Coupling of liquid chromatography and fourier-transform infrared spectroscopy for the characterization of polymers

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2 Liquid-chromatography-based separation techniques for polymers
2.1 Chemical heterogeneity of polymers

In general, (synthetic) polymers are molecules that are built from a repeating sequence of similar building blocks, called monomeric units, prepared in a polymerization process. The number of monomers in a polymer is called the degree of polymerization. This can be different for molecules that are similar in structure, resulting in a molar-mass distribution (MMD). The MMD is influenced by typical characteristics of the polymerization process, \textit{i.e.} kinetic parameters, monomer reactivity, propagation probabilities, \textit{etc.} Different end groups (or functional groups) can be present at the beginning and the end of a polymer chain, for example depending on initial building blocks and the amount(s) and type(s) of end-capper(s) present to terminate the polymerization process. Consequently, next to an MMD a functionality-type distribution (FTD) can be present.

Thus far, it was assumed that only one kind of monomer was present in the polymerization process, resulting in what is called a homopolymer. More-complex distributions are obtained when two – or more – chemically different monomers are used in the synthesis process to form copolymers. The arrangement of the different monomers is dependent on the type of polymerization reaction and different monomer sequences can occur. In a random copolymer the monomers are distributed randomly in the polymer chain. However, when the different types of monomers are concentrated in segments, the polymer is called a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{polymer_structures.png}
\caption{Figure 2.1: Representation of different polymer structures. Spheres represent the monomeric units and end groups are represented as triangles and squares.}
\end{figure}
block-copolymer. A polymer with a combination of random and block aspects is called a statistical copolymer. Alternating copolymers are formed when the monomeric units are alternately grown onto the polymer chain. In the case where (some) monomeric units contain more than two reactive sites, a branched polymer will result. In a similar way, a complete polymer chain can be grafted on an existing polymer, containing residual reactive sites. All polymer architectures mentioned are summarized in Figure 2.1.

2.2 Liquid-chromatographic modes for polymer separations

In liquid chromatography of polymers the separation mechanism plays an especially important role. Depending on the separation mechanism, the different types of distributions described earlier in this chapter can be determined. Two types of interactions with separation columns (i.e. packing materials) can be distinguished. These include entropic (steric exclusion) and enthalpic (adsorption) interactions. The first type of interaction will provide a separation based on size (actually hydrodynamic volume) due to repulsive polymer-surface forces. The second interaction can be used to separate the polymer molecules based on distributions other than size. When both interactions play a role to a different degree, the retention volume of the eluted analytes can be expressed by the retention equation [1]:

\[ V_r = V_i + V_p K_{SEC} + V_s K_{ads} \]  \hspace{1cm} (2.1)

In Equation 2.1, the retention volume \( V_r \) can be described by the interstitial volume \( V_i \), the pore volume of the stationary phase \( V_p \), and the volume of the stationary phase \( V_s \). The chromatographic partition (distribution) coefficients for steric exclusion \( K_{SEC} \) and for adsorption \( K_{ads} \) can be defined for analytes in the stationary phase \( c_s \) and the mobile phase \( c_m \). For the different \( K \) values the stationary and mobile phase are defined differently. For \( K_{SEC} \) the stationary phase is the stagnant mobile phase inside the pores \( V_p \) and the mobile phase is the interstitial volume \( V_i \). For \( K_{ads} \) the stationary phase has a volume of \( V_i \) and the volume of the mobile phase is \( V_m = V_i + V_p \). The chromatographic distribution coefficient, \( K_D \), is usually based on the latter definition of the phase volumes. It can be expressed as

\[ K_D = \frac{c_s}{c_m} = -\exp \left( \frac{\Delta G}{RT} \right) \]  \hspace{1cm} (2.2)

in which \( \Delta G \) is the difference in the partial molar Gibbs free energy (J/mol) for the transfer of analyte molecules form the mobile phase to the stationary phase, which can be written as

\[ \Delta G = \Delta H - T \Delta S \]  \hspace{1cm} (2.3)
where $\Delta H$ (J/mol) and $\Delta S$ (J/K·mol) are the partial molar enthalpy and entropy change, respectively.

Genuine steric exclusion and permeability of the pore volume by the compound will occur when the enthalpic interactions can be suppressed ($K_{ads} = 0$) by using a thermodynamically ‘good’ solvent and strong eluent. This means in thermodynamic terms that $\Delta H = 0$. $K_{SEC}$ varies from 0 for very large molecules that are totally excluded from the pore volume to $K_{SEC}=1$ for very small molecules, which can completely permeate the pores.

On the other hand, when the mobile phase is not a very strong eluent, enthalpic interactions (i.e. adsorption) start to play a role and $K_{ads}$ will be increased. Then the chromatographic mode will change to adsorption ($K_{ads} > 0$). Usually, for larger molecules the retention will be stronger as they contain more monomeric units that can interact with the stationary phase.

It can be derived that mutual entropy-enthalpy compensation can occur for a particular monomeric unit (for a detailed explanation, the reader is referred to [2]). This transition point occurs at a very specific eluent composition and is referred to as liquid chromatography under critical conditions (LCCC) or critical chromatography (CC). It implies that polymers are eluted independent of the number of monomeric. This isocratic mode can be used for the separation of homopolymers exhibiting different end-groups, in which case retention becomes independent of molar mass and an FTD can be obtained [3, 4]. When applying critical conditions for one block of a block-copolymer, a separation can be established according to the block length of the remaining block [5, 6]. The different chromatographic modes are summarized in Figure 2.2.

![Figure 2.2: Isocratic retention modes in liquid chromatography of polymers.](image-url)
2.3 Gradient elution LC of polymers

Nowadays, gradient LC of polymers is a widely accepted technique for the separation of blends and copolymers according to their chemical composition. This was first shown by Van der Maaden et al. who separated homopolymers, such as poly(ethylene terephthalate) and poly(ethylene oxide) according to molar mass and functionality [7]. This was soon followed by the separation of a series of poly(styrene-co-methylacrylate) copolymers according to chemical composition by Teramachi et al. [8]. Since then, several authors have suggested separation mechanisms for this type of separation [1, 9–13], alternately referred to as liquid adsorption chromatography (LAC) [14], high-performance precipitation liquid chromatography (HPPLC) [15] or, gradient polymer elution chromatography (GPEC) [16]. In this section, the separation mechanisms will be briefly discussed. For the applications of gradient LC of polymers, the work of Glöckner [1] is highly recommended. In addition, Philipsen has recently presented an excellent review on the determination of CCDs of polymers [17].

Gradient LC of polymers differs from the LC of low-molar-mass molecules, because additional phenomena contribute to the separation mechanism. The retention of polymers is complex and is affected by solubility effects, exclusion and adsorption [1] (the latter two have been described in the previous section). The solubility of the polymer in the eluent, which can be described by the Flory Huggins theory [18], is limited and plays an important role in obtaining separations. In order to completely retain the polymer at the initial chromatographic conditions, the starting eluent has to be a non-solvent or weak eluent for – at least part of – the polymer [19]. When a non-solvent is used, precipitation occurs while use of a weak eluent results in a phase separation at the top of the LC column [2, 13].

Gradual dissolution and desorption of the polymer is accomplished by increasing the strength of the eluent and solvent. The eluent composition at which the polymer starts to elute is dependent on the chemical composition and on molar mass, and a separation on chemical composition or other structural differences will be the result. Recently, Brun et al. [13] described the gradient elution of polymers and explained the elution according to chemical composition and molar mass as follows. Elution of the polymers can only occur in the vicinity of the critical eluent composition (φ_{crit}, fraction strong eluent at the critical point) and two situations can be discerned for the separation without and with molar mass dependency, respectively. All the polymer fractions will leave the column practically independently of molar mass at an eluent composition close to φ_{crit}. The elution depends on the chemical composition or other structural differences, as structurally different polymers have different critical points. This means that the polymer needs to be fully dissolved and polymer redissolution should occur before φ_{crit} is reached (φ_{sol} < φ_{crit}, where φ_{sol} is the...
fraction of strong solvent yielding complete solubility). In this case, redissolution is followed by polymer adsorption before the gradient at the critical eluent composition can occur. On the other hand, when the polymer is only partly redissolved before the critical eluent composition ($\varphi_{\text{sol}} > \varphi_{\text{crit}}$) due to insufficient affinity of the eluent towards the polymer, the higher molar mass part will elute at an eluent composition with a higher solvent strength. In this case a significant molar-mass dependency is observed.

When using gradient LC for the separation of polymers, one needs to be aware of a few important aspects influencing the chromatographic results. From the above elution mechanism, it is clear that the eluent composition has to fulfill $\varphi_{\text{sol}} < \varphi_{\text{crit}}$ in order to exclude molar mass effects. Furthermore, poor solubility of polymers at the initial stage of separation leading to the possible occurrence of phase separation complicates the prediction of the chromatographic process [13]. In addition, a solid crystalline polymer phase can be formed when (semi-)crystalline polymers are injected in the chromatographic system. Redissolution of crystalline polymers is slow and can lead to anomalous chromatograms [2, 20]. To avoid precipitation of crystalline polymers, it was suggested to use an increased column temperature. Finally, many authors have observed a so-called ‘breakthrough’ peak appearing at the column void volume before the actual (highly) retained polymer peak [19, 21, 22]. This phenomenon was thoroughly investigated by Jiang et al. [23]. Re-injection of both peaks for a narrow-standard sample demonstrated that they exhibit identical molar-mass distributions. It was suggested that for a real (broad) polymer sample, the breakthrough is dependent on the molar mass and chemical composition. To avoid breakthrough peaks it was recommended that (i) a small injection volumes are used with high sample concentrations, (ii) the injection solvent should preferably be a strong solvent but a weak eluent (iii) and the initial chromatographic eluent should be weak or at least weaker than the critical solvent composition.

Analogous to conventional LC for low-molar-mass molecules, two separation modes can be discerned in the LC of polymers, i.e. reversed-phase and normal-phase. Characteristic for reversed-phase LC (RPLC) is the use of a non-polar stationary phase in combination with a more-polar eluent. The retention is based on weak, dispersion interactions of the analyte with the stationary phase, but mostly on strong polar (“solvophobic”) interactions with the mobile phase. Commonly used stationary phases include $C_{18}$ or $C_{8}$-modified silica. RPLC is frequently used for the separation of copolymers according to the (average) chemical composition or when mixtures of polymers differing in polarity (i.e. blends) have to be separated. Contrary to RP adsorbents, the normal-phase stationary phase is polar and it is used in combination with a less-polar eluent. Stationary phases can consist of classical adsorbents (i.e. bare silica), but modified bonded phases, such as diol-, amino-, or cyano-
modified silica, are more frequently used. The separation is based on (strong) polar interactions with the stationary phase and because of the large polarity range for these types of adsorbents, large differences in selectivity can be obtained. Therefore, NPLC is of great value when a separation is necessary to reflect small differences between polymer molecules, such as functional end groups. The elution order of analytes obtained under NP conditions will be (approximately) reversed when the same analytes are separated according to an RP mechanism.

Recently, the use of monolithic columns has been assessed for use in the characterization of polymers to obtain relative molar-mass parameters [24]. Good separations of individual components of polystyrene (PS) and poly(methyl methacrylate) (PMMA) (molar mass range 3,000 to 1,000,000 g/mol) were obtained under gradient-elution conditions when a poly(styrene-co-divinylbenzene) based monoliths was used. However, other precursors used for the preparation of monoliths appeared to be less successful for the separation of polymers. The applicability of monoliths to polymer separations has to be further explored.

2.4 Two-dimensional liquid chromatography

The analysis of polymers by SEC, CC or gradient-elution LC alone will not provide extensive details on the microstructure of complex polymers, which exhibit a dispersity in more than one property. For example, it is impossible to quantitatively distinguish between a copolymer or a blend of two or more homopolymers by SEC [25]. When combining two (different) separation mechanisms in a two-dimensional liquid chromatographic system, the polymer can be separated according to two different distributions [26]. Possible combinations of different LC mechanisms for use in two-dimensional liquid chromatography to obtain such information are summarized in Table 2.1.

<table>
<thead>
<tr>
<th>first dimension</th>
<th>SECC</th>
<th>CC</th>
<th>gradient LC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEC</td>
<td>n.a.</td>
<td>MMD × FTD</td>
<td>MMD × FTD</td>
</tr>
<tr>
<td>CC</td>
<td>MMD × FTD</td>
<td>BLD × BLD*</td>
<td>FTD × CCD</td>
</tr>
<tr>
<td>gradient LC</td>
<td>CCD × MMD</td>
<td>CCD × FTD</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

n.a., not applicable

* Potentially useful for (e.g. for block-length distributions, BLD), provided that two different critical conditions are used.
Table 2.2: Overview of two-dimensional separation techniques and column dimensions used (from 1990).^a^  

<table>
<thead>
<tr>
<th>Coupled Modes</th>
<th>Sample</th>
<th>(1^\text{column} ) LxI.D., mm</th>
<th>(1^\text{F} ) (ml/min)</th>
<th>(1^\text{Vinj} ) ((\mu)l)</th>
<th>(2^\text{column} ) LxI.D., mm</th>
<th>(2^\text{F} ) (ml/min)</th>
<th>(2^\text{Vinj} ) ((\mu)l)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC/LC</td>
<td>PEG</td>
<td>250x10</td>
<td>2 n.s.</td>
<td>100x4.6</td>
<td>n.s.</td>
<td>50</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>CC/SEC</td>
<td>Polyether</td>
<td>250x4</td>
<td>n.s.</td>
<td>300x8</td>
<td>1</td>
<td>100</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>CC/SEC</td>
<td>PEG</td>
<td>250x10</td>
<td>2 n.s.</td>
<td>300x4.6</td>
<td>1</td>
<td>100</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>LC/SEC</td>
<td>SAN</td>
<td>4x n.s.</td>
<td>1 n.s.</td>
<td>700x27</td>
<td>n.s.</td>
<td>n.s.</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>LC/SEC</td>
<td>SMMA</td>
<td>50x4.6</td>
<td>0.5 100</td>
<td>250x8</td>
<td>1</td>
<td>100-250</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>LC/SEC</td>
<td>PS</td>
<td>250x4.6</td>
<td>1 20</td>
<td>300x7.8</td>
<td>(3)</td>
<td>1</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>SEC/LC</td>
<td>SAN</td>
<td>300x7.8</td>
<td>1 500</td>
<td>150x4.6</td>
<td>1</td>
<td>100-175</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>SEC/LC</td>
<td>SEMA</td>
<td>600x7.8</td>
<td>1 200</td>
<td>60x4</td>
<td>0.5</td>
<td>n.s.</td>
<td>32,33</td>
<td></td>
</tr>
<tr>
<td>SEC/LC</td>
<td>S MEMA, SAN</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>SEC/LC</td>
<td>MMA-g-EPDM</td>
<td>600x7.5</td>
<td>1 n.s.</td>
<td>600x4</td>
<td>1</td>
<td>5</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>CC-LC</td>
<td>AE</td>
<td>3x4.6</td>
<td>0.5 100</td>
<td>250x4.6</td>
<td>0.5</td>
<td>n.s.</td>
<td>47,48</td>
<td></td>
</tr>
<tr>
<td>CC×SEC</td>
<td>PEO</td>
<td>250x4</td>
<td>0.04 n.s.</td>
<td>300x8</td>
<td>2</td>
<td>200</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>CC-SEC</td>
<td>BA-g-SBR</td>
<td>250x4(2)</td>
<td>n.s.</td>
<td>300x7.5</td>
<td>n.s.</td>
<td>100</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>CC-SEC</td>
<td>PMMA-b-PrBMA</td>
<td>150x4 + 250x4</td>
<td>0.5 25</td>
<td>300x8(2)</td>
<td>2</td>
<td>n.s.</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>CC-SEC</td>
<td>ENR-g-PS, ENR-g-P MMA</td>
<td>250x4(2)</td>
<td>0.02 n.s.</td>
<td>300x8</td>
<td>1.5</td>
<td>100</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>CC×SEC</td>
<td>PS</td>
<td>250x1</td>
<td>0.004 1</td>
<td>75x4.6</td>
<td>0.6</td>
<td>6.4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>CC×SEC</td>
<td>PS/PS-OH</td>
<td>250x1</td>
<td>0.003 1</td>
<td>50x7.5</td>
<td>0.8</td>
<td>n.s.</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>LC-SEC</td>
<td>MMA-g-EPDM</td>
<td>125x4</td>
<td>1 100</td>
<td>20x50</td>
<td>n.s.</td>
<td>200</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>LC-SEC</td>
<td>PMMA/EP</td>
<td>125x4</td>
<td>1 100</td>
<td>20x50</td>
<td>n.s.</td>
<td>200</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>LC-SEC</td>
<td>16-component mix of star SB</td>
<td>300x8</td>
<td>n.s.</td>
<td>100</td>
<td>n.s.</td>
<td>100</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>LC×SEC</td>
<td>PEG</td>
<td>250x4.6</td>
<td>0.5 n.s.</td>
<td>300x8; 50x8</td>
<td>1-3</td>
<td>500; 1000</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>LC×SEC</td>
<td>PS, PMMA, SMA</td>
<td>150x1</td>
<td>0.004 1</td>
<td>75x4.6</td>
<td>0.6</td>
<td>6.4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>LC×SEC</td>
<td>SMA</td>
<td>150 x 3.9</td>
<td>0.05 10</td>
<td>150 x 6.0</td>
<td>0.8</td>
<td>200</td>
<td>38</td>
<td></td>
</tr>
</tbody>
</table>

^a^ The prescripts used in the table heading refer to the dimension of the separation.

^b^ /, off-line fraction collection; -- , on-line, but not all first-dimension effluent transferred to second dimension (see text); x, on-line comprehensive coupling.

^c^ By means of a splitter a representative fraction from the first-dimension separation was transferred to the second dimension to maintain a comprehensive system.

Abbreviations: AE, alcohol ethoxylates; BA, butylacrylate; ENR, epoxidized natural rubber; EP, ethylene-propylene; EPDM, ethylene-propylene-diene rubber; MMA methyl methacrylate; PEG, polyethylene glycol; PEO, polyethylene oxide; PS, polystyrene; PS-OH, hydroxyl-functionalized PS; PrBMA, poly(i-butyl methacrylate); SEMMA, poly(styrene-co-2-methoxyethyl methacrylate); SAN, poly(styrene-co-acrylonitrile); SBR, styrene-butadiene rubber; SEMA, poly(styrene-co-ethyl methacrylate); SMA, poly(styrene-co-methyl methacrylate).

The coupling of two LC techniques can be performed in an off-line or on-line fashion, each with their own limitations and advantages (see Table 2.2). The off-line mode can be time-consuming due to the extra steps associated with the collection of fractions [27–34], such as
isolation and re-injection in the second chromatograph. However, the advantages of off-line coupling are that a single chromatographic system can be used and that, after the fractions have been collected, they can be redissolved in a suitable solvent for the second-dimension separation to avoid eluent-miscibility problems. Furthermore, a part of the fractions collected can be used for further analysis, for instance using structure-elucidation techniques, or the polymers can be chemically modified.

In the on-line coupling mode an 8- or 10-port interface valve is used, comprising two sample-collection loops. While filling one loop, the fraction collected in the second loop is analyzed in the second dimension (for a detailed experimental set-up, see Chapter 7). However, basically two different approaches can be found in the literature offering a semi-comprehensive and a fully comprehensive two-dimensional chromatography system. The first involves the partial collection of first dimension effluent to be analyzed in the second dimension, using an eight-port interface valve [25, 35-37]. In this set-up, conventional-sized first-dimension columns are used, typically operating at flow rates between 0.5 and 1 ml/min. Although not always explicitly stated, it is obvious that under such conditions, the size of the fraction-collection loop is insufficient to store all the first-dimension effluent during the second-dimension analysis time. Consequently, part of the first-dimension effluent is discarded. From this discussion, it will be clear that the various parameters such as the first-dimension flow rate \( (^1F_{\text{max}}) \), the injection volume in the second dimension \( (^2V_{\text{inj}}) \), and the maximum second-dimension analysis time \( (^2t_{R,\text{max}}) \) must be carefully selected in order to collect all of the first-dimension effluent. For fully comprehensive operation, the second-dimension analysis time and the collection-loop size determine the (maximum) flow rate for the first dimension. Equation 2.4 describes for which conditions a fully comprehensive setup [3, 25, 37, 38] can be obtained.

\[
^1F \leq \frac{^2V_{\text{inj}}}{^2t_{R,\text{max}}} \tag{2.4}
\]

In the on-line coupling mode, gradient-elution LC is most frequently selected as first-dimension separation and SEC as second-dimension separation (LC×SEC) [30, 31, 37, 39]. This specific coupling order has a number of advantages [28, 40] in comparison with SEC×LC. Firstly, gradient-elution LC has more parameters by which to optimize the separation according to chemical composition (e.g. selection of mobile phase and stationary phase, temperature, etc.). Secondly, by adjusting the gradient, rather homogeneous fractions with respect to chemical composition can be obtained. In addition, when gradient-elution LC is used as first-dimension separation in LC×SEC, peak fronting and peak splitting due to the introduction of a large volume of strong (SEC) eluent in the second dimension will be avoided. Next, SEC can be performed in a relatively short time and equation 2.4 is easily
fulfilled, while gradient-elution LC requires long analysis times, including the step to return to initial eluent conditions. Also, detectors that cannot be used under gradient conditions can be used for LC×SEC (i.e. refractive index, flow-cell IR). Finally, the sample load on an LC column can be rather high as compared to a SEC analysis, which will result in a higher signal-to-noise-ratio (SNR) after the second dimension.

In literature, many impressive examples of comprehensive two-dimensional liquid-chromatographic separations have been reported [3, 36, 35], demonstrating the potential of this technique. Nowadays, off-line coupling is rarely used and a trend can be observed towards the on-line (comprehensive) approach (cf. Table 2.2) on which we have focused (see Chapter 7). Depending on which chemical information needs to be revealed, different modes of LC have been coupled. For instance, CC×LC was used to determine the ethoxy-chain-length distribution as function of the aliphatic chain length in technical alcohol ethoxylates. Furthermore, reaction products of a graft polymerization [35, 41, 42] and functionalized polystyrenes [3] were studied by CC×SEC. In the latter case, under "critical" conditions for PS a variation of retention with molar mass was still observed. It was suggested that despite the careful adjustment of the conditions the separation still showed some adsorption characteristics. In addition, it was suggested to use LC×LC to increase our understanding of polymer separation mechanisms [3]. Because of the high separation efficiency of gradient-elution LC, this mode has been applied in combination with SEC to study the molar mass of polymers differing in chemical composition, i.e. blends [3, 36, 43] and copolymers [3, 38]. In such cases, extremely detailed information can be gathered, as was demonstrated by Kilz et al., who separated a 16-component mixture of star-shaped styrene-block-butadiene copolymers [36]. Finally worth mentioning in the context of this thesis is the application of infrared (IR) detection in two-dimensional liquid chromatography, which has been suggested by Fujimoto and Jinno in the early nineties [44]. Recently, the coupling of IR to CC×SEC has been realized, by means of a commercially available solvent-elimination interface, resulting in a semi-on-line detector set-up. More details can be found in Chapter 7.

References

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