

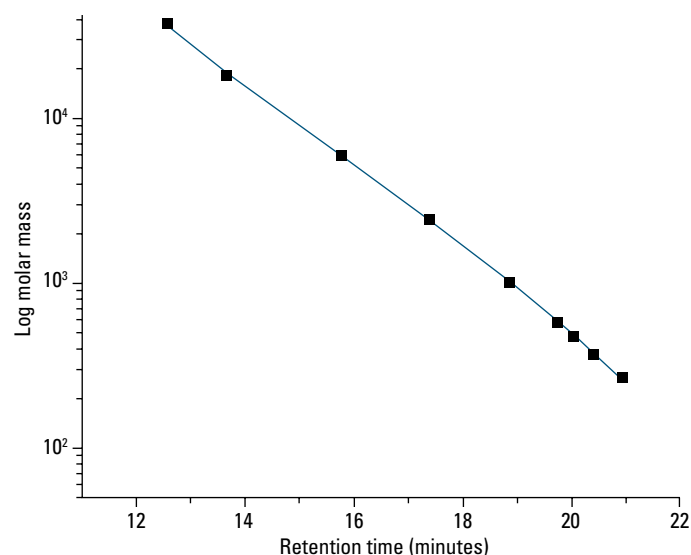
MOLAR MASS MEASUREMENTS OF AN ISOCYANATE MODIFIED POLYURETHANE PREPOLYMER IN LESS THAN 1 HOUR WITH THE EcoSEC® GPC SYSTEM

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INTRODUCTION

Isocyanates are both highly reactive and highly toxic low molar mass chemicals. One common technique used to take advantage of isocyanate reactivity while eliminating safety concerns is to synthesize polyurethane prepolymers for use in subsequent polymerizations. The physical properties of the resultant polymer are influenced to a large degree by the size of the polyol chains in the prepolymer. Harder polymers are formed with larger polyol chains and softer polymers are formed with smaller polyol chains.¹ Here we report on the use of the EcoSEC GPC System to determine the molar mass and molar mass averages of an isocyanate modified polyurethane prepolymer (IMPP) with residual dimethyl sulfoxide (DMSO). The low dead volume of the EcoSEC GPC System combined with the use of semi-micro GPC columns allowed for an efficient separation and characterization of the prepolymer sample in less than 1 hour.

RI CALIBRATION CURVE FOR PStQuick Kit-L POLYSTYRENE STANDARDS AT 0.3 ML/MIN IN THF AT 35 °C



EXPERIMENTAL CONDITIONS

Sample analysis was performed on a system consisting of an EcoSEC GPC System (HLC-8320) equipped with a refractive index detector (RI). Separation of unfiltered 20 μ L injections occurred over a column bank consisting of two 6.0 mm ID $\times$ 15 cm, 3 μ m particle size TSKgel® SuperH3000 (PN 17993) columns preceded by the appropriate guard column (PN 18002) (Tosoh Bioscience). The solvent and mobile phase were tetrahydrofuran (THF) (Fisher Chemical) at flow rates of 0.3 and 0.6 mL/min. Detector, pump oven, and column oven were maintained at 35 °C. For all chromatographic determinations, results are averages of three injections from two separate sample dispersions. Sample solutions were prepared by diluting 99% pure sample with THF for a final sample concentration of approximately 10 mg/mL. Samples were shaken manually for a minute and allowed to sit for 3 hours before analysis was performed. Data was processed with the EcoSEC GPC Workstation Software version 1.08. A RI calibration curve was created using PStQuick Kit-L polystyrene standards (PN 21915) (Tosoh Bioscience LLC) ranging in molar mass from 266 to 37,900 g/mol (Figure 1). Calibration curve data for both 0.3 and 0.6 mL/min were fitted with a cubic function and error values were no greater than 5 %.

SEC ELUTION PROFILE OF IMPP SAMPLE AS MONITORED BY RI (BLUE) AT 0.3 ML/MIN IN THF AT 35 °C

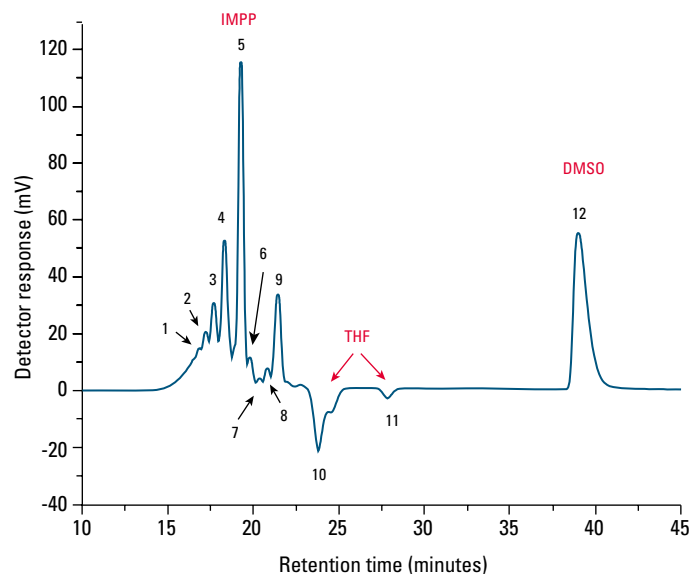


Figure 1

Figure 2

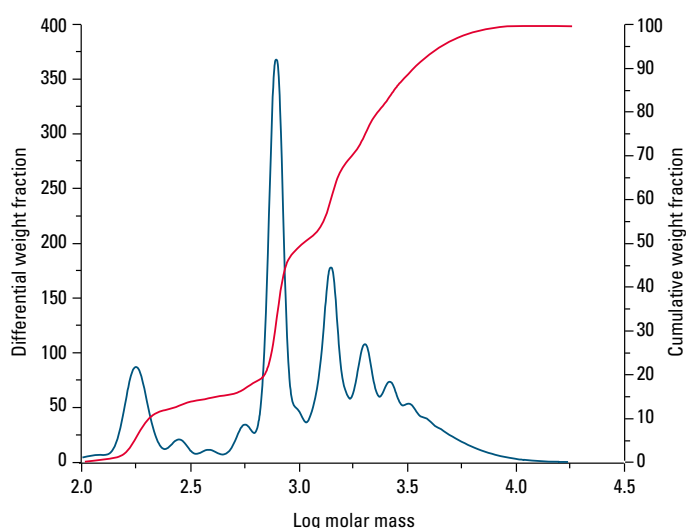
RESULTS AND DISCUSSION

An EcoSEC GPC System encompassing a refractive index detector was used to perform size exclusion chromatography analysis on an IMPP sample composed of 54% urethane prepolymer, 11.5% dimethyl sulfoxide (DMSO), and 34.5% 1,1,1,3,3 pentafluoropropane. As seen in Figure 2, separation of the sample by size exclusion chromatography results in ten positive and two negative chromatographic peaks. The nine positive chromatographic peaks eluting from the column between 14.0 and 22.5 minutes correspond to the urethane prepolymer and 1,1,1,3,3 pentafluoropropane. Peaks 1 through 5 correspond to the urethane prepolymer and peaks 6 through 9 correspond to either the urethane prepolymer or 1,1,1,3,3 pentafluoropropane. The identities of peaks 6 through 9 were not confirmed due to the lack of availability of 1,1,1,3,3 pentafluoropropane.

The two negative peaks at 23.7 and 27.8 minutes are indicative of the sample solvent, THF. Additionally, the latest eluting peak at 39.0 minutes is a result of residual DMSO present in the IMPP sample. Note that the DMSO peak elutes after the void volume of the column (~26.5 minutes) and as such is retained by a non-SEC retention mechanism.

The RI calibrant-relative molar mass averages M_n , M_w , and M_z for the IMPP sample were calculated based on the RI calibration curve, see Figure 1, and are given in Table 1. The weight-average molar mass, M_w , of the IMPP sample ranges from 4,606 g/mol for the earliest eluting peak to 181 g/mol for the latest eluting peak, with an average weight-average molar mass value of 1,531 g/mol. Prior knowledge of the sample predicted the molar mass range to be from 1,000 to 5,000 g/mol.

CUMULATIVE AND DIFFERENTIAL MOLAR MASS DISTRIBUTION FOR IMPP SAMPLE IN THF AT 0.3 ML/MIN



SEC ELUTION PROFILE OF IMPP SAMPLE AS MONITORED BY RI (BLUE) AT 0.6 ML/MIN IN THF AT 35 °C

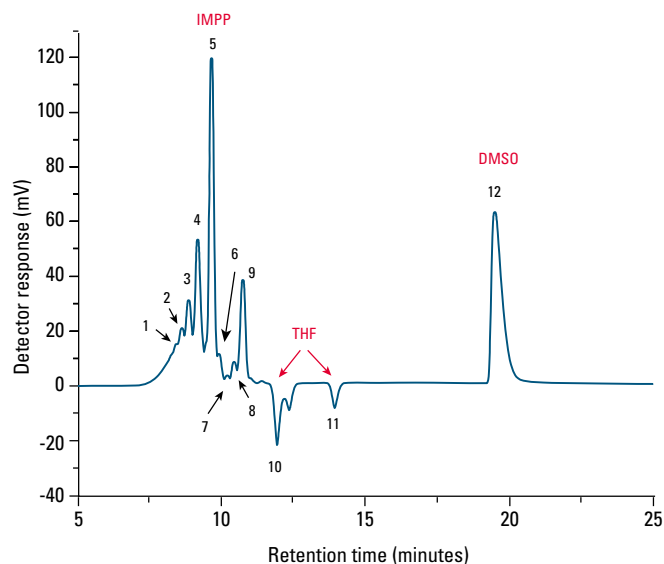


Figure 3

Figure 4

MOLAR MASS AVERAGES, AND POLYDISPERSITY INDEX FOR IMPP SAMPLE IN THF AT 0.3 ML/MIN

Peak	Retention Time (min)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI ^a
1	16.858	4,199 ± 46 ^b	4,606 ± 67	5,214 ± 109	1.09 ± 0.01
2	17.222	2,643 ± 19	2,655 ± 18	2,667 ± 18	1.01 ± 0.01
3	17.688	2,011 ± 16	2,024 ± 16	2,038 ± 16	1.01 ± 0.01
4	18.314	1,387 ± 10	1,403 ± 10	1,418 ± 10	1.01 ± 0.01
5	19.335	798 ± 4	808 ± 5	817 ± 5	1.01 ± 0.01
6	19.790	551 ± 9	554 ± 9	557 ± 9	1.01 ± 0.01
7	20.370	391 ± 9	394 ± 9	397 ± 10	1.01 ± 0.01
8	20.824	278 ± 3	280 ± 3	282 ± 3	1.01 ± 0.01
9	21.439	178 ± 1	181 ± 1	183 ± 1	1.01 ± 0.01
All		676 ± 9	1,531 ± 31	2,873 ± 83	2.26 ± 0.02

^a PDI = M_w/M_n ; ^b Standard deviations from six injections

Table 1

By combining the molar mass information found in Table 1 with prior knowledge of the sample it can be concluded that peaks 1 through 5 are indeed the urethane prepolymer and peak 9 is most likely 1,1,1,3,3 pentafluoropropane. The low molar masses corresponding to peaks 6 through 8 may be oligomers or unreactive material from the synthesis process of IMPP. The polydispersity index, $PDI = M_w/M_n$, for the entire urethane prepolymer sample including 1,1,1,3,3 pentafluoropropane (peaks 1 through 9) was 2.26, while the nine individual components had PDI values ranging from 1.01 to 1.09. From the PDI values it can be concluded that collectively the sample is polydisperse with respect to molar mass but the nine visible components within the IMPP sample are virtually monodisperse with respect to molar mass. The molar mass distribution for the IMPP sample, as obtained at 0.3 mL/min, is shown in Figure 3.

Analysis of the IMPP was initially performed at a flow rate of 0.3 mL/min (the lowest recommended flow rate for the TSKgel SuperH3000 columns) and total analysis was achieved in 45 minutes (Figure 2). In order to increase the throughput of the EcoSEC GPC System the flow rate was increased to 0.6 mL/min (the highest recommended flow rate for the TSKgel SuperH3000 columns) and total analysis was achieved in 22 minutes (Figure 4). As seen by comparing Figures 2 and 4, doubling the chromatographic flow rate had a minimal effect on the chromatographic resolution of the IMPP sample. The only noticeable difference between the chromatograms at 0.3 mL/min and 0.6 mL/min is a slight decrease in chromatographic resolution that occurs between peaks 5 and 6.

CONCLUSIONS

An IMPP sample was analyzed using an EcoSEC GPC System with a refractive index detector. The molar mass averages and polydispersity index of the IMPP sample was determined using a polystyrene relative calibration curve. The chromatogram of the IMPP displayed twelve distinctive peaks. Peaks 1 through 5 were determined to be the urethane prepolymer component of the IMPP and found to have a weight average molar mass ranging from 4,199 to 798 g/mol. The identity of peaks 6 through 9 were not confirmed but are hypothesized to be urethane prepolymer, unreactive species from the synthesis of the sample or 1,1,3,3 pentafluoropropane based on their molar mass range, $M_w = 551\text{--}178$ g/mol. Peaks 10 and 11 and peak 12 are due to the THF used to dilute the IMPP sample and the residual DMSO in the IMPP sample, respectively. The sample was analyzed at two different chromatographic flow rates, 0.3 and 0.6 mL/min. A flow rate of 0.6 mL/min compared to that of 0.3 mL/min resulted in a decrease in analysis time from 45 minutes to 22 minutes. In conclusion, the molar mass averages and polydispersity of the IMPP sample were successfully determined in less than 1 hour using the EcoSEC GPC System.

REFERENCES

- 1.) Extance, A., "Formulating with Polyurethane Prepolymers", SpecialChem4Adhesives.com, July 2, 2008.