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Comprehensive two-dimensional liquid chromatography and hyphenated liquid chromatography to study the degradation of poly(bisphenol A)carbonate

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Abstract

Size exclusion chromatography (SEC), gradient polymer elution chromatography (GPEC) and liquid chromatography at critical conditions (LC-CC) have been developed and applied to observe chemical changes in poly(bisphenol A)carbonate (PC) due to hydrolytic degradation. Especially LC-CC appeared to be very successful to observe differences in functionality of PC as result of hydrolytic degradation. Observed differences due to degradation could be identified by (semi) on-line coupling to matrix assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The differences in functionality could be attributed to the formation of different end-groups, i.e. OH end-groups. In addition, comprehensive two-dimensional liquid chromatography (2D-LC) has been applied successfully to study the hydrolytic degradation of PC. LC-CC × SEC showed that the formation of PC with different end-groups occurred over the whole molecular mass range. This information could not be obtained with the separate liquid chromatographic techniques, thereby illustrating the added value of 2D-LC.

Keywords: Poly(bisphenol A)carbonate; Two-dimensional liquid chromatography; Degradation; GPEC; LC-CC; LC × SEC; MALDI-TOF-MS

1. Introduction

In recent years, the range of analytical liquid chromatographic techniques has been expanded. Besides size exclusion chromatography (SEC), which separates according to molecular size, and indirectly according to molecular mass, liquid chromatographic techniques have been developed that separate polymers on other structural properties of the polymer. For example, gradient polymer elution chromatography (GPEC) has been successfully applied to separate copolymers or polymer blends based on their chemical composition distribution (CCD) [1–4]. Liquid chromatography at critical conditions (LC-CC) has been proven to provide selective information on functionality-type distributions (FTD) [5–7]. Under critical conditions, retention of the polymer is not determined by molecular mass but by chemical heterogeneities. In the case of homopolymers separation can be determined by differences in end-groups. LC-CC has been applied successfully for polymer blends, grafted polymers, functional homopolymers and copolymers [8–11]. Finding the exact critical conditions, if present at all, can be a very extensive job, while maintaining the critical conditions can even be more troublesome. However, separation on differences in functionality is still possible with so-called near critical conditions.

Chemical information obtained with commonly used detection methods, like ultraviolet (UV), refraction index (RI) or evaporative light scattering (ELSD) detection, is often rather limited. Therefore, other detection methods have been coupled to liquid chromatography. For example, infrared (IR) detection can be applied on-line using a flow cell [12] or

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(semi) on-line using a deposition interface [9,13,14]. The same accounts for mass spectrometry (MS), where electrospray ionization time-of-flight mass spectrometry (ESI-TOF) MS has been used on-line [15,16] and matrix assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) has been used (semi) on-line using a deposition interface or after automatic or manual fractionation [10,17–19].

One of the latest developments is the application of comprehensive two-dimensional liquid chromatography, in which preferably GPEC or LC-CC is used in the first dimension and SEC in the second dimension [7,12,20,21]. Especially, the combination of LC-CC × SEC has the advantage that in the first dimension the separation is purely based on functionality and the second dimension on molecular mass leading to complementary information that could not have been obtained using the separation techniques separately. Although this technique is certainly not straightforward with regards to e.g. analysis time and optimization, it has been applied successfully for the characterization of functional homopolymers [22], copolymers [12,20,21] and grafted polymers [11,13,23,24].

As stated earlier, the various liquid chromatographic techniques have been successfully applied for various types of (co)polymers. However, for commonly used and thus industrially relevant thermoplastic polymers like polyethyleneterephthalate, polycarbonate, polyvinylchloride or polyamides there are only a few papers that describe the characterization with liquid chromatographic techniques like GPEC or LC-CC [25,26], in contrast to many papers on characterization of these polymers using SEC. This can probably be attributed to their semi-crystallinity or semi-crystalline behaviour so that the application of liquid chromatography is not straightforward for these types of polymers.

Polymer degradation is a complex process, which is characterized by a large range of chemical and physical changes that may occur depending on the type of polymer and the specific degradation conditions. Various studies are published on the degradation of poly(bisphenol A)carbonate (PC) focusing on UV-degradation [27,28] and thermal degradation at high temperatures to mimic injection molding conditions [29]. Analytical techniques that are commonly used in degradation studies of PC are UV- and IR-spectroscopy and SEC [30]. Montaudo and co-workers [29,31–33] have used in addition MALDI-TOF-MS to identify chemical changes in PC due to degradation. However, these authors focused only on the low molecular weight part of the material.

In this paper, various liquid chromatographic techniques will be developed for PC as an example of a commonly used thermoplastic polymer showing semi-crystalline behaviour. The aim was to develop liquid chromatographic methods to characterize PC and to detect small chemical changes in the polymer as a result of ageing at an early stage. The methods will be demonstrated for the hydrolytic degradation of PC.

2. Experimental

2.1. Samples and sample pretreatment

Commercially available poly(bisphenol A)carbonate containing small amounts of process stabilizer Irgafos 168 was used.

Hydrolytic degradation of the PC samples was carried out in a thermostatted oven at 100 °C in moist air (∼50%, v/v water) for various periods ranging from 0 to12 weeks.

The polymer samples were dissolved in chloroform prior to analysis resulting in polymer solutions with a concentration of about 10 mg/ml.

2.2. Normal phase gradient polymer elution chromatography (NP-GPEC)

The liquid chromatographic system consisted of a Waters 2690 Separations Module (Milford, MA, USA), equipped with a vacuum degasser and a thermostatted column compartment. UV-detection at 265 nm was performed with a Waters PDA model 2996.

NP-GPEC separations were carried out on a Chrompack Hypersil Silica column (dimensions: 250 mm × 3.0 mm, 5 μm particles) using a gradient of 98%/2% chloroform/isopropanol to 98%/2% dichloromethane/isopropanol at 2%/min and a flow-rate of 0.25 ml/min. The injected sample volume of the polymer solutions was 10 μl. The temperature of the column compartment was maintained at 45 °C. All solvents were HPLC grade from Biosolve.

2.3. Liquid chromatography at critical conditions

The liquid chromatographic system was identical to that used for NP-GPEC. LC-CC separations were carried out on a Alltech Platinum Silica column (dimensions: 150 × 3.2 mm, 5 μm particles, pore size 300 μm) using a isocratic flow of chloroform/diethylether (98.5/1.5%, v/v) at a flow rate of 0.3 ml/min. The injected sample volume of the polymer solutions was 2 μl. The temperature of the column compartment was maintained at 33 °C. All solvents were HPLC grade from Biosolve.

2.4. Two-dimensional liquid chromatography (LC-CC × SEC, NP-GPEC × SEC)

The experimental conditions and set-up of the two-dimensional liquid chromatography (2D-LC) system were described earlier in more detail [12]. The first-dimension LC system consisted of a Waters 2695 Separations Module (Milford, MA, USA). This system was used for LC-CC and NP-GPEC separation. The same columns and eluents were used as described above. The flow-rate for LC-CC and NP-GPEC was 10 μl/min in order to obtain a comprehensive LC × SEC set-up.

SEC separations were carried out on a Waters HSPgel-RT MB-L/M column (150 mm × 6.0 mm i.d., 3 μm) with chloroform as eluent at a flow-rate of 0.8 ml/min and using a Dionex model P580 pump (Germering, Germany) preceded by a vacuum degasser (Alltech, Deerfield, IL). With this set-up high speed SEC was possible with good resolution [12]. The injected sample volume of the polymer solutions was 50 μl. The temperature of the column compartment was maintained at 30 °C.

Comprehensive coupling of LC and SEC was achieved by means of a helium-actuated VICI two-position 10-port valve (Valco, Schenkon, Switzerland) with a port diameter of 0.25 mm. Two injection loops of 200 μl each were connected to the 10-port valve. The 10-port valve was switched every 5 min by means of an electronic pulse from the LC system. This resulted in injection of 50 μl into the second dimension. For example, the peaks observed in the first dimension with LC–CC were analyzed in the second dimension in approximately 4–5 fractions.

2.5. Matrix assisted laser desorption ionization time-of-flight mass spectrometry

MALDI-TOF-MS was coupled semi on-line with the LC system using a LCT LabConnection deposition interface that has been used in an earlier paper for coupling of IR [14]. After liquid chromatographic separation of the sample a solution containing both matrix and salt, i.e. trans-3-indoleacrylic acid (IAA) and NaI in acetone, were mixed with the eluent using a T-connection and deposited on a metal MALDI probe. A Bruker Biflex II MALDI-TOF-MS was used to obtain mass spectra in the reflector mode.

3. Results and discussion

3.1. Liquid chromatography

Chemical differences in polymers due to e.g. degradation may lead to changes in molecular mass (MMD), chemical composition (CCD) and/or functionality (FTD) distribution. As explained earlier, the three different forms of liquid chromatography, i.e. SEC, GPEC and LC-CC, can reveal these differences, if present.

SEC analysis was carried out for PC as a start to study the influence of hydrolytic degradation on the molecular mass (MM) and molecular mass distribution (MMD) (data not shown). As expected the molecular mass decreased significantly due to the applied degradation conditions. For example, for virgin PC a molecular mass of 41.500 Da was determined, while for PC aged for 12 weeks a molecular mass of 33.000 Da was calculated (not shown). The molecular masses have been obtained by conventional calibration using PS standards. Although it is known that the absolute molecular mass of PC deviates strongly from values obtained with conventional calibration using PS standards [31,34], differences in molecular mass can still be determined.

3.1.1. NP-GPEC

With NP-GPEC the separation can to a large extent be based on chemical composition and less on molecular mass, although molecular mass effects can influence the separation, especially for lower molecular weights up to about 50 kDa depending on the pore size of the column. If PC is precipitated on the column after injection and when starting the gradient with a bad solvent for PC, redissolving this polymer was observed to be rather troublesome and at least irreproducible, as was also observed for semi-crystalline polymers [3]. Therefore, it was considered necessary to retain PC on the column in a 'gel-like' state which can be redissolved in a more reproducible way. This can be achieved by using an injection solvent and starting eluent of the gradient that are good solvents, but weak eluents. Next, a gradient to a good solvent and strong eluent should lead to a good and reproducible separation and elution of PC without any breakthrough peaks, in accordance with the solvent selection scheme of Jiang et al. [35]. This was successfully carried out using a gradient from chloroform to dichloromethane with a constant trace of iso-propanol. An isocratic flow of 100% chloroform lead to adsorption of PC on the column and reproducible elution of PC was not possible. It was observed that addition of small amounts of iso-propanol was essential to obtain reproducible elution of PC. It was thought that the small amount of iso-propanol interacts with active sites on the silica column. Especially these active sites may cause strong adsorption of PC on the column. By adding small amounts of iso-propanol these active sites are hindered and strong adsorption of PC on the column is prohibited. In principle, the only parameter that is changed during the gradient is the eluent strength.

Fig. 1 shows the NP-GPEC chromatograms of virgin PC and PC aged for 6 weeks and 12 weeks. A characteristic NP-GPEC chromatogram can be observed for virgin PC

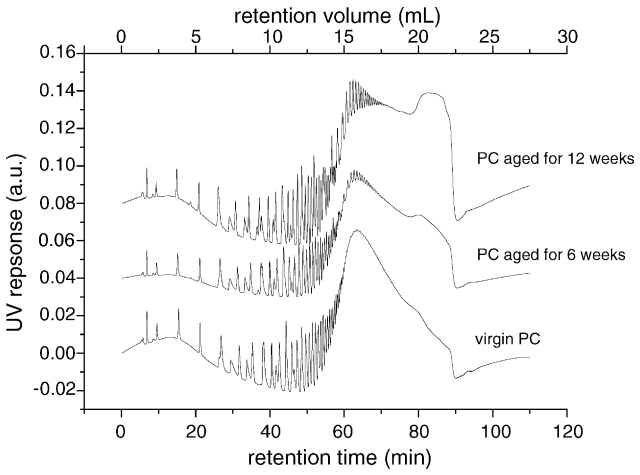


Fig. 1. NP-GPEC–UV (λ = 265 nm) chromatograms of virgin PC, PC aged for 6 weeks and PC aged for 12 weeks.

in which molecular mass effects are strongly visible, i.e. oligomers/low molecular polymers are well separated and elute first, followed by PC with a higher molecular mass that elutes as a broad feature. The NP-GPEC chromatograms of aged PC show an additional broad unresolved feature around t_r = 80–90 min. Furthermore, the fine structure of the broad peak around t_r = 60–70 min increases significantly with degradation. The latter may be due to a decrease in concentration. Although differences as a result of degradation could be observed, it is difficult to address these differences to specific chemical changes. This is due to the fact that NP-GPEC separation is based on both chemical composition and molecular mass and it is very difficult to distinguish between the two effects. As a result it is not clear whether the appearance of the broad peak around t_r = 80–90 min is due to PC with a different chemical composition and/or different molecular mass. However, a NP-GPEC method allowing the separation of high molecular weight PC was developed and applied successfully for the hydrolytic degradation of PC although the method may give more valuable information for other applications, e.g. batch-to-batch differences or competitor analysis.

3.1.2. LC-CC

As stated earlier, LC-CC provides selective information on the functionality of polymers. LC-CC uses conditions where the number of monomeric units of a certain polymer does not contribute to the retention of the polymer; the elution behavior of the polymer is only influenced by the type and number of functional groups and/or end-groups. Differences in these functional groups or end-groups due to degradation should therefore be detectable with LC-CC.

The critical conditions for some commonly used polymers, like polyethyleneglycol, polystyrene and polymethylmethacrylate are more or less known [7]. However, for PC this is not the case and finding the critical conditions can be rather time-consuming. While there are no commercially available well defined polymer standards with known end-groups for PC, the virgin PC sample was fractionated by SEC into a few fractions with different molecular mass. These fractions were used to find the critical conditions for PC. An isocratic run of 100% chloroform on a silica column did not elute PC, probably because chloroform is a good solvent but a relatively weak eluent. For NP-GPEC it was already observed that addition of small amounts of other solvents had a strong influence on the elution behaviour. It appeared that the addition of a small trace of weaker solvent, but stronger eluent, e.g. diethyl ether, to chloroform was sufficient to obtain the critical conditions for PC. The addition of 1.5%, v/v of diethyl ether was found to be optimal. In addition, other critical parameters, such as column temperature, injection volume and eluent temperature were studied and optimized.

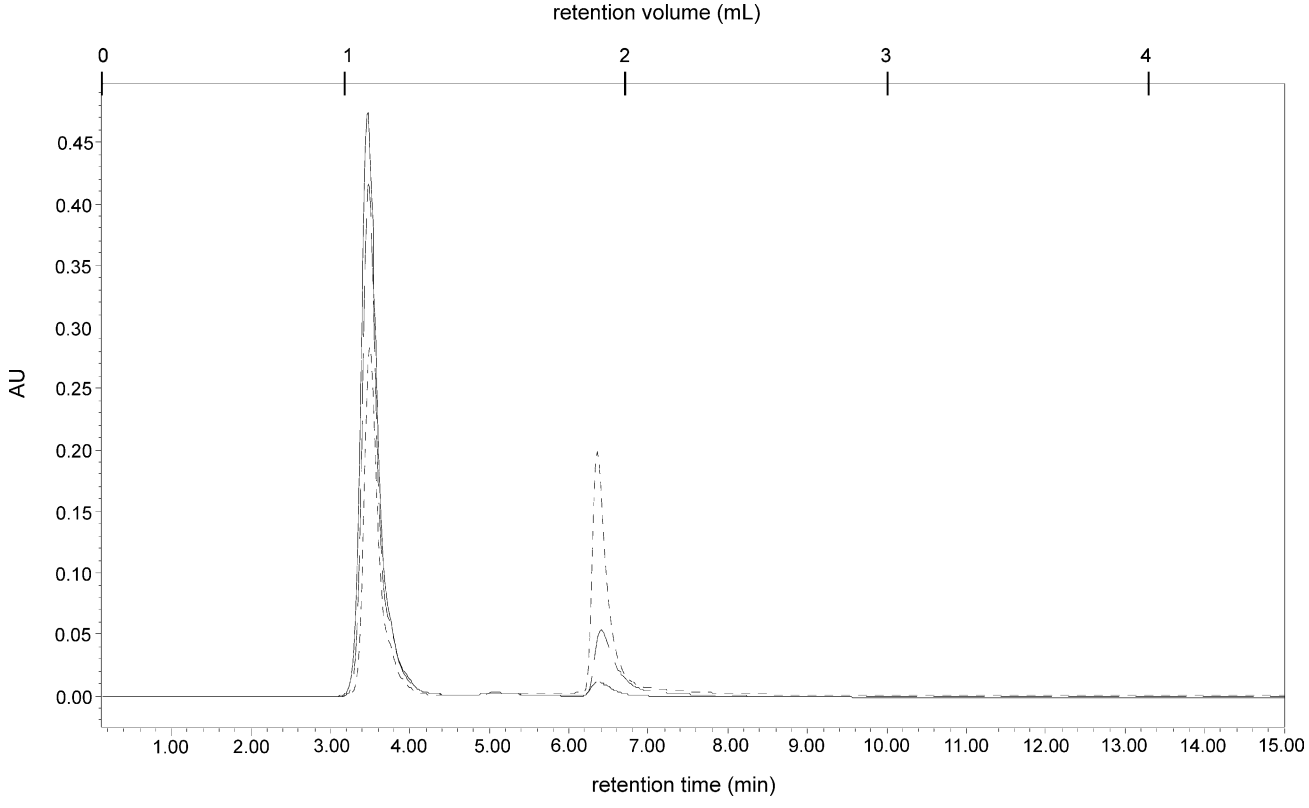


Fig. 2. Overlay of LC-CC–UV (λ = 265 nm) chromatograms of PC ref (—), PC aged for 6 weeks (— — —) and PC aged for 12 weeks (- - -).

In the LC-CC–UV chromatogram of virgin PC a small intense peak at very short retention time ($t \sim t_0$) showed up (Fig. 2). In the LC-CC–UV chromatograms of PC aged for 6 weeks and 12 weeks an additional peak at higher retention times ($t \sim 7$ min) showed up next to the peak at $t \sim t_0$ (Fig. 2). This additional peak increased in height with increasing degradation time. Hence, it was concluded that this peak was caused by PC with different functionality due to hydrolytic degradation.

Note that virgin PC elutes around $t \sim t_0$ and thus shows no significant retention. In principle only the PC with different functionality due to degradation shows retention.

3.2. Identification of chemical changes using LC-CC × MALDI-TOF-MS

The additional peak observed with LC-CC was identified by semi on-line coupling of LC-CC to MALDI-TOF-MS by using a deposition interface that has also been used for the coupling of LC to FT-IR [14]. The interpretation of the MALDI-TOF-MS spectra revealed that the peak at short retention times ($t \sim t_0$) could be assigned to unaged PC, i.e. PC with t-butyl end-groups and cyclic PC oligomers (Fig. 3 and Table 1). The peak observed at a retention time of about 7 min for aged PC could be assigned to PC containing one t-butyl

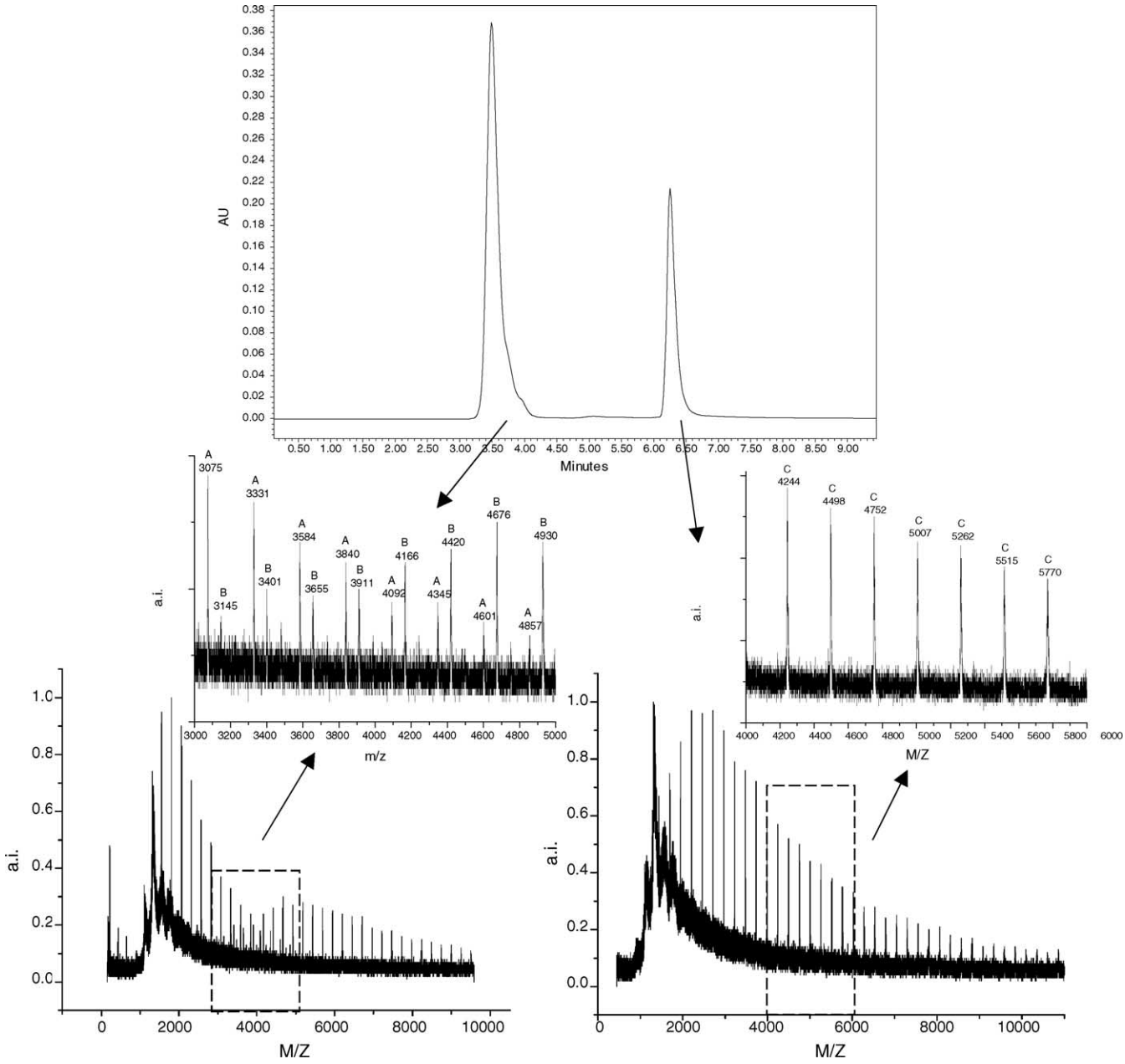
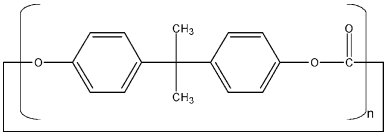
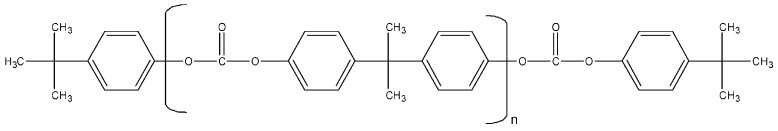
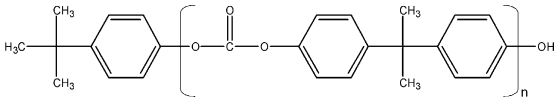


Fig. 3. Identification of the peaks observed with LC-CC using semi on-line coupling of MALDI-TOF-MS.

Table 1
Structural assignments of mass peaks determined with MALDI-TOF-MS

Mass series	Polymer structure	Theoretical end-group mass (Da)	Experimental end-group mass (Da)
A		0	0 ± 5
B		326.44	326 ± 5
C		150.22	150 ± 5

end-group and one OH end-group, which are expected to be present after hydrolytic degradation [30]. No evidence of PC with two OH end-groups was found with LC-CC. Moreover, SEC × MALDI-TOF-MS analysis did not show any evidence either of PC with two OH end-groups. Note that MALDI-TOF-MS might discriminate between PC with different end-groups. No clear explanation for the absence of PC with two OH end-groups can be found. Possibly the concentration of PC with two end-groups is too low to be detected. The results obtained with LC-CC show the ability to separate PC on different end-groups. In this case LC-CC could discriminate PC with polar OH end-groups from PC with non-polar end-groups, i.e. tert-butyl, or cyclic oligomers of PC, due to their stronger interaction with the stationary phase. However, no information regarding molecular mass or molecular mass distribution can be obtained with LC-CC.

3.3. Two-dimensional liquid chromatography (2D-LC)

As discussed above the different types of liquid chromatography are separating according to different properties, i.e. molecular mass, chemical composition and functionality, and sometimes according to a combination of these effects. To obtain more insight from the complementary information of various one-dimensional liquid chromatographic techniques, comprehensive on-line two-dimensional liquid chromatography (2D-LC) was used in such a way that the polymer sample was analyzed completely in both dimensions. In principle, the 2D-LC set-up described earlier for the analysis of copolymers using FT-IR detection was used [12]. As described in that paper, a slow separation in first dimension was combined with a fast separation in the second dimension in order to achieve a comprehensive 2D-LC set-up. As a fast GPEC gradient is often affecting the separation significantly, a combination of LC-CC or GPEC in the first dimension combined with a fast SEC analysis in the second dimension using a high speed SEC column was chosen [12].

For the first dimension the same NP-GPEC and LC-CC methods were used as described above, although some parameters had to be changed in order to have a comprehensive 2D-LC method. Most importantly, the flow rate of the first dimension had to be decreased significantly, i.e. 10 μl/min, to match with the fraction volume and the runtime of the SEC analysis.

It should be mentioned that the columns used in the first dimension are normally used for flows of ∼0.5 ml/min. A significantly slower flow rate, i.e. 10 μl/min, can result in peak broadening effects. For LC-CC separations the effect of peak broadening is not expected to be dramatic, while the peaks observed for LC-CC are small and show no further details. However, for NP-GPEC the effect may be larger due to the presence of the well separated oligomer pattern that may partially disappear due to peak broadening.

3.3.1. NP-GPEC × SEC

With NP-GPEC × SEC using UV detection for virgin PC and PC aged for 12 weeks (Fig. 4) a pattern similar to the NP-GPEC chromatograms in Fig. 1 are obtained, i.e. some narrow peaks are eluted at short retention times and a large unresolved feature at higher retention times. In addition, on the *y*-axis the molecular mass distribution of the various fractions NP-GPEC chromatogram are shown and it can be seen that the peaks that elute at short retention times in NP-GPEC have relatively low molecular mass and the molecular mass increases with increasing retention times. Hence, it can be concluded that with NP-GPEC PC is already separated to a large extent on molecular mass. This information cannot be obtained from the separate SEC and NP-GPEC measurements and hence shows the additional information that can be obtained with 2D-LC.

As stated earlier, peak broadening may play a significant role due to the low flow rate. Despite the fact that the number of separated peaks is larger for the one-dimensional GPEC chromatograms in Fig. 1 compared the two-dimensional

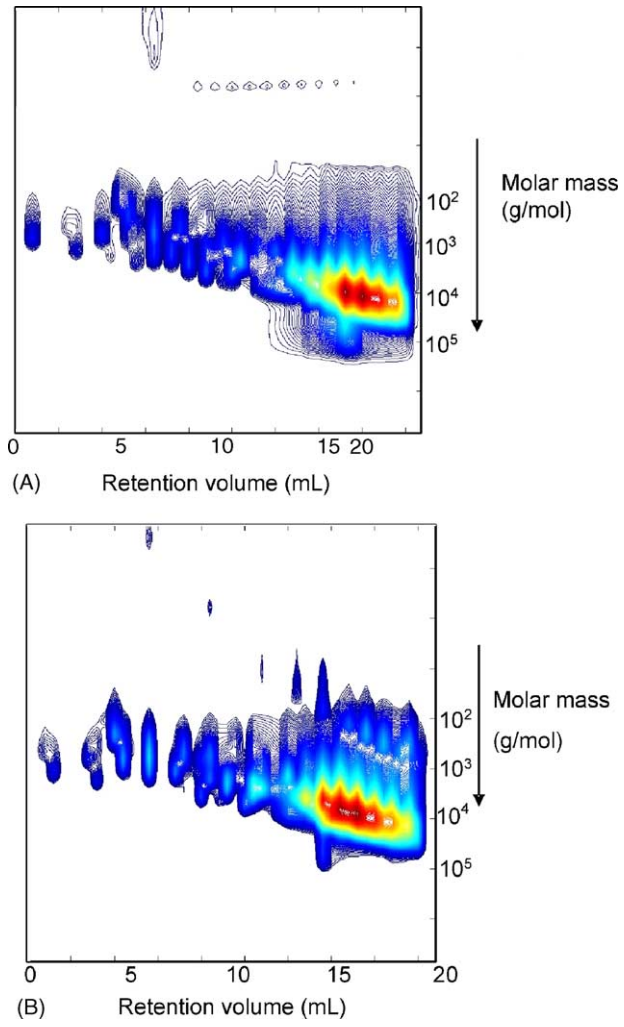


Fig. 4. NP-GPEC × SEC–UV (λ = 265 nm) chromatograms of (A) virgin PC and (B) PC aged for 12 weeks.

chromatograms in Fig. 4, the pattern of resolved peaks is still visible in Fig. 4 and thus indicates that peak broadening is taking place but not to a very large extent.

The NP-GPEC × SEC chromatogram of aged PC shows more or less the same pattern compared to virgin PC. Close inspection of the NP-GPEC × SEC chromatogram showed a small second distribution of peaks for aged PC at high retention times just above the intense series of peaks, i.e. with a somewhat lower molecular mass, as indicated in Fig. 4. This distribution is present around the same retention time as the additional feature observed in NP-GPEC (see Fig. 1). However, this additional feature for aged PC could not be clearly identified as was explained earlier for NP-GPEC.

One critical remark should be made. The sensitivity of 2D-LC can be less compared to the one-dimensional method due to the dilution of the sample as a result of the two-dimensional set-up, i.e. each fraction in the first dimension is separated again, in the second dimension. In principle, it should be possible to counterbalance this dilution effect partially by using higher sample loads. However, sample loads are very critical for both NP-GPEC and LC-CC separations and for the present set-up it was actually found that the sample load could not be increased. This might explain the fact that the extra feature observed for aged PC is more pronounced with NP-GPEC than with NP-GPEC × SEC.

Altogether, it can be concluded that the information obtained with NP-GPEC × SEC is not providing more detailed insight in the polymer microstructure. The combination of the separation mechanisms of NP-GPEC and SEC are obviously not orthogonal, as both techniques separate mainly on molecular mass in the case of PC. Due to the dilution effect that is always present in 2D-LC, the small differences observed for NP-GPEC alone are more difficult to observe in the two-dimensional set-up. Still, the developed comprehensive two-dimensional liquid chromatographic method could be applied to poly(bisphenol A)carbonate and might prove its value for other applications.

3.3.2. *LC-CC × SEC*

In order to be able to fully profit from the advantages of 2D-LC, LC-CC × SEC was applied to the PC samples. With LC-CC, separation by molecular mass effects is excluded while the SEC separation is primarily based on molecular mass. Therefore, these separations are expected to be orthogonal and thus combination of LC-CC and SEC should result in complementary information. Fig. 5 shows the LC-CC × SEC chromatograms obtained with UV detection of virgin PC and PC aged for 12 weeks. The 2D-LC chromatogram of virgin PC shows one feature that looks like a series of peaks. However, the separation between the 'peaks' is due to subsequent fractions that are analyzed. In principle, the feature is due to one peak, identical to the one observed with LC-CC (see Fig. 2). Separation in the second dimension, i.e. SEC, reveals that there is a small molecular mass effect in this peak, viz. the molecular mass increases with increasing retention times. Therefore, near-critical rather than critical separation is achieved for PC. Still the separation on functionality is much stronger than on molecular mass, as will be shown further on.

The LC-CC × SEC chromatogram of PC aged for 12 weeks in Fig. 5 shows the same peak as virgin PC but additionally there is a feature at higher retention times that was also visible with LC-CC and was identified with MALDI-TOF-MS as PC with one OH end-group and one t-butyl end-group. It can be observed from Fig. 5 that PC with one OH end-group and one t-butyl end-group is present over the whole molecular mass range rather than e.g. only in the low molecular range. The latter information could not be obtained from the separate SEC or LC-CC chromatograms of the complete sample. Hence, this example illustrates the complementary information that can be obtained by using LC-CC × SEC.

All methods shown in this paper can be applied for other types of degradation, e.g. photo-oxidation, outdoor weathering. Furthermore, the liquid chromatographic techniques can be coupled to other detection methods like e.g. FT-IR, to ob-

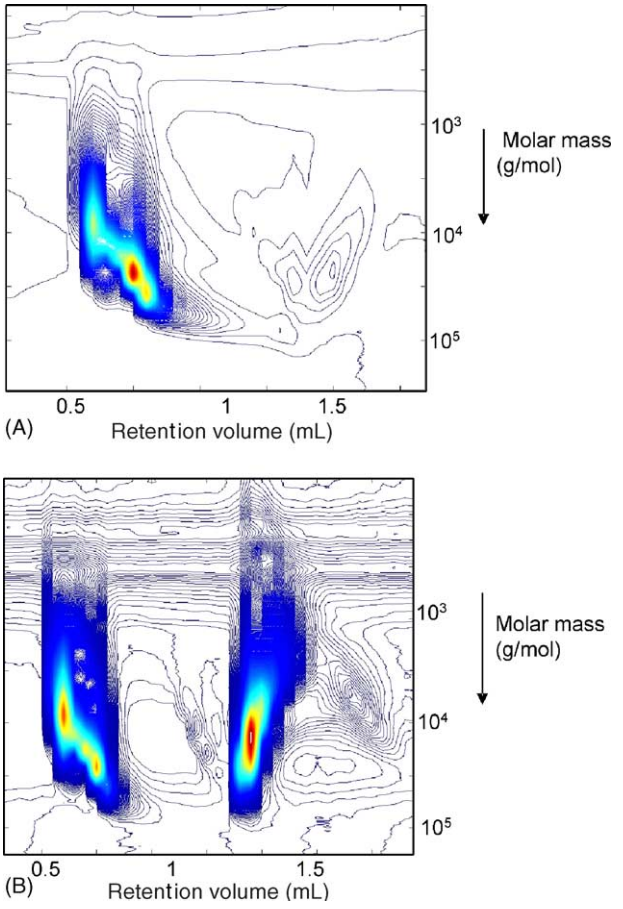


Fig. 5. LC-CC × SEC–UV (λ = 265 nm) chromatograms of (A) virgin PC and (B) PC aged for 12 weeks.

tain some more specific chemical information. This will be the subject of future investigations.

4. Conclusions

NP-GPEC, LC-CC and comprehensive 2D-LC methods have been developed for poly(bisphenol A)carbonate. The developed methods were applied to identify chemical differences in PC due to hydrolytic degradation.

NP-GPEC analysis showed a characteristic chromatogram in which oligomers/low molecular species elute first followed by high molecular weight polymer. It was concluded that PC was separated to a large extent based on molecular mass. Differences due to degradation could be observed with NP-GPEC but the differences could not easily be explained, due to the presence of two separation modes, i.e. molecular mass and polarity.

LC-CC, which separates on functionality, showed the formation of an additional peak at higher retention times, i.e. increase in functionality. Coupling of LC-CC to MALDI-TOF-MS showed that the additional peak in LC-CC could be assigned to PC with one OH end-group and one t-butyl end-group.

The additional information that can be obtained using comprehensive two-dimensional liquid chromatography was clearly demonstrated by successful on-line coupling of NP-GPEC × SEC and LC-CC × SEC. Using a comprehensive set-up it was shown that NP-GPEC separation was mainly based on molecular mass. With LC-CC × SEC it was shown that aged PC, i.e. with one OH end-group and one t-butyl end-group, is present over the whole molecular mass distribution. This information cannot be obtained from the separate liquid chromatographic techniques.

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