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Fast determination of functionality-type × molecular-weight distribution of propoxylates with varying numbers of hydroxyl end-groups using gradient–normal-phase liquid chromatography × ultra-high pressure size-exclusion chromatography

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ABSTRACT

Understanding the relation between chemical characteristics and properties of synthetic polymers is one of the challenges faced by analytical chemists in industry. This is a complex task, as polymers are not synthesized as single molecule, but are populations of chemically similar compounds with distributions over several properties. The latter include, for example, molecular weight, nature of end-groups (functionality), and chemical composition.

In this paper, comprehensive two-dimensional liquid chromatography was used to determine the combined functionality-type and molecular-weight distributions of hydroxy–functionalized propoxylates. Propoxylates derived from different initiators (one up to eight terminal hydroxyl groups) were separated in the first dimension using a gradient normal-phase LC separation (NPLC). In the second dimension ultra-high pressure size-exclusion chromatography separation (UHPSEC), further speciating distributions based on molecular size. The developed NPLC × SEC method with evaporative light-scattering detection can be used for the fast screening (< 30 min) of mutually dependent functionality-type and molecular-weight distributions of unknown propoxylates.

1. Introduction

Polyether polyols have been studied extensively by liquid chromatography (LC) to determine chemical distributions such as molecular-weight distribution (MWD), end-group-functionality distribution (FTD) and chemical-composition distribution (CCD) [1–4]. Different chromatographic modes have been developed to provide information on such distributions, including gradient-elution liquid chromatography (GELC), liquid chromatography at critical conditions (LCCC), size-exclusion chromatography (SEC) and other techniques [5,6]. Although the obtained chromatograms provide information on one specific chemical property (or a convolution of several properties), relating the interdependence of two or more chemical features remains difficult, if not impossible.

Comprehensive two-dimensional liquid chromatography (LC × LC) has shown to be a crucial technique to obtain information on several mutually dependent chemical properties [7–9]. Especially the combination of size-exclusion chromatography (SEC) with other modes of LC, such as GELC and LCCC, has been used extensively to obtain two-dimensional MWD × FTD distributions of synthetic polymers [10,11].

Although several research articles describe the characterization of ethoxylate-based polyether polyols, such as poly(ethylene glycol), surfactants, *etc*., by both one- and two-dimensional LC [12,13], to our knowledge very few methods have been described in literature for the analysis of propylene-oxide-based polyether polyols ("propoxylates"). Only reversed-phase liquid chromatography (RPLC), normal-phase liquid chromatography (NPLC) and SEC have been described, providing mainly or exclusively information on the size of the analyte [14–17]. In this study, LC × LC methodology has been developed to characterize propoxylate formulations, resolving analyte molecules based on the number of hydroxyl end-groups

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Table 1
Studied propoxylates derived from different initiators.

#	Initiator	Functionality (*f*)	Average Molecular weight (Da)	Sample name
1	Butanol	1	750	ButPO-0.75kDa
2	Butanol	1	3000	ButPO-3kDa
3	Water	2	1000	PPG-1kDa
4	Water	2	2000	PPG-2kDa
5	Water	2	8000	PPG-8kDa
6	Glycerol	3	450	GlyPO-0.5kDa
7	Glycerol	3	1000	GlyPO-1kDa
8	Sorbitol	6	700	SorbPO-0.5kDa
9	Sorbitol	6	10,000	SorbPO-10kDa
10	Sucrose	8	1000	SucPO-1kDa

(providing information on the initiator used) and molecular size simultaneously. To provide a fast LC × LC method (shorter than 30 min), gradient normal-phase LC and ultra-high-pressure size-exclusion chromatography (UHPSEC) were exploited in the first and second dimension, respectively.

2. Experimental

2.1. Chemicals and samples

The solvents used included 2,2,4-trimethylpentane (isooctane, > 99.5%, HiperSolv grade) and tetrahydrofuran (THF, > 99.7% unstabilised, HiPerSolv grade), both obtained from VWR International (Leuven, Belgium). To study the separation of –OH functionalized propoxylates, various products with known initiators and molecular weights were used including butanol-initiated propylene oxide (ButPO), polypropylene glycol (PPG), glycerol-initiated polypropylene oxide (GlyPO), sorbitol-initiated polypropylene oxide (SorbPO) and sucrose-initiated polypropylene oxide (SucPO). The samples used throughout this study are summarized in Table 1 and were kindly provided by Dow Benelux B.V. (Terneuzen, The Netherlands). Chemical structures of the studied polyether polyols are shown in Fig. 1. To test the broad applicability of the developed analytical methods, samples were selected so as to span a wide range of both molecular weights (0.5 kDa – 10 kDa) and functionalities (1 to 8 terminal hydroxyl groups).

For one-dimensional gradient-NPLC method development, samples were prepared at a concentration of 5 mg/mL in 35% v/v THF in isooctane and injected separately. For developing the fast SEC second-dimension method, mixtures of (*i*) all three available PPG samples and (*ii*) GlyPO samples were prepared separately at a concentration of 5 mg/mL in THF. To study the effects of solvent and injection volume on the SEC performance, a dilution series of a mixture of PPG-1 kDa, −2 kDa and −8 kDa at the levels of 10.0, 5.0, 2.0, 0.5 and 0.25 mg/mL was made (in THF). An additional sample was made in 35% v/v THF in isooctane at a concentration of 5 mg/mL to study injection solvent effect on the SEC separation. For LC × LC analysis, all the available samples were combined in solution at the following concentrations in 35% THF (v/v) in isooctane to obtain comparable detector-intensities between the various distributions: ButPO-0.75 kDa 2.0 mg/mL, ButPO-3 kDa 2.0 mg/mL, PPG-1 kDa 5.0 mg/mL, PPG-2 kDa 5.0 mg/mL, PPG-8 kDa 5.0 mg/mL, GlyPO-0.5 kDa 15 mg/mL, GlyPO-1 kDa 5.0 mg/mL, SorbPO-0.5 kDa 10 mg/mL, SorbPO-10 kDa 10.0 mg/mL, SucPO-1 kDa 10.0 mg/mL. All materials were used as received. Mobile phases were not filtered prior to use.

2.2. Instrumentation

All experiments were performed using an Agilent 1290 Infinity 2D-LC system (Agilent Technologies, Waldbronn, Germany). The system comprised of a high-speed binary pump (G7120A) and a binary pump (G7112B) for solvent delivery. Other components included an multicolumn thermostat (G7116A), autosampler (G71676A) and an evaporative light-scattering detector (ELSD, G7102A). An Agilent 2D-LC ASM valve (G4243A) connected with two distinct multiple heart-cutting valves with 40-µL loops installed were used for modulation and operated in comprehensive 2D-LC mode.

For one-dimensional analysis, the separation was coupled directly to the detector, instead of to the modulation valve. NPLC method development was carried out using the 1260 binary pump (G7112B) and an Ascentis Expres OH5 (50 × 2.1 mm I.D., 2.7 µm particle size) column (Sigma-Aldrich, Zwijndrecht, The Netherlands), while one-dimensional fast SEC analyses were performed using the 1290 high-speed binary pump (G7120A) and a Waters APC XT 45 Å (150 × 4.6 mm I.D., 1.7 µm particle size) column (Waters, Milford, MA, USA).

2.3. Analytical conditions

For one-dimensional NPLC, 2.0 µL of the solute were injected on the column operating at a flow rate of 0.2 mL/min and thermostatted at a temperature of 22 °C. The following gradient was programmed from 35% v/v THF in isooctane (mobile phase A) to THF (mobile phase B): 0.0–1.0–5.0–6.0–6.01–8.0 min 0.0–0.0–95.0–95.0–0.0–0.0%B. For one-dimensional SEC experiments, the column was thermostatted at 50 °C and operated at a flow of 1.8 mL/min and 100% THF (isocratic conditions). The default injection volume was 1.0 µL, but this was varied from 1.0 to 40.0 µL for studying injection band-broadening effects.

For LC × LC experiments, the two developed separations were combined. The gradient-NPLC first dimension (^{1}D) was themostatted at 22 °C and operated at a flow rate of 40 µL/min with a gradient of 0.0–5.0–25.0–30.0–30.01–45.0 min, 0.0–0.0–95.0–95.0–0.0–0.0%B. The modulation time was set to 30 s, corresponding to a modulation volume of 20 µL. The UHPSEC second dimension (^{2}D) was operated at 50 °C, with 100% THF using a flow rate of 1.8 mL/min. For fast LC × LC separations, the ^{1}D conditions were slightly modified. The ^{1}D flow rate was increased to 80 µL/min, resulting in a modulation volume of 40 µL (overfill conditions). The gradient was adjusted accordingly: 0.0–2.5–12.5–15.0–15.01–20.0 min, 0.0–0.0–95.0–95.0–0.0–0.0%B. For both one-dimensional LC and LC × LC experiments, ELSD conditions were as follows: evaporator temperature 60 °C, nebulizer temperature 60 °C, gas flow rate 1.60 SLM, data acquisition rate 40 Hz, smoothing 0.1.

2.4. Data treatment

Both LC-ELSD and LC × LC-ELSD data were exported as space-separated files and processed using MatLab 2018a (Mathworks, Woodshole, MA, USA). One-dimensional NPLC chromatograms were smoothed using a moving average filter (function smooth-

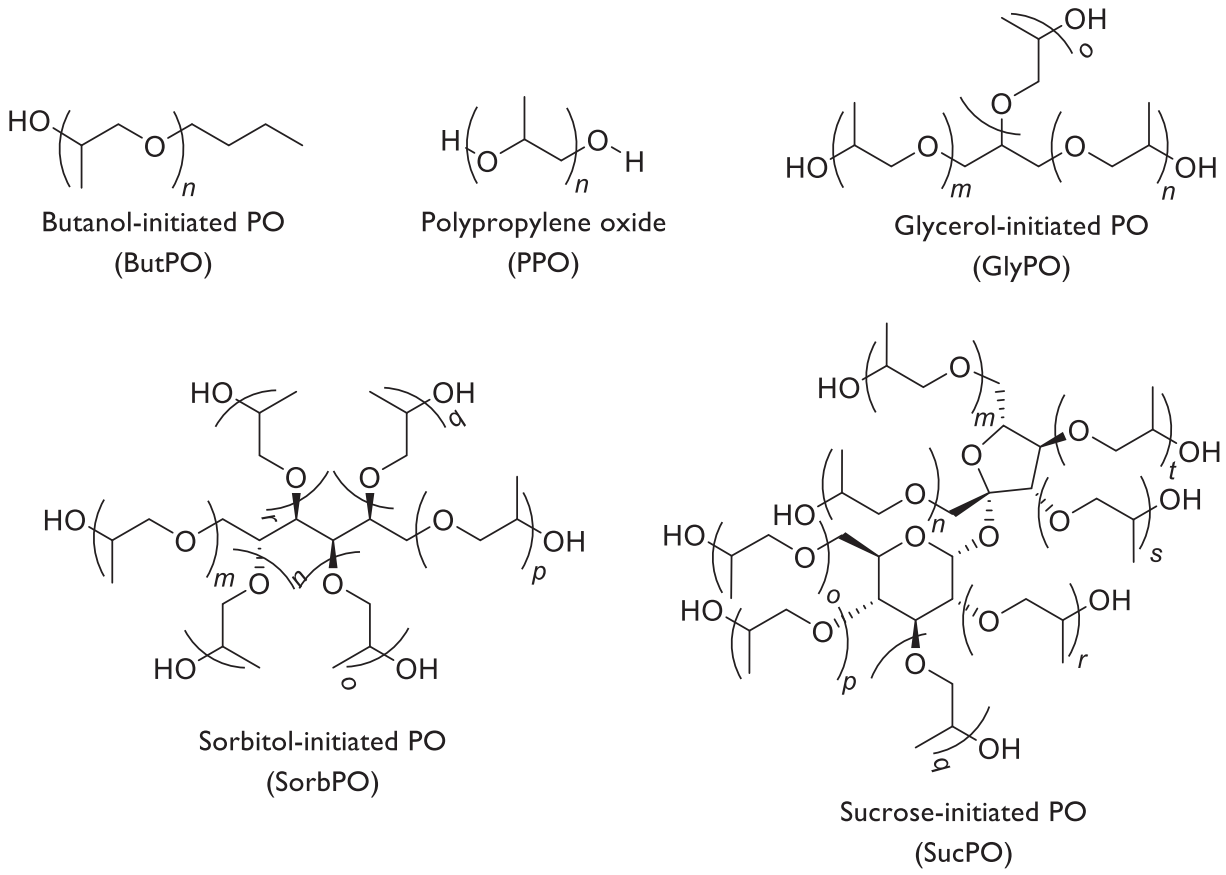

Fig. 1. structures of the studied polyether polyols.

data) with a smoothing factor of 0.0005. In-house written code was used to construct the LC × LC plots.

3. Results and discussion

3.1. One-dimensional gradient NPLC and SEC method development

To study the separation of propoxylates based on the number of –OH end-groups, samples with varying functionality were selected (1 to 6 terminal hydroxyl groups). Furthermore, for both PPG and GlyPO an additional sample with a different average molecular weight was selected to study the dependence of the separation on molecular weight (MW). The performance of the SEC separation for the potential use in the second dimension was studied using PPG and GlyPO samples with varying MW.

The results for the gradient-NPLC separation are shown in Fig. 2a. Using a gradient from 35% THF in isooctane (v/v) to 95% THF on an Ascentis Express OH5 column, the different propoxylate species were separated according to functionality, with analytes with increasing numbers of terminal –OH groups eluting at longer retention times. For the PPG-1 kDa and PPG-2 kDa samples, elution times were nearly identical confirming elution at near-critical conditions, with little to no effect of the molecular weight of the propoxylate species. On the other hand, glycerol-initiated propoxylates did exhibit molecular-weight dependency of the separation. Low MW GlyPOs (GlyPO-0.5 kDa) elute at longer retention times than GlyPO-1 kDa. A possible explanation for this is that with decreasing MW, the interaction of the terminal –OH groups with the stationary phase becomes dominant, resulting in increased retention compared to higher MW species.

Ideally, in LC × LC the ^{2}D separation should have short cycle times to sample the ^{1}D effluent sufficiently. Therefore, a fast and efficient SEC separation was developed, shown in Fig. 2b. Using a Waters APC 45 Å column (150 × 4.6 mm, 1.7 µm d_p) and the maximum allowable flow rate of 1.8 mL/min (according to the care and use manual provided by the column manufacturer), analytes of interest were separated within 0.9 min. For both PPG and GlyPO, three samples with representative MW across the MW range of interest (0.5 kDa – 10 kDa) were separated with sufficient resolution. As can be seen, the SEC separation does not use the separation space between 0.0 and 0.5 min. This can be advantageously used in LC × LC, performing overlapping injections, as no separation is expected to occur outside the SEC range of the column [9]. The total column volume was approximately 1.5 mL while the exclusion limit was around 0.86 mL. Therefore, the range of SEC separation will not greatly exceed a volume of 0.64 mL, corresponding to 22 s at a flow rate of 1.8 mL/min. Based on these findings a modulation time of 30 s was chosen. This implies that the column typically contains two modulations simultaneously, significantly reducing the ^{2}D run time.

As the SEC separation will be applied in the second dimension, the ^{1}D effluent should be compatible with the ^{2}D separation. To ensure that the changing effluent in the ^{1}D does not jeopardize the ^{2}D sparation (*e.g.* due to adsorption), the effects of the injection-solvent composition and volume were studied (see Figs. 3a and 3b). For PPG 1 to 8 kDa, samples were prepared in both 35/65% THF in isooctane (v/v) and 100% THF, representing the starting and final conditions of the ^{1}D gradient-NPLC separation, respectively. As shown in Fig. 3a, no effects of the solvent were observed on the retention times and peak shapes when changing solvent, proving that the NPLC gradient is compatible with SEC for the LC × LC separation. Furthermore, the effect of injection volume was studied on the SEC separation, as increased modulation volumes allow for faster ^{1}D flow rates, and, thus, reduced LC × LC cycle times.

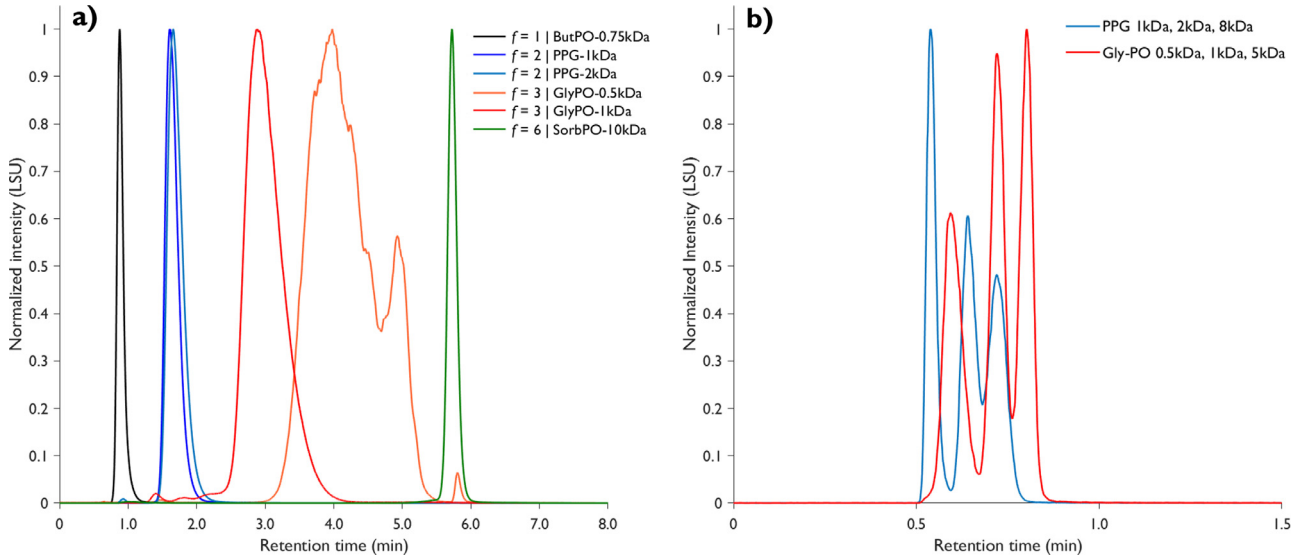

Fig. 2. a) gradient NPLC separation of propoxylates with varying functionality ranging from one to six –OH end-groups: mono-ol (black, ButPO-0.75 kDa), diol (blue, PPGs with different MWD), triol (red, glyPO with varying MWD) and hexol (green, SorbPO-10 K). b) SEC separation of analytes with different molecular weights using APC column technology and maximum allowable flow rate. For detailed chromatographic conditions, see the Experimental Section.

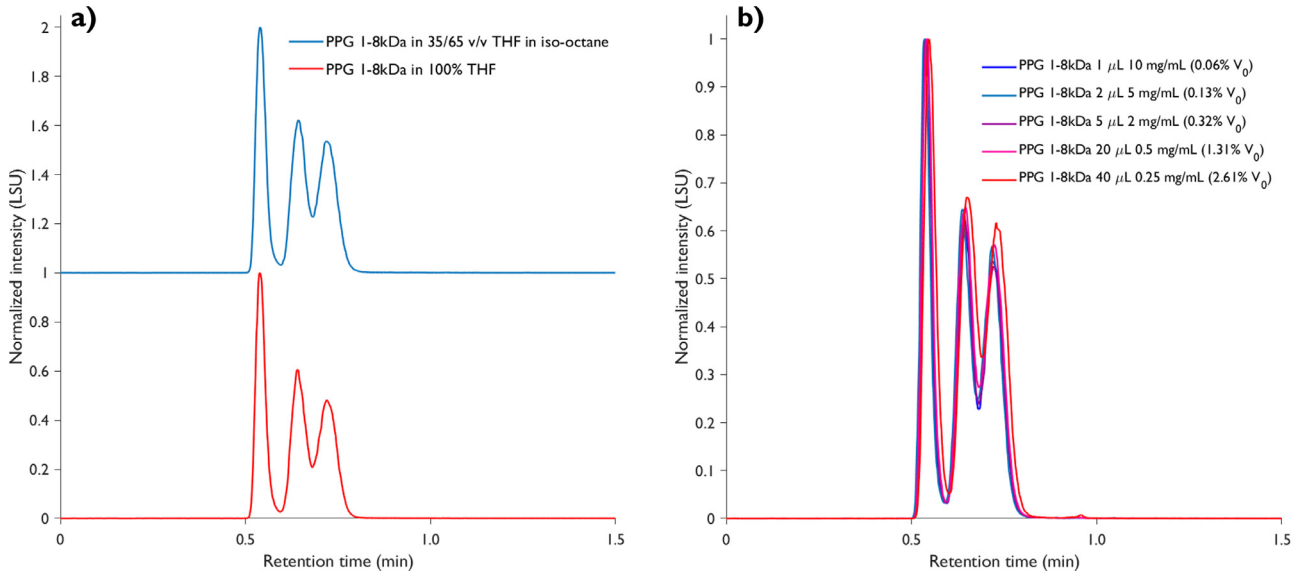

Fig. 3. UHPSEC separations to study the effects of injection solvent (a) and injection volume (b). For detailed chromatographic conditions, see the Experimental Section.

A dilution series of PPG samples between 1 and 8 kDa was prepared to allow different injection volumes between 1 µL and 40 µL, while the injected amount on column remained constant (0.1 mg on column). As can be seen in Fig. 3b, the separation with the 40 µL injection shows slightly reduced resolution compared to the 1, 2, 5 and 20 µL injections. Both the 20 µL and 40 µL modulation volumes were considered good candidates for LC × LC separation, allowing relatively fast ^{1}D analysis (25 to 45 min), while maintaining sufficient sampling of the ^{1}D effluent when using overlapping injections on the ^{2}D column.

3.2. Gradient NPLC × SEC for FTD × MWD of –OH funtionalized propoxylates

The developed methods as discussed in Section 3.1 were combined in a LC × LC system. The flow rate of the ^{1}D was set to 40 µL/min and the gradient program was adjusted accordingly. Using overlapping injections on the ^{2}D column, the ^{2}D cycle time could be reduced to 30 s, corresponding with a 20 µL modulation volume. A total analysis time of 45 min was achieved as shown in Fig. 4.

Overall, the LC × LC method was able to separate ten different propoxylate species varying in functionality from one to eight terminal hydroxyl groups and in MW from 0.5 kDa to 10 kDa. At low ^{1}D retention times, the mono-ol and diols species were eluted (peaks 1 & 2 for mono-ol and peaks 3, 4 & 5 for diol). Although different MW species of each group were overlapping in the ^{1}D, the ^{2}D SEC separation was able to resolve those peaks. Based on the LC × LC chromatogram the separation of both mono-ol and diols species was performed at near-critical conditions before the onset of the gradient, resulting in little to no dependence of the ^{1}D retention time on the MW. In contrast to the mono-ols and diols, the triols, hexols and octols eluted under gradient-NPLC conditions with retention times increasing with increasing number of hydroxy end-groups and decreasing with increasing MW.

The LC × LC method proved to be crucial for the separation of sorbitol- and sucrose-initiated propoxylates. Using gradient NPLC only, the two distribution would overlap completely. Using the ad-

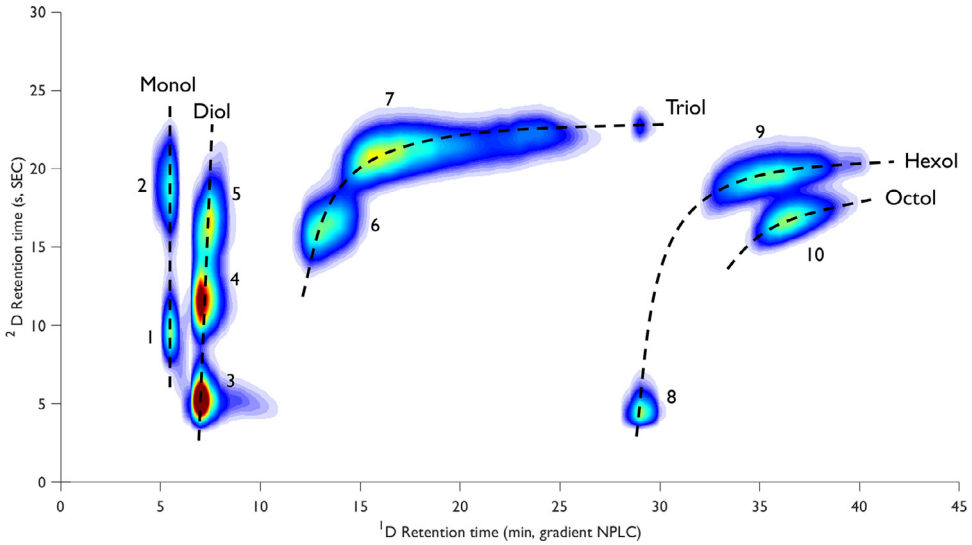

Fig. 4. Gradient NPLC × SEC separation of mixed propoxylates showing that the mutually dependent –OH end-group functionality distribution (FTD) and MWD (after calibration of SEC retention times) can be characterized in a single run. At lower retention times, the separation of mono-ols and diols are achieved at critical isocratic conditions, while the later eluting analytes are resolved by gradient LC. Peak identifications 1: ButPO-3 kDa, 2: ButPO-0.75 kDa, 3: PPG-8 kDa, 4: PPG-2 kDa, 5: PPG-1 kDa, 6: GlyPO-1 kDa, 7: GlyPO-0.5 kDa, 8: SorbPO-10 kDa, 9: SorbPO-0.5 kDa, 10: SucPO-1 kDa (see Table 1 for a description of the samples). For detailed chromatographic conditions, see the Experimental Section.

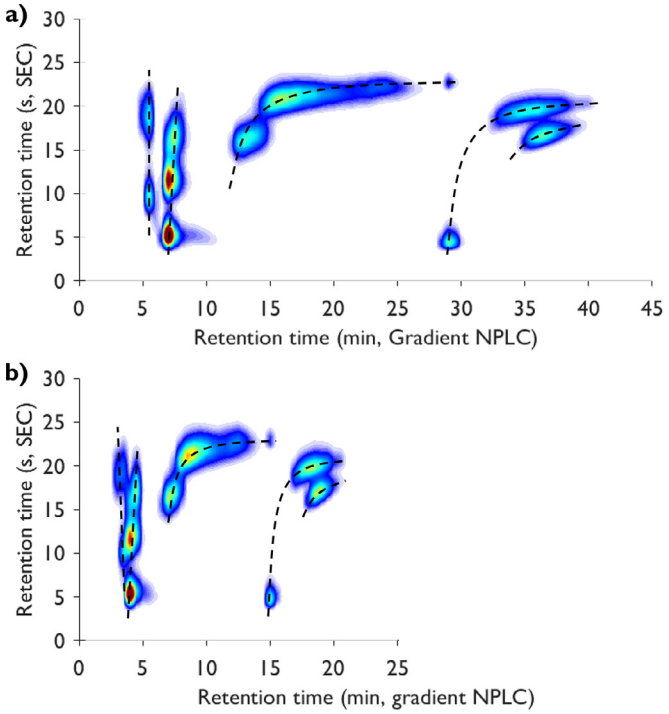

Fig. 5. Comparison of (a) the conventional gradient NPLC × SEC method and (b) a modified method employing increased ^{1}D flow rate, reducing the total LC × LC analysis time to 25 min. For detailed chromatographic conditions, see the Experimental Section.

ditional ^{2}D SEC separation, the analytes could be separated based on size, clearly depicting two separate distributions. Furthermore, the separation of glycerol-initiated 450 Da and 1 kDa propoxylates was slightly improved by employing the LC × LC method.

As previously discussed (Section 3.1), an injection volume of 40 µL showed slightly less resolution in the SEC separation compared to an injection volume of 20 µL. However, increasing the modulation volume from 20 to 40 µL could result in a two-fold reduction of the total LC × LC analysis time. By simply increasing the flow rate in the ^{1}D from 40 µL/min to 80 µL/min and adjusting the gradient program accordingly, a fast LC × LC method was tested for the measurement of propoxylates.

In Fig. 5 separations with modulation volumes of 20 and 40 µL are compared. As can be seen, the total analysis time is significantly reduced from 45 to 25 min, while maintaining all two-dimensional information with respect to functionality and molecular weight. Only the ButPO-3 kDa and PPG-2 kDa were not completely resolved in the LC × LC separation space. A slightly longer isocratic hold may suffice to resolve these two peaks. The developed 25-min method allows fast screening of unknown propoxylated oligomeric samples.

4. Conclusion

In this paper, the use of comprehensive two-dimensional liquid chromatography was demonstrated for the separation of alcohol-functionalized propoxylates up to a molecular weight of 10 kDa. Using a gradient normal-phase LC separation in the first dimension, solutes were separated based on the number of terminal –OH groups, separating mono-ol, diol, triol, hexol and octol species. The fractions were further speciated by molecular weight using a second-dimension size-exclusion chromatography separation. The NPLC × UHPSEC method could be used for the (high-throughput) screening of mutually dependent functionality-type and molecular-weight distributions of unknown propoxylates.

Declaration of Competing Interest

Statement: "The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper."

CRediT authorship contribution statement

Gino Groeneveld: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization, Project administration. **Ron Salome:** Conceptualization, Methodology, Resources, Writing – review & editing. **Melissa N. Dunkle:** Conceptualization, Resources,

Writing – review & editing, Supervision. **Mubasher Bashir:** Conceptualization, Resources, Writing – review & editing. **Andrea F.G. Gargano:** Conceptualization, Writing – review & editing, Supervision. **Matthias Pursch:** Conceptualization, Writing – review & editing, Supervision. **Edwin P.C. Mes:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition. **Peter J. Schoenmakers:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

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