Coupling of liquid chromatography and fourier-transform infrared spectroscopy for the characterization of polymers
Kok, S.J.

Citation for published version (APA):
Kok, S. J. (2004). Coupling of liquid chromatography and fourier-transform infrared spectroscopy for the characterization of polymers

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
1 Introduction
1.1 Introduction

During the last decades, important progress in the production of polymers has been made and nowadays the applications of polymers seem almost unlimited. Polymer products can be made in almost every shape and can be applied in a great variety of circumstances, while their initial properties should be maintained. Clearly, at present polymers are indispensable and greatly influence our way of living.

During the lifetime of a polymer changes in the optical, mechanical and chemical properties can occur. These changes can limit their usable period. To help extend the service-life-time, it is important to reveal the underlying changes in microstructure of a polymer. As polymers are complex molecules and typically consist of multiple distributions, their characterization is a challenging task. For example, a molar-mass (MMD) and chemical-composition distribution (CCD) are simultaneously present in copolymers.

In order to determine the microstructure of polymers a variety of analytical techniques can be used. Among these are spectroscopic techniques, such as Fourier-transform infrared (FTIR) and nuclear-magnetic-resonance (NMR), and mass-spectrometric techniques. However, spectroscopic techniques only provide information on the average composition of the polymer and the spectra are difficult to interpret as they contain all the features of the polymer. To characterize distributions, (liquid-chromatographic, LC) separation techniques are necessary. These can be based on a separation according to hydrodynamic volume (which is related to molar mass), as in size-exclusion chromatography (SEC). On the other hand, gradient-elution LC can be used for separations according to chemical composition, while isocratic LC can be used to separated according to functionality. The identity of the separated molecules still remains unknown when universal detectors are used. A sophisticated coupling to the aforementioned spectroscopic and spectrometric detectors is therefore essential to obtain detailed information on the microstructure of the polymer. As most of the changes during the polymer life-time are due to changes in functional groups, the combination of LC and FTIR spectroscopy is an obvious choice.

1.2 Scope and outline of the thesis

The objective of the work described in this thesis was the application of interfacing LC and FTIR spectroscopy to reveal functionality differences between polymers. For this purpose, research has mainly focused on the quantitative and qualitative aspects of LC–FTIR. The LC techniques included SEC and gradient-elution LC. The LC–FTIR interfaces used in these studies have been commercial interfaces, viz. an off-line solvent-elimination interface and on-line flow-through cells.
In Chapter 2 a brief overview is given of LC techniques used for the separation of polymers. In Chapter 3 LC and FTIR spectroscopy interfaces, which have been and are being used are reviewed. The early on-line interfaces based on flow cells are discussed with respect to their various designs, their limitations and applicability. Thereafter, the developments in off-line solvent-elimination interfaces are discussed extensively. The most successful solvent-elimination interfaces involve a nebulizer in which the eluent is rapidly evaporated by means of a heated nebulizer. Analyte deposition is preferably carried out on inert, water-resistant substrates, such as zinc selenide or germanium, and IR spectra can be acquired in the transmission as well as in the transfection mode. It has been reported that the highest sensitivity can be obtained when using micro-LC and FTIR microscopy. However, recent developments in solvent-elimination LC–FTIR have shown the potential of an ink-jet-printer-like interface for coupling with micro-LC.

Chapter 4 describes the use of a solvent-elimination interface as a quantitative detector in SEC–FTIR. Several aspects have been investigated. The influence of the substrate moving speed on the chromatographic resolution was assessed based on the analysis of a series of polystyrene standards by SEC–FTIR. The optimum substrate moving speed strongly depends on the eluent and on the eluent flow rate and it has to be optimized for every experimental set-up. However, once all interface parameters have been optimized, the chromatographic resolution was essentially maintained upon analyte deposition. It also became apparent that varying concentration profiles are obtained across and along the deposit trace. This effect can be reduced by working at low eluent flow rates (i.e. 100 μl/min). At reduced flow rates an increased response was observed, due to the smaller areas across which analytes were deposited. In practice, however, such low flow rates are rarely used in SEC. When conventional-sized SEC columns are used, a typical operating flow rate is 1 ml/min.

For quantitative analysis the use of absolute absorption-band intensities is not allowed due to the varying concentrations along the deposit. To overcome these concentration effects the use of absorption-band ratios is suggested. Quantification using absorption-band ratios should be very well applicable to the compositional analysis of copolymers. However, inconsistent absorption-band ratios were found for a homopolymer when the injected quantity was varied. Different aspects have been investigated in order to obtain consistent absorption-band ratios. To this end, research has focused on the effects of using different substrates, the occurrence of molecular orientation upon deposition, the influence of an irregular deposit, and the effect of the layer thickness of the analyte deposit. In addition, the influence on the spectral integrity has been examined by acquiring spectra in the transmission and transfection modes. It was revealed that the layer thickness can influence
the absorption-band intensity and thus the absorption-band ratios. Specifically, this occurred at layer thicknesses below 10 μm (corresponding to approximately 37 μg of polymer deposited) with the solvent-elimination used. The characteristic concentration profile described in this chapter led to an underestimation of the true absorption-band intensity. It can be concluded that the use of LC–FTIR as a quantitative detector is rather limited, as deposits from LC–FTIR experiments are usually smaller than the layer thickness indicated. Furthermore, the observed effects are possibly dependent on the physical properties of the polymer, i.e. the tendency to form a smooth film or to spread across the substrate.

The use of LC–FTIR as a qualitative detector is discussed in Chapter 5. A new multivariate-data-analysis method, DifSub, based on principal component analysis (PCA), is introduced to reveal subtle differences between large SEC–FTIR data sets. DifSub was successfully applied to aged poly(vinyl chloride) (PVC) samples and a reference PVC sample in order to reveal molar-mass-dependent differences between the aged PVC samples. Because DifSub uses FTIR spectra without pretreatment (such as mean-centering or scaling), interpretable ‘difference spectra’ were obtained. In principle, the DifSub method can be used in combination with any type of separation technique with spectroscopic detection.

In the second part of Chapter 5, LC–FTIR was used as a valuable functional-group-screening tool, to verify the presence of different classes of additives (e.g. hindered amines, hindered phenols, or phosphorous-containing anti-oxidants) in an artificial additive mixture. The selection of additives covered a wide range of polarity and molar mass. Successful deposition was accomplished for the majority of the additives and the corresponding FTIR spectra could be used for identification purposes. However, FTIR spectra of certain additives were different from the corresponding KBr-reference spectra, which was ascribed to the polymorphic nature of these additives. The functionality screening was applied to a real polymer sample, containing 1.2% (w/w) Irganox 1076. It was demonstrated that the polymer sample could be analyzed by gradient-elution LC–FTIR in one single step without sample preparation. The FTIR spectrum obtained for Irganox 1076 was successfully identified after comparison with KBr-reference spectra.

The use of a flow cell for coupling of LC and FTIR spectroscopy as an alternative for solvent-elimination LC–FTIR is often disregarded. However, flow cells can be of high value in isocratic analysis, provided that an IR-transparent eluent “window” is available for detection of the functional groups of interest. Therefore, the two types of interfaces were assessed in Chapter 6 by analyzing a polycarbonate/aliphatic polyester blend and a polycarbonate-co-polydimethylsiloxane copolymer. The chromatographic integrity (i.e.
peak asymmetry and chromatographic resolution) of the two systems was compared. It was demonstrated that the peak asymmetry was comparable to the peak asymmetry obtained by UV detection. However, the chromatographic resolution for oligomers was reduced in both types of interfaces. Quantitative and qualitative aspects have been examined. A linear relationship was obtained from a plot of the absorption-band intensity vs. the concentration. The injected quantity was higher than the critical value described in the second part of Chapter 4, so that consistent absorption-band intensities were obtained. The detection limit was found to be lower for the solvent-elimination interface than for the flow-cell interface. However, the latter interface showed a better repeatability and allowed some qualitative information to be obtained. From this study, it can be concluded that a flow-cell can be of high value in SEC–FTIR. Moreover, because of the possible occurrence of inconsistent absorption-band intensities in solvent-elimination LC–FTIR spectra, it is foreseen that a flow cell can provide quantitative analysis for a large number of polymers. Besides, it offers a cheap and easy-to-operate alternative for solvent-elimination interfaces.

In order to reveal differences in molar mass and chemical composition of copolymers simultaneously, a comprehensive two-dimensional gradient-elution LC and SEC chromatography system (gradient-elution LC×SEC) was used in Chapter 7 in conjunction with FTIR spectroscopic detection. Because a short second-dimension analysis time and a large number of second-dimension fractions are typical for comprehensive two-dimensional LC, FTIR coupling via a solvent-elimination interface is of limited use. For example, it is foreseen that the chromatographic resolution cannot be fully maintained and the available deposition space of the currently used solvent-elimination LC–FTIR interface is not adequate. For the latter aspect, a flow cell was used in interfacing gradient-elution LC×SEC and a sufficient number of spectra could be acquired during a long elution time. The potential of gradient-elution LC×SEC–FTIR has been demonstrated by the analysis of a series of styrene-co-methylacrylate copolymers with varying chemical composition. The contour plots for styrene have been compared to the corresponding contour plots obtained by UV detection and FTIR detection was shown to yield comparable results. By extracting functional-group contour plots from two-dimensional LC×SEC–FTIR analysis, changes in functionality can be easily revealed across multiple distributions.