as polymer end-use properties. Infrared spectroscopic fingerprints proved to be very useful for accelerating polymer analyses including characterization of polymer molecular architectures as well as non-destructive testing of the mechanical, thermal and other end-use polymer properties. Such spectroscopic fingerprints represent important components of effective on-line quality control systems. With ATR-FT-IR probes on-line monitoring of catalytic olefin copolymerization was performed in solution to measure in real time copolymerization kinetics, catalyst productivities, catalyst deactivation as well as copolymerization parameters and copolymer sequence distributions. Monomer consumption and comonomer incorporation were monitored simultaneously. Advanced fingerprint technology can reduce significantly the need for time- and money consuming polymer testing and can also stimulate the search for new catalyst systems and polymeric materials.

Keywords: combinatorial chemistry; data mining; high throughput screening; IR spectroscopy; multivariate calibration; polypropylene

Introduction

An important objective in catalyst as well as polymer development is to reduce the costs and the time required for identifying new products and bringing them from the lab to the market place. High throughput methods were introduced in drug development to prepare and screen a

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large number of small molecules with respect to their biological activities.[1] High throughput methods and combinatorial chemistry was also introduced in materials development.[2] While automated reactors and data mining tools are established in polymer reaction engineering and process research at pilot plant facilities, many catalyst and polymer research labs are still employing manually operated reactors with inadequate process control and tedious, time-consuming data acquisition, especially with respect to the characterization of polymer properties. Today inexpensive computing power is at hand to facilitate work in research labs by means of automated reactors equipped with computer guided process control and automated acquisition of polymerization data as well as product properties.

High-Output Polymer Screening (HOPS)[3]

Most high throughput systems increase screening speed at the expense of process-relevant information. The High-Output Polymer Screening (HOPS)[3], developed at the Freiburg Materials Research Center jointly with BASF AG and Basell, employs process-relevant reactors equipped with precise process control and data acquisition of both polymerization data as well as polymer properties in a data base system ("electronic notebook"). The basic concept of HOPS is displayed in Figure 1. Virtually any lab reactor can be upgraded to perform HOPS. Special miniaturized reactors and sophisticated reactor arrays are not required. This is important to assure process relevant results. Since polymerization reactions are very well controlled, it is possible to generate a large number of well-defined and well-characterized polymer samples within very short time. This enhances the yield of useful information per experiment, which can be employed in data analysis. Also this information can be used to improve the templates for molecular modeling of catalysts and to facilitate simulations of polymerization processes. An important objective of this research was to search correlations of spectroscopic data with polymer architectures and polymer properties.

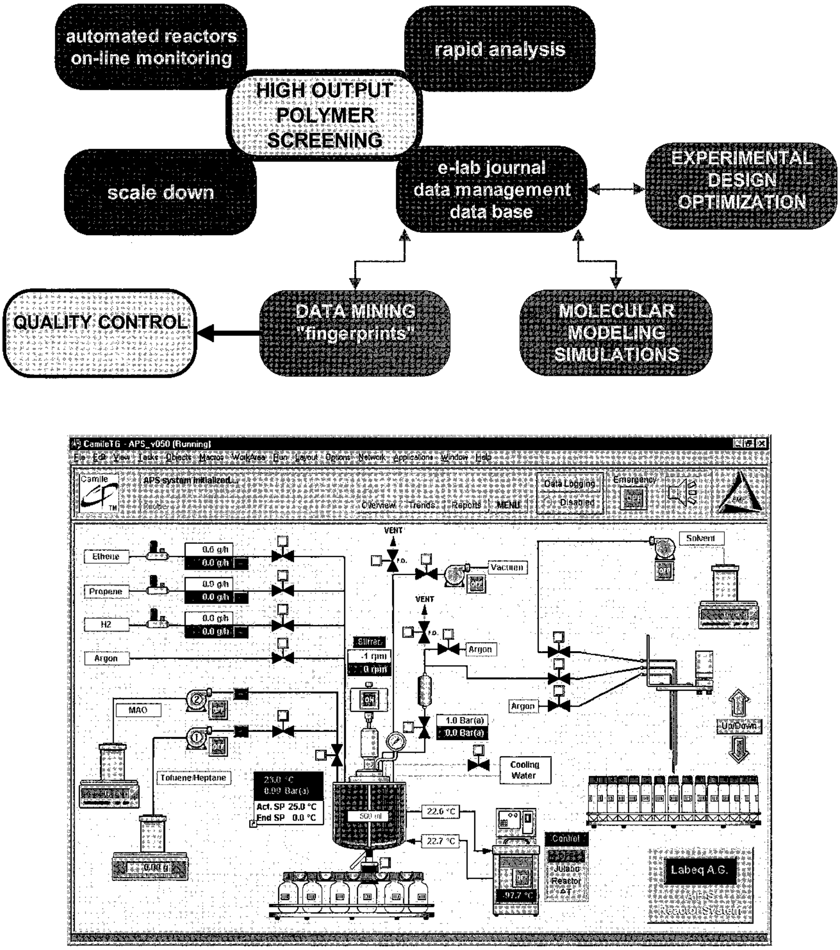

Figure 1. High-Output Polymer Screening (HOPS)

Fingerprint Technology and Rapid Polymer Characterization

Automated reactors significantly improve the effectiveness of lab reactor operations. However, the increased number of samples caused severe bottleneck situation in polymer characterization. Especially NMR spectroscopic investigations require measurements requiring several hours per sample. Infrared (IR) spectroscopy is being used for polyolefin characterization since the pioneering days of Natta's group.[4,5] At that time the preparation of IR samples was rather tedious because it required either time-consuming compression molding of KBr pellets or film formation, e.,g. by casting solutions onto mercury surfaces. This traditional bottleneck was eliminated by employing the attenuated total reflection IR spectroscopy, also known as "Golden Gate".[6] As shown in Figure 2, the polymer sample is added to the top of a dense crystal platform and the IR beam is directed to the bottom of the crystal at an angle greater than the systems critical angle, which depends on the refractive properties of both the crystal and the polymer. This causes a total reflection of the wave, minus what is absorbed by the sample. It was demonstrated for ethene/1-hexene copolymers that 40 samples can be processed per hour. Using multivariate calibration ("fingerprint") of model copolymers, analyzed by means of NMR spectroscopy, the accuracy of this methods was improved considerably. Also MIR and NIR spectroscopy were used successfully to establish fingerprints for copolymer microstructure analysis.[7]

Another time- and money-consuming bottleneck relates to the measurement of end-use properties such as mechanical and thermal properties, density, crystallinity, hardness, etc. . Frequently, also wet chemical analysis must be performed to measure properties such as gel content and soluble fractions. Here multivariate calibration combined with a well-characterized large number of polymer samples, obtained by means of HOPS, offers interesting opportunities. The approach is rather simple. Instead of expensive high-resolution NMR, inexpensive spectroscopy such as IR and industrial magnetic resonance are being used to correlate the spectroscopic data with polymer properties in order to identify spectroscopic "fingerprints". Clearly the versatility of this fingerprint technology depends on the individual polymer systems and the quality and easy availability of a fairly large number of "model" samples. With HOPS such model samples are readily available. Fingerprints were established for the non-destructive rapid determination of tensile strength, Shore hardness, flexural modulus and density of polypropylenes.[3] In a similar approach, Pandy, Kumar and Garg evaluated melt flow index, Izod impact strength, and flexural modulus by means of multivariate statistical analysis.[8] Karlsson and Camacho measured number average weight and crystallinity of recycled HDPE by means of non-destructive testing and fingerprints originating from NIR and MIR spectroscopy combined with multivariate partial least square calibration.[9] With HOPS technology it is very easy to adopt fingerprint technology in research labs as well as pilot plants because of the availability of large sample numbers required to sharpen the data mining tools. As seen in Figure 4, also fingerprint correlations between catalyst compositions and polymer properties are feasible.

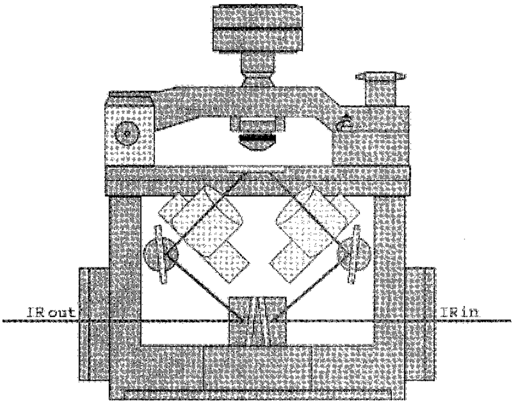

Figure 2. ATR-FTIR analysis of polymer powders and pellets

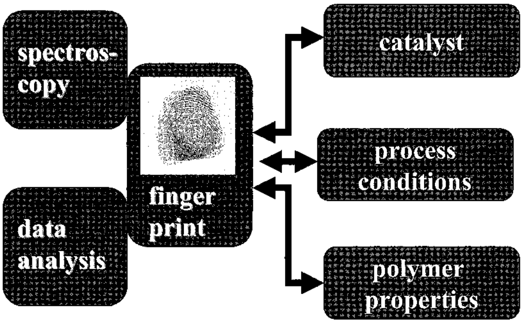

Figure 3. Fingerprint technology: “fishing for correlations”

On-Line Monitoring of Solution Copolymerizations[10]

For solution polymerizations and copolymerizations it is possible to insert ATR-FT-IR probes, e.g., ReactIR from Mettler) into the reactor. The reactor system is displayed in Figure 4. Although IR – in contrast to Raman - does not detect ethylene, it is possible to monitor the consumption of 1-hexene and simultaneously the incorporation of ethene and 1-hexene into the copolymer. Fingerprint technology and data processing were employed successfully in order to monitor polymerization kinetics as well as copolymer composition and copolymer sequence analysis. The results are in good agreement with time-consuming NMR measurements. When the differential equations of copolymerization reactions were modified to take into account the time-dependent variation of catalyst activity during polymerization it is also possible to identify living polymerization processes and catalyst deactivations. This HOPS system proved to be useful for the development of solution processes and the formation of elastomers.

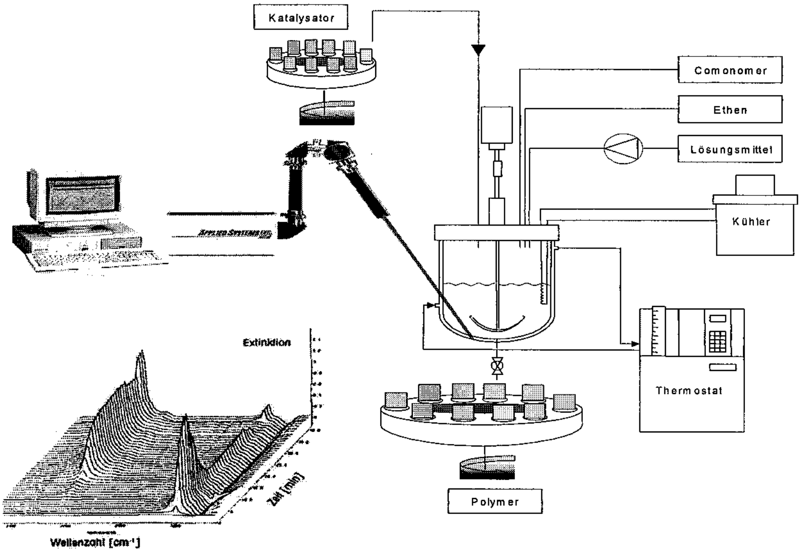

Figure 4. On-line solution copolymerization monitoring by means of ATR-FTIR-probes

Outlook

HOPS and fingerprint technology make research labs much more effective with respect to rapid feedback of experimental results and lower costs and less environmental pollution due to the non-destructive evaluation of polymeric materials. The large amount of polymers, which are readily available using process- relevant and well-controlled polymerization conditions, facilitate implementation of fingerprint technology. On one hand, fingerprint technology speeds up polymer characterization. On the other hand, the fingerprint technology offers new opportunities of pinpointing the influence of catalyst variations and changes of process conditions on the end-use properties of polymers. This information can be used to achieve better quality control and also to stimulate catalyst and polymer developments.

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