MEASURING OXIDE RATIOS IN MIXED-OXIDE POLYOLS BY SOLVERE LIQUID CHROMATOGRAPHY DETECTOR

Application Note

GPC Analysis of Polymers

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Abstract

The Solvere liquid chromatography detector was evaluated for the determination of the relative carbon content of a series of polyols produced with varying ratios of different molecular weight (and carbon number) oxides. This was accomplished by a gel permeation chromatographic separation followed by refractive index or Solvere detection, analyses completed separately. The peak area ratios of the RI and Solvere signals were compared to measured carbon content based on CHN combustion analysis. This relationship was roughly linear (R^2 = 0.87) for the 14 polyols investigated.

Introduction

Polymer analysis can be a costly endeavor for companies specializing in materials or polymer precursors. These measurements become even more important when the components being analyzed are the product of co-monomers. Having the correct ratio of monomers can be the key to a successful product or an off-grade material. Examples of these type of co-monomer products would be ethylene-vinyl acetate, styrene-acrylonitrile, or mixed oxide polyols, as well as many others on the market.

Nuclear Magnetic Resonance Spectroscopy (NMR) analysis is often used to measure the co-monomer ratios as it provides a unique measurement of either the carbon or proton from each monomer. Additionally, it can directly yield quantitation based on the response, so no external calibration is necessary. However, very few labs have NMR capabilities, and the measurements can be time consuming to make. Other analytical measurements can be made with certain polymers (e.g., Fourier Transform Infrared Spectroscopy [FTIR] with modeling), but those can also be very time consuming to set up.

The Solvere liquid chromatography (LC) detector can make these measurements in a simpler fashion depending on the monomer system used. Separating polyol polymers by Gel Permeation Chromatography (GPC) followed by a mass-sensitive detector (e.g., refractive index [RI]) and using the Solvere to measure carbon content should allow one to measure the ratio of oxides with different numbers of carbon, short-chain oxides vs. a longer-chain oxide, in the polyol. For example, a polyol of a given molecular weight (MW) that is made from 100% of a longer-chain oxide will have a higher carbon content than one of the same MW that is made from 100% of a shorter-chain oxide. The amount of each oxide can be determined by comparing the measured mass (or mass response) of the polymer to the detected carbon signal. This concept could be used for any co-monomer system where the monomers had a fixed number of heteroatoms (e.g., oxygen) and varying amounts of carbon.

The advantage of using this type of measurement for determining the content of each monomer is that, in addition to the MW information typically obtained by GPC, it also can provide chemical composition

distribution information. For example, one could determine the ratio of the different oxides at each point along the MW distribution of the GPC. This gives the researcher information about the composition homogeneity (or heterogeneity) of each monomer at each MW slice. Neither NMR nor IR can provide that same MW or composition distribution data.

To investigate this measurement, a range of polyols containing varying ratios of two different oxides were collected and analyzed using both the Solvere and a RI detector. As GPC typically uses isocratic solvent delivery, a split system would deliver solvents at a fixed split ratio since there are no major viscosity changes in solvent throughout the separation. However, since the Solvere detector was not located on the same system as the RI detector, two separate instruments were used to collect the RI-detected and Solvere-detected chromatograms. Care was taken to run both systems under identical conditions.

Experimental

All polyol solutions were prepared by dissolving approximately 0.2 grams of each polyol into 20 mL of THF and mixing the solution well.

The LC system used for GPC in this study is shown in Table 1.

Table 1. Liquid chromatography, GPC system

GPC System:	Agilent 1260 (Binary pump, autosampler, column oven, variable wavelength detector [VWD], RI detector)
Column:	Agilent PLgel MiniMix-D (4.6 x 250 mm, 5 µm)
Eluent:	tetrahydrofuran (THF)
Flow Rate:	0.4 mL/min
UV Detector:	Agilent VWD, 270 nm, 5 Hz data collection
RI Detector	Agilent RID
Solvere™ Detector:	Interfaced through Agilent 35900E A/D (5 Hz)

Once analyzed, the Solvere signal was adjusted by subtracting the average baseline value from 0 to 0.8 minutes from the raw signal to remove the baseline offset for data visualization. The resulting signal was multiplied by a constant value of 950 for each chromatogram so that the signal magnitudes would be on a similar scale as the RI signal. All data analysis was done on the non-corrected chromatograms. Absolute peak area as determined by the chromatographic data system software was used for the ratio measurements. Elution time for the Solvere signal was adjusted by subtracting time from the retention axis to match the peak maximum for the Solvere signal to the RI signal. This was necessary because of the time offset of the Solvere signal that arises from the delay between peak elution onto the disk and the rotation of the disk to get the peak to the combustion zone and subsequent detection. This does assume that the detectors generate the same peak maximum (same retention time).

Results

Examples of chromatograms taken from each detector to demonstrate changes in the peak ratios are shown in Figure 1, Figure 2, and Figure 3. Figure 1 represents chromatograms from low MW Polyol 1 which is made exclusively with short-chain oxide. Figure 2 shows chromatograms of Polyol 13 made with a blend of the short-chain oxide and longer-chain oxide. Figure 3 is from Polyol 4 made exclusively with the longer-chain oxide.

There are several things to note about these example chromatograms. First, as the amount of the longer-chain oxide in the formulation increases, the ratio between the Solvere signal to the RI signal also increases. The peak area for the Solvere for Polyol 1 is larger than that for the RI signal compared to Polyol 13, reflecting the change between an 85% and a 100% longer-chain oxide with higher relative carbon content.

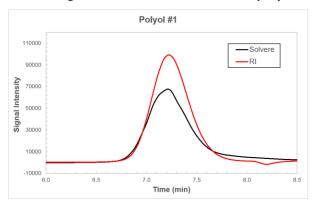**Figure 1.** Overlay of a RI-detected chromatogram and a Solvere-detected chromatogram of a 100% low MW oxide polyol.

Polyol #1

Figure 2. Overlay of a RI-detected chromatogram and a Solvere-detected chromatogram of a polyol containing 85% of the higher MW oxide.
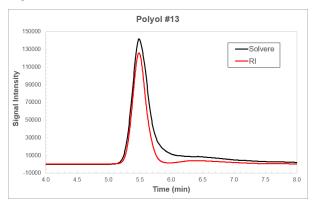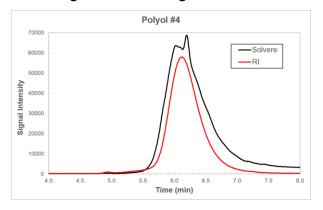

Polyol #13

Figure 3. Overlay of a RI-detected chromatogram and a Solvere-detected chromatogram of a 100% higher MW oxide.

Polyol #4

The ratio of peak areas for the two detectors was plotted for the polyols shown in Table 2. Initially, the

calculated carbon fraction was used to test the feasibility of this measurement. However, these calculations were based on production targets and did not necessarily reflect the actual carbon content of the polyols. To compensate for this, all samples were measured for carbon content by CHN analysis and the directly measured carbon fraction was used for the calculations. The comparison of the data is shown in Table 2 and the graphical results are shown in **Figure 4**

Table 2. Polyols used to evaluate carbon measurements by the Solvere. Carbon fraction was measured by CHN.

Polyol Sample	MW	Measured Carbon Percent	Peak Area Ratio (Solvere/RI)
1	600	52	0.876
2	600	53	0.873
3	1000	56	0.908
4	5000	57	1.242
5	1800	58	1.455
6	4600	59	1.176
7	3000	61	1.458
8	3000	62	1.385
9	3000	62	1.458
10	4600	63	1.748
11	5000	63	1.600
12	2000	64	1.539
13	6100	65	1.755
14	6100	67	1.984

Figure 4. Plot of the peak area ratio of the Solvere to RI detector as a function of measured carbon fraction of each polyol.
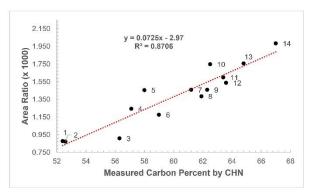

$y = 0.0725x - 2.97$
$R^2 = 0.8706$

Figure 4 shows a good fit to the linear least-squares (LLS) line across the entire x axis range. Evaluating individual data points in **Figure 4** for outliers, there are 3 that could be statistically excluded for being

>2σ away from the LLS line. Excluding Polyols 3, 5, and 10 the model, the correlation coefficient would increase to 0.94. However, aside from the lack of fit, there is no known reason to exclude those points. Further work with the detector is needed to better understand if these measurements were an anomaly or if they are reproducible as the data presented here are based on single analyses. In either case, we observe a linear trend in the data and that the fraction of carbon within a polyol can be predicted using the Solvere detector. Additionally, the trend of carbon content follows the ratio of the two oxides used to make these polyols.

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For more information or to purchase a Solvere™ system, please contact us at 612-787-2721 or contact@activatedresearch.com.

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