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Heterogeneity analysis of polymeric carboxylic acid functionality by selective derivatization followed by size exclusion chromatography

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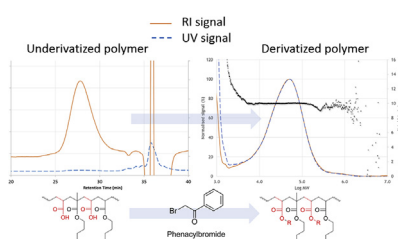
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HIGHLIGHTS

- Distribution of carboxylic acid functionality over molecular weight.
- Derivatization of carboxylic acid functionality with phenacylbromide.
- Simple sample preparation performed by mixing reagent/catalyst at room temperature.
- Acid distribution analysis independent of type and amount of comonomers.

GRAPHICAL ABSTRACT



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ABSTRACT

Waterborne polymers are increasingly applied in our society, replacing traditional solvent-borne coatings and thus reducing environmental impact of coatings. The majority of waterborne dispersions are stabilized by the incorporation of neutralizable carboxylic acid functionality. The characterization of synthetic waterborne polymer systems can be performed by a wide variety of chromatographic and spectroscopic techniques. However, none of these approaches is able to determine the acid functionality distribution over the molecular-weight distribution directly. In this research, an innovative approach is developed which enables this analysis. The approach is based on the specific and complete derivatization of carboxylic acid functionality with phenacylbromide.

Size exclusion chromatography (SEC) analysis of the derivatized polymers is performed followed by ultraviolet- (UV) and refractive index (RI) detection, enabling the quantitative determination of the acid content per molecular weight fraction. The applicability of the developed protocol is shown for various polymer systems.

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1. Introduction

Waterborne polymer systems are sustainable alternatives to solvent-borne polymers and thus are becoming increasingly more important. Their use results in a significantly decreased release of

volatile organic compounds to the atmosphere. Waterborne polymers are used for a wide variety of applications, such as coatings for packaging, printing, decorative and industrial use. These polymers can be synthesized using different polymerization methods, including emulsion radical polymerization [1–7], step-growth polyurethane polymerization [8–10] or hybrids of these mechanisms [11–15]. The obtained polymers are dispersed in water and yield particles of nanometer to micrometer size. The most common method to achieve aqueous dispersibility of these non-water-

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soluble polymers is incorporation of acidic groups, such as (meth) acrylic acid in the case of polyacrylic emulsion polymers or dimethylolpropanoic acid (DMPA) in waterborne polyurethanes. These acidic groups may be neutralized by the addition of water-soluble base, such as ammonia, triethylamine (TEA) or potassium hydroxide which results in water-soluble ionic domains within a polymer chain thus stabilizing the polymer particles in aqueous environments.

The distribution of these incorporated hydrophilic acidic monomers over the molecular-weight distribution (MWD) plays a crucial role in polymer particle formation and colloidal stability. Presence of hydrophilic domains in a coating however may severely impact coating application properties, such as durability and adhesion [16–18]. To ensure that the coating properties meet the application-specific requirements, it is important that the acid distribution throughout the MWD can be determined [19]. The analysis of ionic groups in synthetic polymers is complicated, as commercial polymer systems are comprised from a large number and variety of comonomers [20]. Also, the presence of multiple distributions, such as molecular-weight, end-group, sequence and/or functionality-type distributions complicate the chemical characterization of these polymers. Established techniques such as gradient size-exclusion chromatography [21,22] and gradient polymer-elution chromatography [23–28] are valuable for the analysis of ionic groups in simple acid-functionalized copolymers. However, application of these techniques to contemporary, highly complex polymers, which often contain many different comonomers next to the acid monomer, is less suitable as retention and elution behavior are strongly related to the overall polymer composition. From a synthesis-, application- and commercial perspective, there is a strong need to obtain more information about the incorporation of these ionic groups over the molecular-weight distribution.

In our previous study [29], we have demonstrated the applicability of a carboxylic-acid selective derivatization protocol for the unambiguous identification of the type of acid used during the synthesis of waterborne acrylic polymers. This derivatization protocol may be further exploited to investigate the heterogenic incorporation of the anionic groups over the MWD. By selectively reacting the anionic groups with a UV-absorbing group, the acid distribution can be made visible by employing UV detection.

In this work, an analysis method for the rapid quantification and characterization of acidic monomer groups in synthetic polymers by SEC-dRI-UV is described. Quantitative aspects of the protocol are investigated, as well as the application of the developed method to characterize commercial waterborne polymer types.

2. Experimental

2.1. Materials

n-Methylpyrrolidone (NMP, peptide synthesis grade), triethylamine ($\geq 99.5\%$), phenacylbromide (PB, $\geq 99\%$), phenacyl acetate (PA, $\geq 98\%$), lithium bromide (LiBr, $\geq 99\%$), butyl methacrylate (BMA, $>99\%$), methyl methacrylate (MMA, $>99\%$), methacrylic acid (MAA, $>99\%$), sodium lauryl sulfonate (32% (w/w) in water) and ammonia (25% in water) were purchased from VWR (Amsterdam, The Netherlands). 1-Dodecane thiol ($\leq 100\%$), ammonium persulphate ($\geq 98\%$) were purchased from Merck (Amsterdam, The Netherlands).

2.2. Synthesis of waterborne polymers

Copolymers were synthesized by reacting butyl methacrylate, methyl methacrylate and methacrylic acid in various weight ratios

(φ , see Table 1) using emulsion polymerization. Water containing 2.3% (w/w) sodium lauryl sulfonate was heated to 80 °C prior to addition of the monomer seed, which consists of 5% of the total monomer feed. Targeted total concentration of polymer is 30% (w/w) in water, further to be named solid content. Directly after addition of the monomer feed, 0.5% (on monomer) of ammonium persulphate was added to the mixture over 3 min to initiate the reaction. Remaining monomer feed (containing 0.5% (w/w) of 1-dodecane thiol as chain transfer agent) was added for 90 min while maintaining reaction temperature at 85 °C. Reaction temperature was kept at 85 °C for 60 min after completion of the monomer feed, after this time the batch is cooled to 30 °C. At this stage, the neutralizing agent (ammonia) is added until a pH between 7.5 and 8.5 is obtained. Solid content was measured by making a mass balance of 1 g of polymer before and after drying in a 120 °C oven for 2 h.

2.3. Instrumentation

Size-exclusion chromatography (SEC) was performed on a modular Agilent 1260 HPLC system, equipped with autosampler, pump, column compartment, multi wavelength UV detector and a 1260 multi-detector system (Amstelveen, The Netherlands) consisting of a RI detector, viscosity detector and 2 light scattering detectors which utilize different angles. The eluent was n-Methylpyrrolidone with 0.01 M lithium bromide at 0.75 mL min⁻¹ and a column temperature of 60 °C. Three 300 mm × 7.5 mm i.d. PLgel Mixed-B columns packed with 10 μm particles (Agilent, Amstelveen, The Netherlands) were used in series. A 50 mm × 7.5 mm i.d. PLgel guard column was used (packed with 5-μm particles). The injection volume was 100 μL. The UV wavelength used for selective detection of functionalized acid groups was 280 nm. System control was performed using Agilent GPC/SEC software, version A.02.01, data processing was performed using home-built macros in Microsoft Excel (2016 Edition).

2.4. Procedures

Derivatization of acid-functional polymers with phenacylbromide was performed by dissolving 200 mg of acid-functionalized polymer, with a known amount of incorporated acid and solid content, in 8 mL NMP, thus resulting in a known dilution factor. TEA was added in 4-fold stoichiometric excess with respect to absolute acid amount. After 1 h of stirring, a similar stoichiometric excess of phenacyl bromide was added to the mixture and mixed for 10 min. This solution was used for SEC analysis without any further sample preparation. For samples with an unknown acid content, 100 mg of phenacylbromide and 100 μL of TEA were added using the described procedure.

Calculation of incorporated-acid content by selective derivatization of the acid functionality was performed by preparing a stock solution of PA in NMP. A 10-point calibration curve (concentration range 14 mg kg⁻¹ to 600 mg kg⁻¹) was prepared from this stock solution. To obtain the acid concentration from the PA calibration curve, the PA concentrations were corrected for molar mass:

$$Conc_{Target\ acid} = \frac{MW_{Target\ acid}}{MW_{PA}} * Conc_{PA}$$

In this equation, $Conc_{Target\ acid}$ is the calculated concentration of target acid present in the calibration point, $MW_{Target\ acid}$ is the molecular weight of the acid (72.1 g/mol for acrylic acid, 86.1 g/mol for methacrylic acid and 134.1 g/mol for DMPA), MW_{PA} is the molecular weight of phenacylacetate (178.2 g/mol) and $Conc_{PA}$ is the calculated phenacylacetate concentration in the calibration point.

Table 1
Composition of model polymer systems.

MMA-MAA copolymers				BMA-MAA copolymers			
Sample	ϕ MMA % (w/w)	ϕ MAA % (w/w)	Solid content % (w/w)	Sample	ϕ BMA % (w/w)	ϕ MAA % (w/w)	Solid content % (w/w)
MMA 1	100.0	0.0	28.5	BMA 1	100.0	0.0	29.2
MMA 2	98.0	2.0	29.6	BMA 2	98.0	2.0	29.5
MMA 3	96.0	4.0	29.1	BMA 3	96.0	4.0	29.3
MMA 4	94.0	6.0	29.0	BMA 4	94.0	6.0	29.4
MMA 5	92.0	8.0	28.1	BMA 5	92.0	8.0	29.4
MMA 6	90.0	10.0	28.7	BMA 6	90.0	10.0	29.3

These standards are analyzed using the described SEC setup, integrating the low molecular weight PA peak in the UV trace. The UV peak area of the polymeric fraction (see Fig. 1b, dotted line between t_R 23–32 min) was integrated and corrected for the solids content and the dilution factor which was calculated for each polymer.

3. Results and discussion

3.1. Total acid content determination by SEC-UV-RI

To detect the presence of acids in a polymer, the phenacyl bromide functionalization protocol will result in a distinct UV signal at 280 nm which is visible during elution of the polymer. This is illustrated in Fig. 1. Fig. 1a shows the chromatograms of both refractive index- and UV 280 nm trace of sample MMA 2 without derivatization, while Fig. 1b is the same sample after derivatization with phenacylbromide.

The polymer sample without derivatization shows no significant UV absorbance at polymer elution times (t_R 24–32 min), whereas a clear elution band can be observed for the derivatized polymer. Remaining derivatization agent and catalyst elute around t_0 and are shown as positive peaks on both RI- and UV traces. It can also be noted that the elution time, and thus the hydrodynamic volume, of the polymer (refractive index signal) did not change significantly as a result of the derivatization. Peak intensity in refractive index signal was found to increase, which can be explained by the more favourable detector response increment (dn/dc) of the aromatic functionality compared to the bare incorporated carboxylic acid monomer [30].

The UV peak of the polymer was integrated (as shown in Fig. 1b) and compared to the phenacyl acetate calibration curve (linear fit, $R^2 = 0.99998$, $y = 104.11x + 470.28$), as described in the Procedures section. In Table 2, results from the SEC-dRI-UV analysis are displayed.

From the obtained results, it can be concluded that the derivatization protocol performs well for the detection and quantification of acid functionality. Results using this protocol are in good agreement with the theoretical acid content values (which are established gravimetrically during the synthesis of the polymers) with a relative deviation between 0 and 10%. We did not find significant reactivity of phenacylbromide with other possible functional groups in waterborne polymers (e.g. hydroxyl, amine, urethane, urea and sulfonic acid), but as this is considered out of scope of this study it should be investigated in more detail in further research.

3.2. Acid distribution analysis

Additional information about distribution of carboxylic acid groups from SEC analysis may be obtained by the addition of an additional concentration detector next to the UV detector. In this research, a refractive index detector was used to detect the polymer

concentration. The assumption is made that refractive-index response for a single polymer across the polymer molecular weight is constant. Significant deviations of the refractive index of a certain polymer fraction slice compared to the polymer bulk are only expected in the low molecular weight region [31], as molecular weight build-up will rapidly average out the composition and thus the polymer refractive index. More generic SEC solvents with lower refractive indices, such as tetrahydrofuran (THF) may be used in the derivatization protocol, yet would be accompanied by drastically different reaction kinetics of anionic groups [29], easily requiring several days before complete derivatization is obtained. For practical reasons, the decision was made to perform the derivatization and analysis in NMP.

Both RI and UV signals are aligned by correcting the elution time for the interdetector delay, after which the peak area under the polymer is determined for both detectors. For every fraction of the molecular weight distribution, the area of the UV signal is divided by the total UV peak area, which in turn is divided by the area of the RI signal divided by the total RI peak area. The result is multiplied by the acid content (ϕ_{total}) as determined by the external standard UV calibration using phenacylacetate (see section 3.1).

$$\phi_{slice} = \frac{A_{280\text{ nm}} / \sum A_{280\text{ nm}}}{A_{RI} / \sum A_{RI}} * \phi_{total}$$

The output for this calculation is the acid content per data slice, an example of this output is shown in Fig. 2.

The polymer appears to contain an evenly distributed acid content over the molecular weight, which means that every polymer chain contains the same relative concentration of acid. There is an increase in apparent acid content visible in the low molecular weight ($M_w \sim 2000$ kDa), which is mainly caused by the presence of excess derivatization agent. This could be counteracted by using an optimized SEC column setup for increased low molecular weight resolution between reagent and polymer or by sample clean-up prior to SEC analysis. It must be mentioned that also the non-derivatized sample (Fig. 1a) displays some UV absorption in the low molecular weight region. Towards the higher molecular weight region, scattering of data points is observed. This indicates that accuracy of the acid content determination is lower compared to the bulk of the polymer. This is caused by the relatively low signals for both RI and UV detectors in this molecular weight region.

All model systems were analyzed using the derivatization protocol and SEC-dRI-UV, resulting in the acid distribution plots shown in Fig. 3 (MMA-MAA copolymers) and Fig. 4 (BMA-MAA copolymers). All polymers show a homogeneous acid distribution over the molecular weight with the clear difference of a different acid content.

3.3. Industrial sample analysis

Using the developed protocol, an unidentified commercially available resin and a polyurethane prepolymer were analyzed.

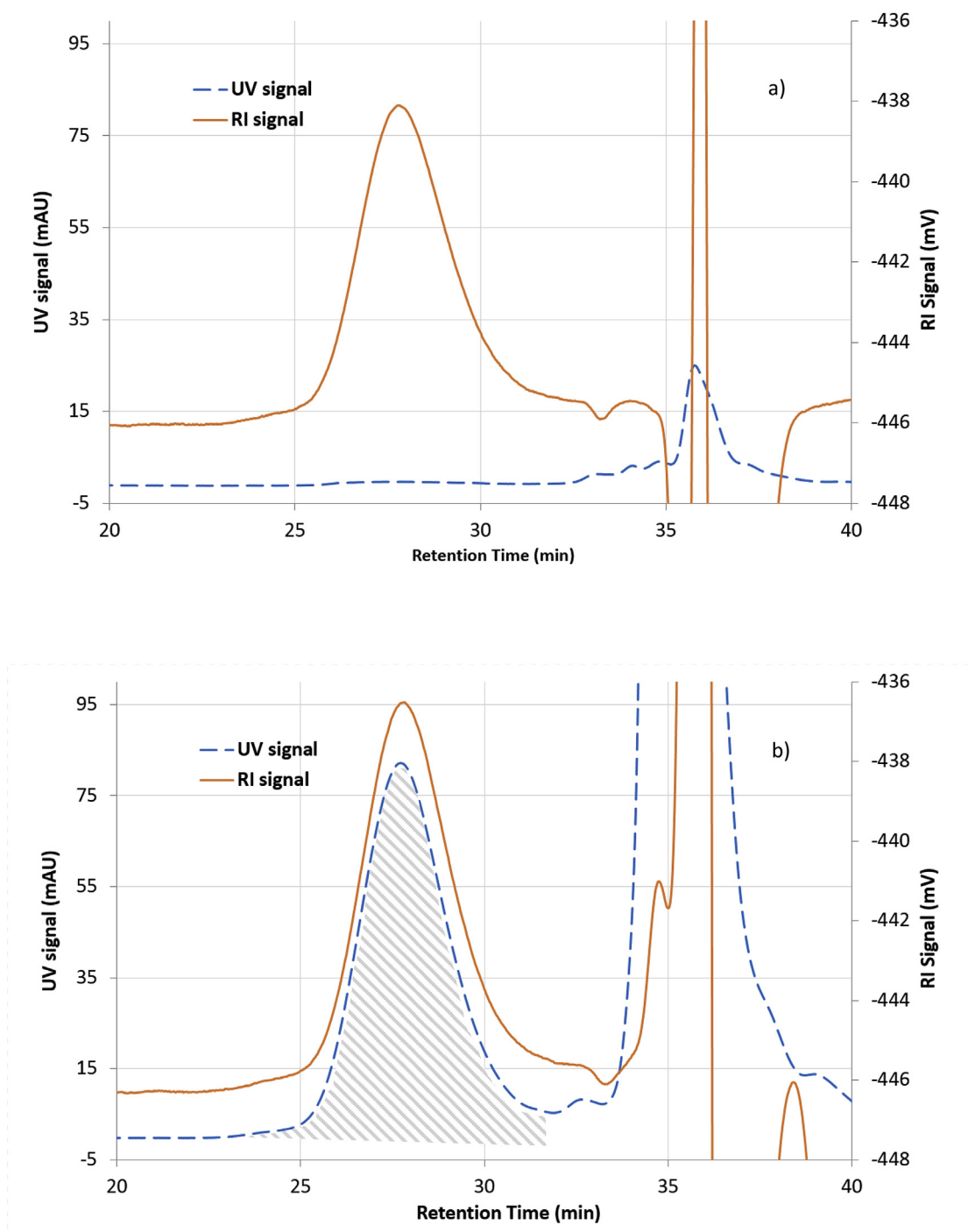


Fig. 1. Refractive index- and UV chromatograms at 280 nm of model polymer MMA 2 (2% (w/w) MAA). a) sample MMA 2 without derivatization, and b) sample MMA 2 after derivatization.

Table 2

Acid content (weight fractions) in model polymer systems. Theoretical values compared with the SEC protocol.

MMA-MAA copolymers			BMA-MAA copolymers		
Sample	ϕ MAA Synthesis % (w/w)	Average ϕ MAA SEC % (w/w) ^a	Sample	ϕ MAA Synthesis % (w/w)	Average ϕ MAA SEC % (w/w) ^a
MMA 1	0.0	—	BMA 1	0.0	—
MMA 2	2.0	1.9	BMA 2	2.0	2.0
MMA 3	4.0	4.0	BMA 3	4.0	3.7
MMA 4	6.0	6.1	BMA 4	6.0	5.5
MMA 5	8.0	8.5	BMA 5	8.0	8.1
MMA 6	10.0	10.3	BMA 6	10.0	10.0

^a Samples are analyzed in 6-fold, relative standard deviations below 2%.

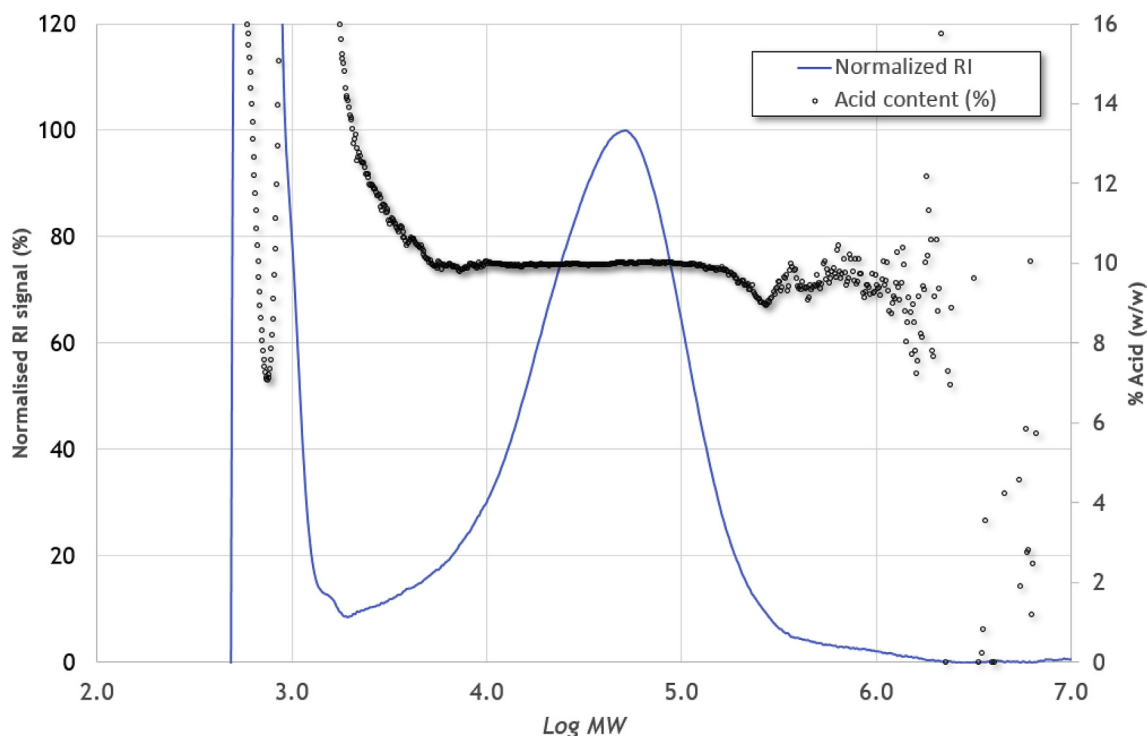


Fig. 2. Acid distribution as a function of molecular weight of model polymer BMA6 (10% w/w acid monomer. Refractive index signal (blue trace) is displayed to show polymer elution profile. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

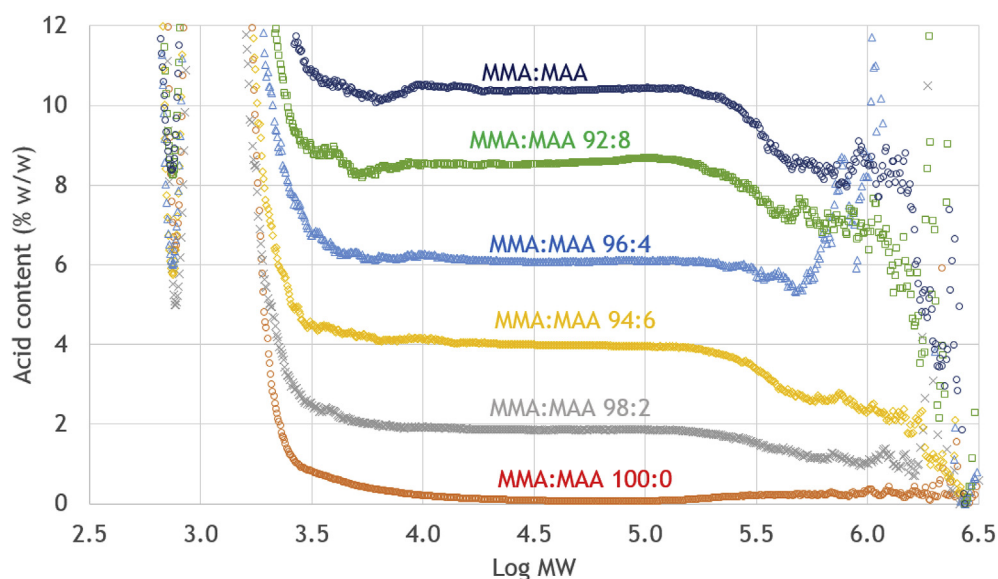


Fig. 3. Acid distribution overlay of model polymers MMA 1 to 6.

Results for the commercially available resin are shown in Fig. 5, which shows the sample being based on the oligomer-polymer concept [19] with respective molecular weights of the oligomer and polymer of approximately 10 kDa and 100 kDa. Using the UV-signal and the phenacyl acetate calibration together with confirmed acid identity (acrylic acid) from our previously published pyrolysis method [29], the total polymer acid content was calculated to be 6.7% (w/w). Calculation of the acid distribution shows a relatively acid-rich oligomer containing roughly 9% (w/w) of acrylic acid, and a polymer which also contains acrylic acid in

approximately 4.5% (w/w) content. Presence of an acid-rich oligomer is common for oligomer-polymer systems, but the presence of acid in the polymer is encountered less often. This crucial information about polymer architecture helps explain polymer properties and performance, and would not be available without the developed protocol.

Applicability of the developed protocol is not limited to acrylate polymers, but may also be used for the characterization of other carboxylic acid-containing polymers. An example is shown in Fig. 6 which shows the analysis of a polyurethane prepolymer. This

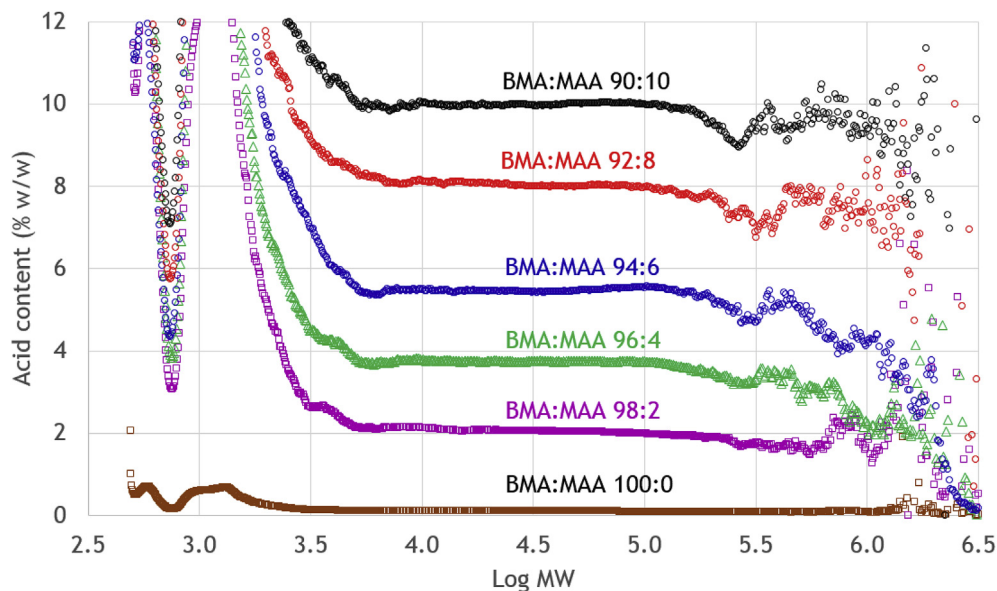


Fig. 4. Acid distribution overlay of model polymers BMA 1 to 6.

prepolymer was prepared in-house and consists of the reaction content of the polymers. Sample preparation is simple and yields

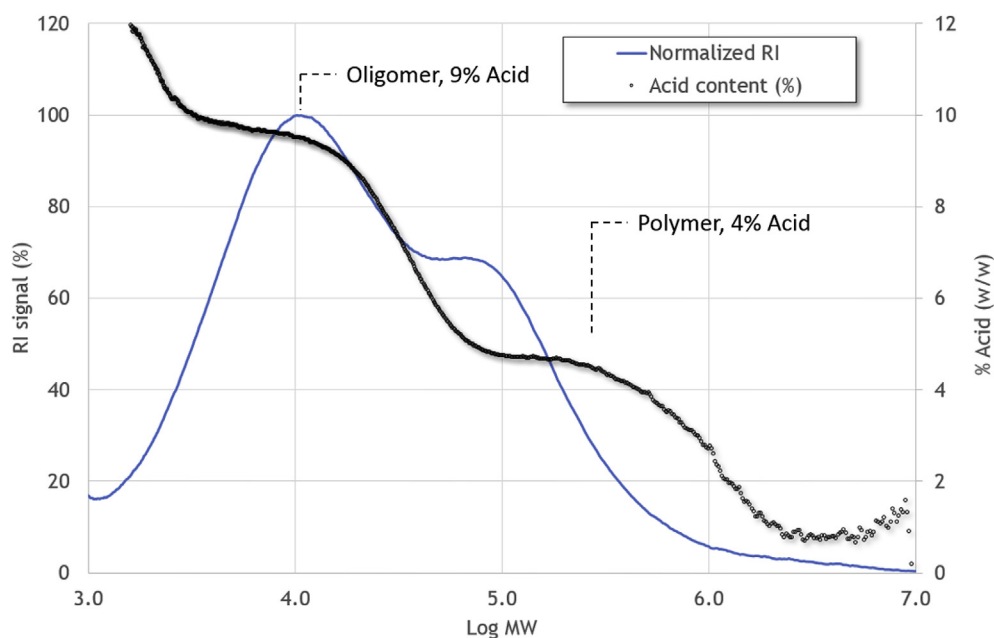


Fig. 5. Acid distribution of commercial resin A. Bimodal molecular weight distribution with an acid-rich oligomer indicates an oligomer-polymer system.

product of isophorone diisocyanate, polytetrahydrofuran (pTHF) 1000 and DMPA. The UV trace shows acid content to be approximately 2% (w/w), which was consistent with the polymerization recipe. Also, a homogeneous incorporation of acid with respect to molecular weight was observed.

4. Discussion and conclusion

A specific derivatization protocol was established and used for the quantitative determination of acid content in waterborne polymers. Obtained results correspond well to the theoretical acid

quantitative information, and only requires addition of reagent and catalyst to the dissolved polymer in excess amounts. A possible drawback could be that the SEC analysis requires the polymer sample to be fully soluble to obtain repeatable and accurate results whereas titration requires at least swelling of the polymer. The SEC analysis cannot be applied for (pre)crosslinked polymers as these will not dissolve in any solvent.

By incorporation of a concentration detector such as a RI next to a UV detector which specifically detects presence of acid, the acid distribution across the molecular weight can be determined. The compositional influence on RI signal is a drawback of the use of RI

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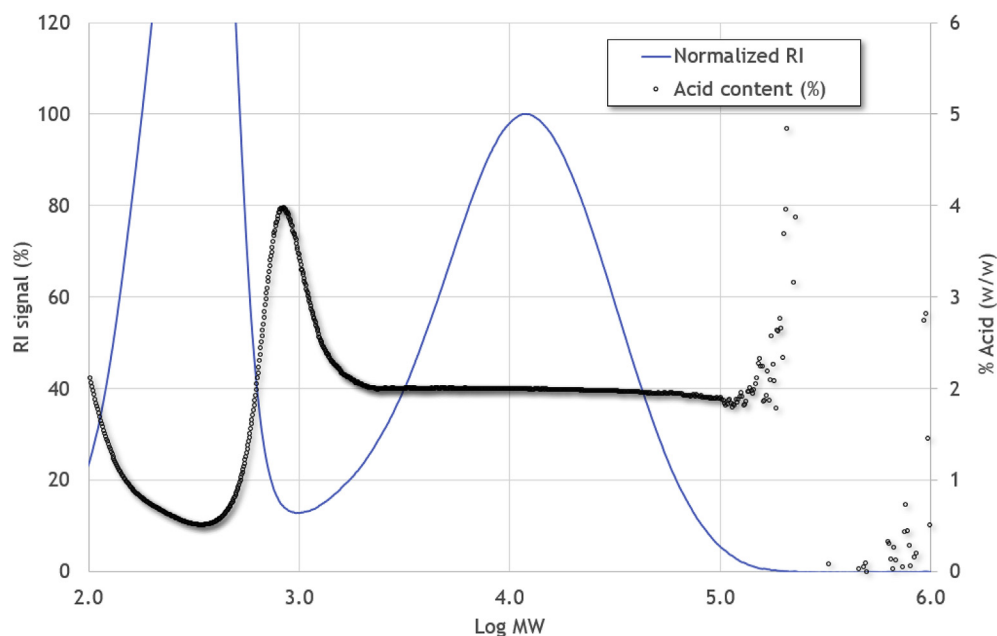


Fig. 6. Acid distribution of a polyurethane prepolymer, consisting of Isophorone diisocyanate, pTHF1000 and DMPA.

refractive index solvents such as NMP. The model polymer systems used in this research were prepared in such a way, that a homogeneous composition over molecular weight is obtained. Polymers prepared in a different way, may exhibit a variation in acid distribution and/or a compositional variation of the comonomers. This will have an effect on both RI- and UV detector signals, but it must be noted that UV-signal differences between derivatized and non-derivatized acid functionality will be significantly larger than any difference in refractive index caused by compositional drift. Detection techniques such as high-temperature evaporative light scattering detection (HT-ELSD) are theoretically better suited as concentration detector compared to RI detection, as there is no significant influence of polymer composition on the detector signal [32,33] and detector signal can be linearized.

The described protocol is able to provide molecular weight, acid content and acid distribution of a polymer sample in a single analysis run. This combined information is not readily obtainable using other methods of instrumental analysis. The reported protocol provides more information on the chemical heterogeneity of the incorporated acid monomers, and may be utilized regardless of type, number and polarity of comonomers which makes it a valuable addition to polymer analysis laboratories.

Declaration of interests

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.

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