Analysis of Complex Polymers by Multidimensional Analytical Techniques

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SUMMARY: Complex polymers are distributed in more than one direction of molecular heterogeneity. In addition to the molar mass distribution, they are frequently distributed with respect to chemical composition, functionality, and molecular architecture. For the characterization of the different types of molecular heterogeneity it is necessary to use a wide range of analytical techniques. Preferably, these techniques should be selective towards a specific type of heterogeneity. The combination of two or more selective analytical techniques yield multidimensional information on the molecular heterogeneity.
The article presents the principle ideas of combining different analytical techniques in multidimensional analysis schemes. Most promising protocols for hyphenated techniques refer to the combination of two different chromatographic methods and the combination of chromatography and spectroscopy. The basic principles of two-dimensional chromatography and the hyphenation of liquid chromatography with selective detectors will be discussed and a number of applications will be given.

Introduction

Synthetic polymers are highly complex multicomponent materials. They are composed of macromolecules varying in chain length, chemical composition, and architecture. By definition, complex polymers are heterogeneous in more than one distributed property (for example, linear copolymers are distributed in molar mass and chemical composition). Depending on the composition of the monomer feed and the polymerization procedure, different types of heterogeneities may become important. For example, in the synthesis of tailor-made polymers frequently telechelics or macromonomers are used. These oligomers or polymers usually contain functional groups at the polymer chain end. Depending on the preparation procedure, they can have a different number of functional endgroups, i.e. be mono-, bifunctional etc. In addition, polymers can have different architectures, i.e. they can be branched (star- or comb-like), and they can be cyclic.

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Different from low molar mass organic samples, where single molecules are to be determined, for complex synthetic polymers the analytical task is the determination of a distributed property. The molecular heterogeneity of a certain complex polymer can be presented either in a three-dimensional diagram or a so-called "contour plot". For a telechelic polymer these presentations are given in Figure 1.

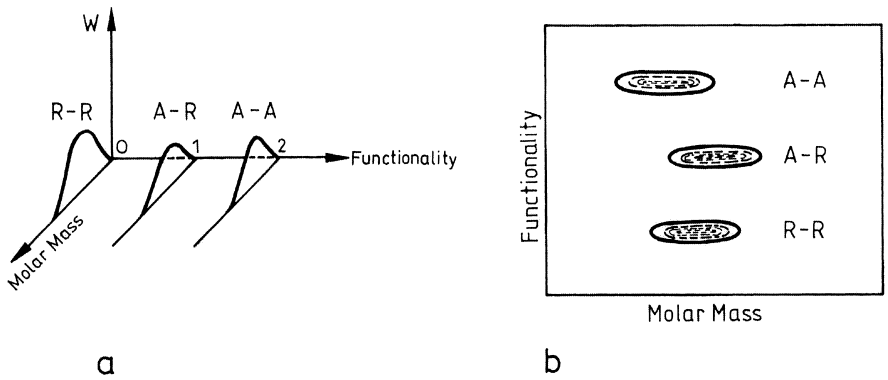


Fig. 1: Schematic representation of the molecular heterogeneity of a telechelic polymer in a 3D diagram (a) and a contour plot (b) [1)]

For copolymers, in particular random copolymers, instead of discrete functionality fractions a continuous drift in composition is present. To determine this chemical composition drift in correlation with the molar mass distribution, a variety of analytical techniques must be used, including chromatographic separation combined with spectroscopic detection.

Another most efficient approach is the chromatographic separation of complex polymers by combining different separation mechanisms. A possible separation protocol for a complex polymer mixture is presented in Fig. 2. The sample under investigation comprises molecules of different chemical compositions (different colours) and different sizes. In a first separation step this mixture is separated according to composition yielding fractions which are chemically homogeneous. These fractions are transfered to a size-selective separation method and analysed with respect to molar mass. As a result of this two-dimensional separation, information on both typs of molecular heterogeneity is obtained.

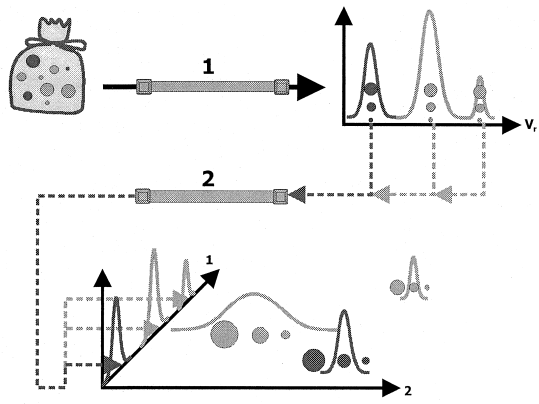


Fig. 2: Schematic separation protocol for the analysis of a complex polymer mixture [1)]

Two-dimensional Chromatography

By the use of different modes of liquid chromatography it is possible to separate polymers selectively with respect to hydrodynamic volume (molar mass), chemical composition or functionality. Using these techniques and combining them with each other or with a selective detector, two-dimensional information on different aspects of molecular heterogeneity can be obtained. If, for example, two different chromatographic techniques are combined in a "cross-fractionation" mode, information on chemical composition distribution (CCD) and molar mass distribution (MMD) can be obtained.

One of the very selective modes of liquid chromatography of polymers is liquid chromatography at the critical point of adsorption (LC-CC) [2-4)]. LC-CC relates to a chromatographic situation, where the entropic and enthalpic interactions of the macromolecules and the column packing compensate each other. To describe this phenomenon the term "chromatographic invisibility" is used, meaning that the chromatographic behaviour is not directed by the size but by the inhomogeneities (chemical structure) of the macromolecules. Under such chromatographic conditions it is possible to determine the heterogeneities of the polymer chain selectively and without any influence of the polymer chain length. LC-CC has been successfully used for the determination of the

functionality type distribution of telechelics and macromonomers, for the analysis of block copolymers, macrocyclic polymers, and polymer blends [5,6].

Thus, LC-CC represents a chromatographic separation technique yielding fractions which are homogeneous with respect to chemical composition but distributed in molar mass. These fractions can readily be analysed by SEC which for chemically homogeneous fractions provides true molar mass distributions without interference of CCD or functionality type distribution (FTD). Therefore, the combination of LC-CC and SEC in a 2D set-up can truely be regarded as "orthogonal" chromatography provided that LC-CC comprises the first dimension [7]. Consequently, for functional homopolymers being distributed in functionality and molar mass, coupled LC-CC vs. SEC can yield combined information on FTD and MMD. This type of dual information is of significant importance, for example, for the quality control of epoxy resins [8,9].

Epoxy resins are distributed with respect to molar mass, functionality and branching. A functionality type separation can be achieved by LC-CC, resulting in functionality fractions P1-P4 which are identified as corresponding to the bisepoxy (P1), epoxy-diol (P2) and bisdiol (P3,P4) functionality fractions by MALDI-TOF mass spectrometry, see Fig. 3.

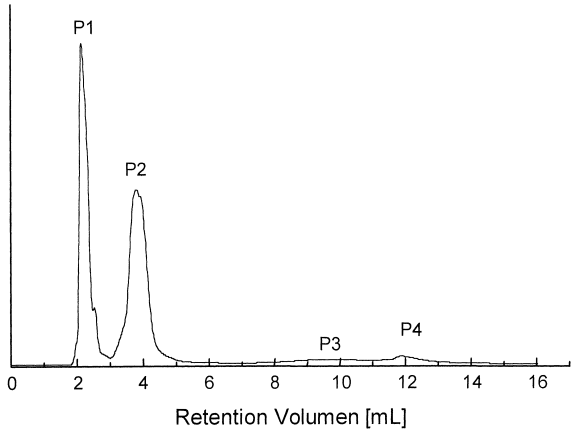


Fig. 3: Functionality type separation of an epoxy resin by LC-CC [8]

The combination of this type of separation with SEC in a 2D chromatography experiment results in a contour plot, where in addition to the different functionality and molar mass fractions branching can be detected, see Fig. 4.

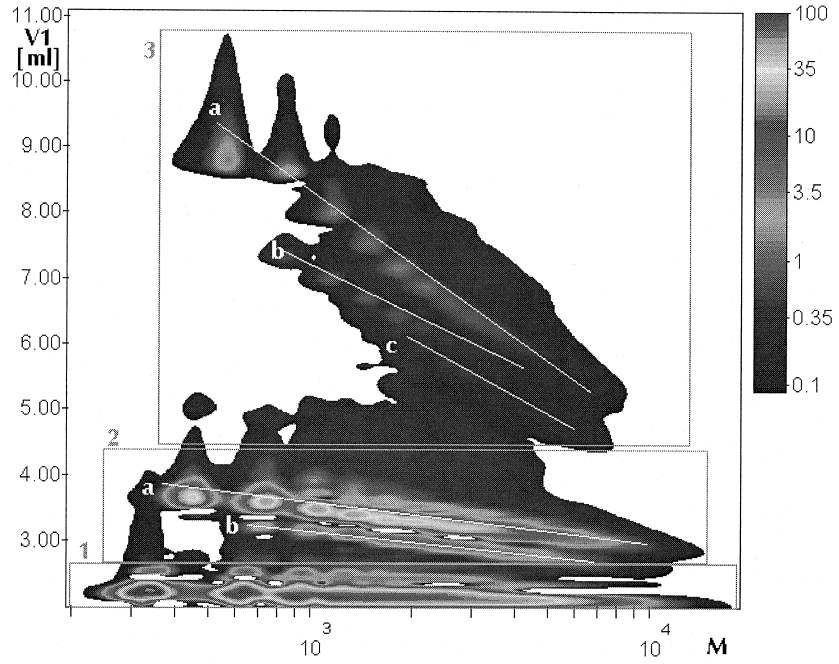
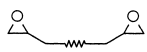
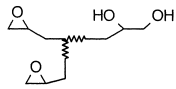
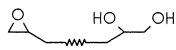
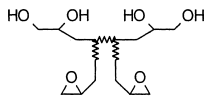
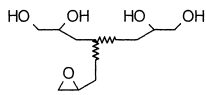
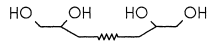


Fig. 4: Contour plot LC-CC (vertical) vs. SEC (horizontal) separation of an epoxy resin [9)]

In addition to the linear oligomer series **1**, **2a** and **3a** the contour plot reveals branched functionality fractions **2b**, **3b** and **3c**. **2b** can be assigned to a mono-branched epoxy-diol fraction, while **3b** and **3c** correspond to a mono-branched and di-branched bisdiol fraction, respectively. The concentration of each fraction is presented by a color code and can be determined directly from the contour plot. Calibrating the SEC dimension, the molar mass distributions for all functionality fractions can be calculated, see Table 1.

Table 1: Quantification of the 2D separation of an epoxy resin

	Structure	Amount	M_n	M_w	D
1		65	860	1.720	1,99
2		4	1.690	2.620	1,55
		26	1.130	1.840	1,62
3		1	2.990	3.680	1,23
		1	1.360	1.590	1,17
		3	1.100	1.990	1,81
Total	All	100	953	1811	1,90

Hyphenation of Liquid Chromatography with Spectroscopic Methods

The determination of compositional changes across the molar mass distribution of a polymer or the detection of a specific component in a complex polymer mixture is of considerable interest. This information allows to predict physical properties and ultimately the performance of the polymer. Several analytical techniques are of use in determining these properties. Mass spectrometry, NMR, and infrared spectroscopy can be used to provide data about the compositional details of the sample.

The direct coupling of HPLC and FTIR spectroscopy is possible by using the LC-Transform interface of Lab Connections. The design concept of the interface is shown in Fig. 5.

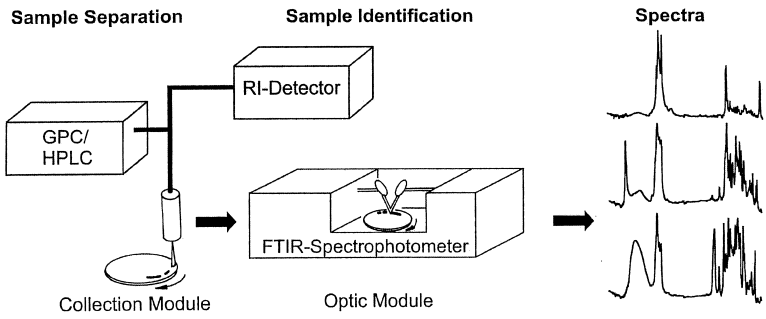


Fig. 5: Schematic representation of coupled liquid chromatography and FTIR spectroscopy [1)]

The system is composed of two independent modules, the sample collection module and the optics module. The effluent of the liquid chromatography column is split with a fraction going into the heated 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. Data collection is readily accomplished with software packages presently used for GC-FTIR. 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. As a result of the investigation a complete FTIR spectrum for each position on the disc and, hence, for each sample fraction is obtained [10,11)]. 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.

The analysis of the chemical composition of a binary polymer blend by coupled SEC-FTIR using the LC Transform is shown in Fig. 6. After separating the sample with respect to molecular size, the fractions were deposited on the germanium disc and FTIR spectra were recorded continuously along the sample track. In total, a set of about 80 spectra was obtained which can be presented in a three-dimensional plot. The projection of the 3D plot on the retention time-IR frequency coordinate system yielded a two-dimensional representation, where the intensities of the absorption peaks were given by a colour code. Such a contour plot

readily provides information on the chemical composition of each chromatographic fraction. It was obvious that the chromatographic peaks 1 and 2 had different chemical structures. By comparison with reference spectra which are accessible from corresponding data bases, component 1 could be identified as polystyrene, while component 2 was polyphenylene oxide.

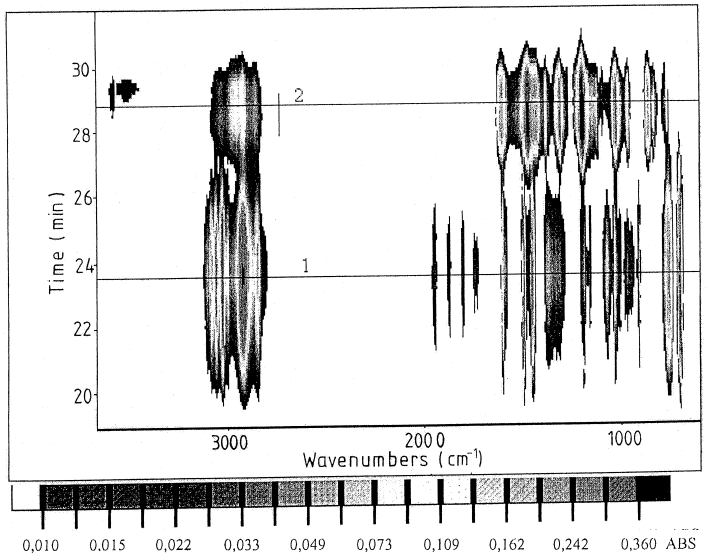


Fig. 6: SEC-FTIR analysis of a binary blend, contour plot representation

Nuclear magnetic resonance (NMR) spectroscopy is by far the most powerful spectroscopic technique for obtaining structural information about organic compounds in solution. Its particular strength lies in its ability to differentiate between most structural, conformational and optical isomers. Early experiments of coupled HPLC-^{1}H-NMR in polymer analysis were conducted in a stop-flow mode or with very low flow rates to accumulate a sufficient number of spectra per sample volume. With the development of more powerful spectrometers and efficient solvent suppression techniques it is now possible to run on-flow experiments. For these experiments the ^{1}H-NMR spectrometer is directly coupled via capillary tubing to the HPLC. The injection of the sample into the HPLC system is automatically initiated by the NMR console via a trigger pulse when starting acquiring NMR data [12,13].

The investigation of the tacticity of oligostyrenes by on-line HPLC-^{1}H-NMR has been reported recently [14]. The oligomer separation was carried out by hydrophobic interaction

chromatography using isocratic elution with acetonitrile on a reversed phase column RP-18. The chromatogram of an oligostyrene is shown in Fig. 7. The first oligomer peak was identified as being the dimer (n=2), the next peak was identified as the trimer (n=3) and, accordingly, the following peaks were assigned to the tetramer, pentamer etc. The dimer peak appeared uniform, whereas for the following oligomers a splitting of the peaks was obtained. For n=3 and n=4 a splitting into two peaks was observed. For n=5 and further a splitting into three or more peaks occured, which could be attributed to the formation of different tactic isomers.

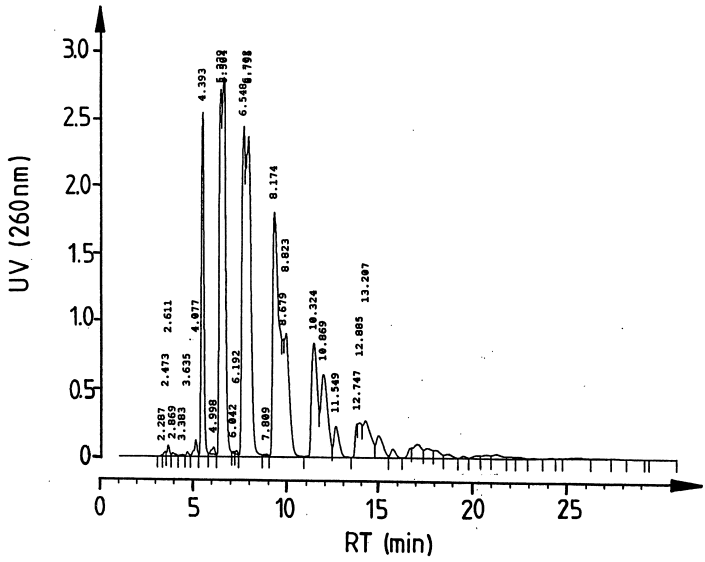


Fig. 7: HPLC chromatogram of oligostyrene PS 530 separated on a RP-18 column [14)]

The analysis of the isomerism of the oligomers by HPLC-NMR is given in Fig. 8. In this experiment conventional HPLC grade acetonitrile was used as the eluent and no deuterium lock was applied. These conditions required high stability of the NMR instrument and a very efficient solvent suppression technique since 100 % acetonitrile must be suppressed. The obtainable structural information related to the entire chemical shift region, however residual signals of the eluent were obtained at 1.8-2.4 ppm and 1.3 ppm due to acetonitrile and its impurities. The contour plot clearly revealed two signal regions, which could be used for analysis. These were the region of the methyl protons of the sec. butyl endgroup at 0.6-0.8 ppm and the aromatic proton region of the styrene units at 6.5-8.0 ppm. For the generation of the contour plot every 8 seconds a complete spectrum was produced by co-adding 8 scans.

Accordingly, for the structural analysis 128 spectra were available over the entire retention time range. These spectra bear selective information on the tacticity, even without completely separating the tactic isomers chromatographically.

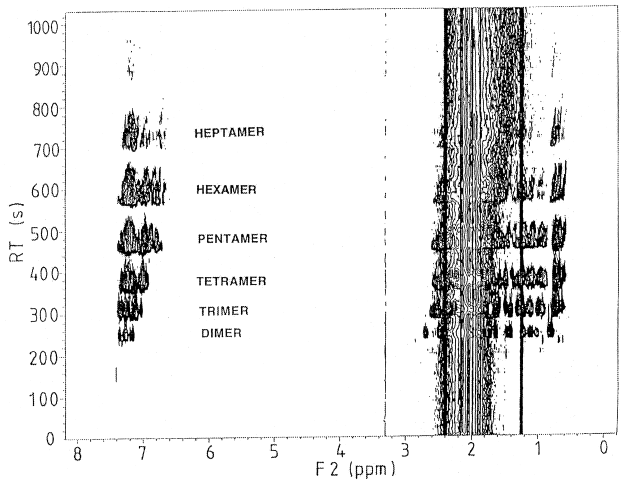


Fig. 8: Contour plot of chemical shift vs. retention time of the on-line HPLC-NMR analysis of PS 530 [14)]

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