

Polyether polyols as GPC calibration standards for determination of molecular weight distribution of polyether polyols

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ABSTRACT: Average molecular weights (M_n , M_w and M_p) are important characteristics of oligomers and polymers, and therefore there is a need to have a precise and reliable determination method. A gel permeation chromatography (GPC) coupled with a single refractive index detector was used to determine the molecular weight distributions of commercial polyether polyols calibrated against a series of polyether polyols with known molecular weights and low polydispersity. Results of these GPC analyses were compared to the ones calibrated against the commercially available polystyrene (PS) standards. The number-average molecular weights (M_n) obtained with GPC using polyether polyols calibration were closer to the theoretical values than the M_n obtained using PS as calibration standards. Hence, these GPC analyses using polyether polyols as calibration standards can provide reliable determination of molecular weight distribution of polyether polyols and can be potentially applied to natural oil-based polyols, including palm oil-based polyols.

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INTRODUCTION

Oligo-polyols, such as polyether polyols and polyester polyols, are one of most important raw materials in production of polyurethane polymers, and thus need to be well-characterized in terms of the concentration of reactive terminal hydroxyl groups as well as their molecular weights (MWs) and molecular weight distributions (MWDs).^{1–5} Today, the MWD and the MW averages of synthetic polymers are commonly determined with gel permeation chromatography (GPC), where synthetic macromolecules are separated according to their size as solution flows through a packed bed of porous gels.⁶

Separation through GPC is ideally achieved by differential pore permeation. The volume of the pore, which is effectively accessible, is greater for small molecules than for large ones. Therefore, larger molecules have shorter retention times in the pores of the packing than smaller ones.^{6,7} The need for reproducible and accurate determination of MWD and the MW averages of polymers have led to the development of different configurations of GPC systems used in different laboratories in terms of column packing, detection types and MW calibration methods.^{6,7}

Various types of detectors have been used to continuously monitor the column effluent and to produce a signal which depends on the amount and/or MW of the polymer in the detector cell. GPC system, coupled with a MW-sensitive multi-angle laser light scattering (MALLS) detector, has been used to determine weight-average molecular weight (M_w) and polydispersity (PD) of heparins.^{8,9} There was also a breakthrough approach where GPC was combined with light scattering and viscosity detector to give direct universal calibration. Even though the universal calibration gives the molecular weight distributions without a mathematical correction, it still requires a column calibration and a series of narrow standards but the latter no longer need to be the same chemical composition as the sample polymer.¹⁰

Different sets of column packing were also applied to obtain a good separation. For example, bio-based polyols were eluted into a set of four Phenogel columns installed in series.^{11–21} Above all, a GPC system needs to have accurate calibration method in order to eliminate systematic errors in MW determination due to inaccurate inter-detector delay values.

Calibration using polystyrene (PS) standards is widely used since these standards are commercially available.^{11,21–30} Ionescu *et al.* (2011) reported that the MWs of polyester polyols

Table I. Batch Numbers and Properties of Commercial Polyether Polyols Reported by Suppliers

Commercial polyether polyols	Supplier	Batch No.	Reported properties				
			Hydroxyl number (mg KOH g ⁻¹)	Functionality	Acid number (mg KOH g ⁻¹)	Water content (%)	pH
Acclaim [®] 8200N ^a	Bayer	PD82000229	14.5	2	0.008	0.012	-
Acclaim [®] 6300N	Bayer	PD82000125	27.2	3	0.008	0.013	-
Poly-G [®] 85-29	Arch	10DR208763	27.7	3	0.008	0.03	6.3
Poly-G [®] 85-34 ^a	Arch	10DR145253	35.0	3	0.002	0.00	7.3
Acclaim [®] 3300N ^a	Bayer	PD82000092	57.7	3	0.002	0.013	6.9
Acclaim [®] 2220N	Bayer	84004002	48.8	2	0.007	0.026	-
Poly-G [®] 76-120 ^a	Arch	10DR117018	118.0	3	0.006	0.00	7.1
Lumulse [®] POE 26	Lambent	G175973	129.53	3	0.151	0.04	-
Poly-G [®] 30-168 ^a	Arch	10DR017121	170	3	0.01	0.01	6.3
Poly-G [®] 30-240 ^a	Arch	10DR255222	233	3	0.016	0.01	5.4

^aPolyols used as calibration standards.

Table II. Batch Numbers and MW Values of PS Standards Reported by the Supplier

Name of PS standards	Batch No.	Reported MW values			
		M_p	M_n	M_w	PD
M_p 580	20122-25	580	580	645	1.12
M_p 970	20123-17	970	935	1,005	1.07
M_p 1,530	20124-20	1,530	1,400	1,490	1.07
M_p 5,120	20127-12	5,120	4,960	5,090	1.03
M_p 19,640	20121-10	19,640	19,210	19,620	1.02
M_p 70,950	20134-13	70,950	67,350	69,200	1.03

calculated against PS standards were indicative but they were not correct.¹⁶ Polymethyl methacrylate (PMMA) standards were also used as calibration standards.³¹ On the other hand, polyols standards are not commercially available and this issue was highlighted by Ionescu *et al.* (2011).¹⁶ There are reported uses of polyether polyols with known MW as standards for GPC cali-

bration.^{32,33} However, a calibration method was not reported and the results obtained with the polyether polyols calibration were not compared with the conventional PS calibration.

This paper discusses the GPC results of polyether polyols using polyether polyols as standards for calibration curves as an alternative to the commercially available PS standards. The MWs of polyols obtained via GPC analysis using polyether polyols calibration are expected to be closer to the theoretical MWs compared to the results obtained using PS standards.

Table III. Theoretical MWs of the Polyether Polyols Used as Calibration Standards

Polyether polyols	Calculated ^a	
	Equivalent weight	Theoretical MW
Acclaim [®] 8200N	3869	7738
Poly-G [®] 85-34	1603	4809
Acclaim [®] 3300N	972	2917
Poly-G [®] 76-120	475	1426
Poly-G [®] 30-168	330	990
Poly-G [®] 30-240	241	722

^aFor hydroxyl values of polyether polyols and their stoichiometrically defined functionalities, refer Table I.

EXPERIMENTAL

Materials

Commercial polyether polyols with their reported properties are tabulated in Table I. The hydroxyl value, acid value, water content and pH for each polyether polyol was obtained from their certificates of analysis. The reported functionalities are defined stoichiometrically.

Six PS standards (Varian Inc.) with reported MW ranging from 580 to 70,950 Da are listed in Table II. The MWs, including molecular weight at the peak (M_p), number-average molecular weight (M_n) and weight-average molecular weight (M_w) were obtained from the certificates of analysis.

Table IV. Theoretical MWs of the Polyether Polyols Used as Calibration Standards and MWs (M_p , M_n and M_w) Obtained from GPC Analysis Using PS Calibration

Polyether polyols	Theoretical MW	Calibration against PS			PD
		M_p	M_n	M_w	
Acclaim [®] 8200N	7738	15835	14465	15550	1.08
Poly-G [®] 85-34	4809	8690	7885	8465	1.07
Acclaim [®] 3300N	2917	5185	4725	5000	1.06
Poly-G [®] 76-120	1426	2080	1790	2010	1.12
Poly-G [®] 30-168	990	1275	1185	1275	1.08
Poly-G [®] 30-240	722	850	795	855	1.08

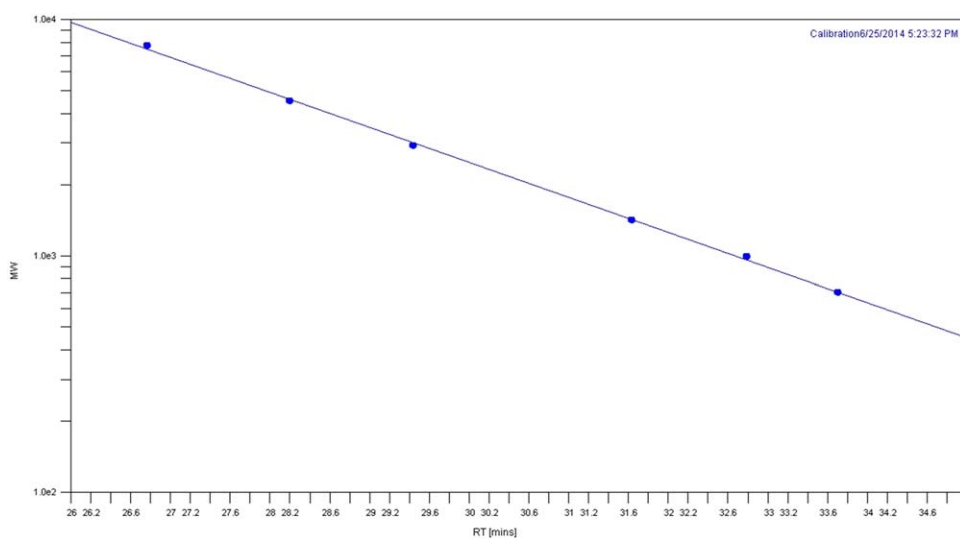
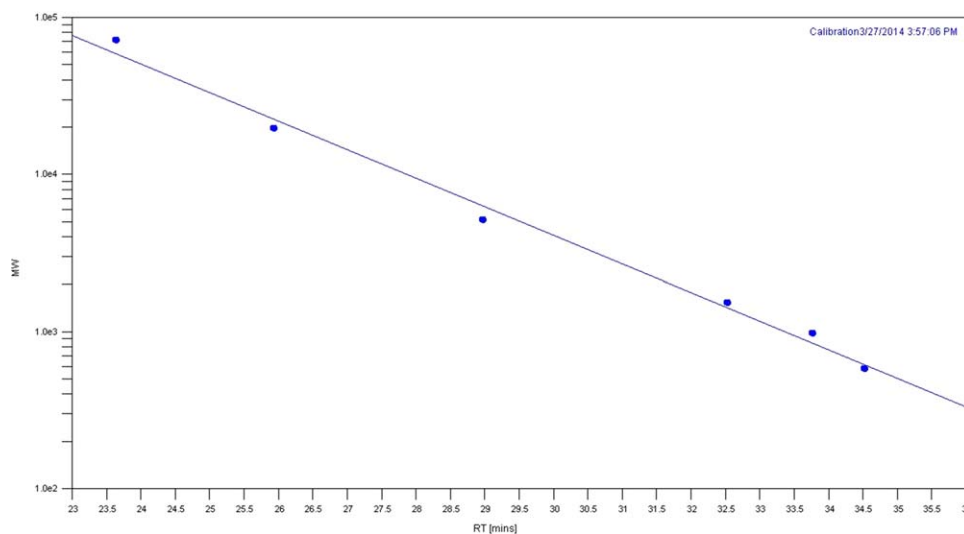
**Figure 1.** Calibration curve using polyether polyols as standards. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 2.** Calibration curve using PS standards. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Theoretical MWs of the Commercial Polyether Polyols and MWs (M_p , M_n and M_w) Obtained From GPC Analysis Using Polyether Polyols and PS Calibration

Commercial polyether polyols	Theoretical MW	Calibration against polyether polyols				Calibration against PS			
		M_p	M_n	M_w	PD	M_p	M_n	M_w	PD
Acclaim [®] 8200N ^a	7738	7480	6995	7335	1.05	15835	14465	15550	1.08
Acclaim [®] 6300N	6188	5225	5215	6050	1.16	10200	9985	12555	1.26
Poly-G [®] 85-29	6011	6095	5495	5760	1.05	12315	10770	11570	1.07
Poly-G [®] 85-34 ^a	4809	4585	4265	4465	1.05	8690	7885	8465	1.07
Acclaim [®] 3300N ^a	2917	3010	2805	2910	1.04	5185	4725	5000	1.06
Acclaim [®] 2220N	2299	2290	2225	2390	1.07	3710	3540	3945	1.11
Poly-G [®] 76-120 ^a	1426	1430	1280	1380	1.08	2080	1790	2010	1.12
Lumulse [®] POE 26	1299	1120	1025	1070	1.04	1540	1375	1465	1.06
Poly-G [®] 30-168 ^a	990	960	910	955	1.05	1275	1185	1275	1.08
Poly-G [®] 30-240 ^a	722	690	655	690	1.05	850	795	855	1.08

^aPolyols used as calibration standards.

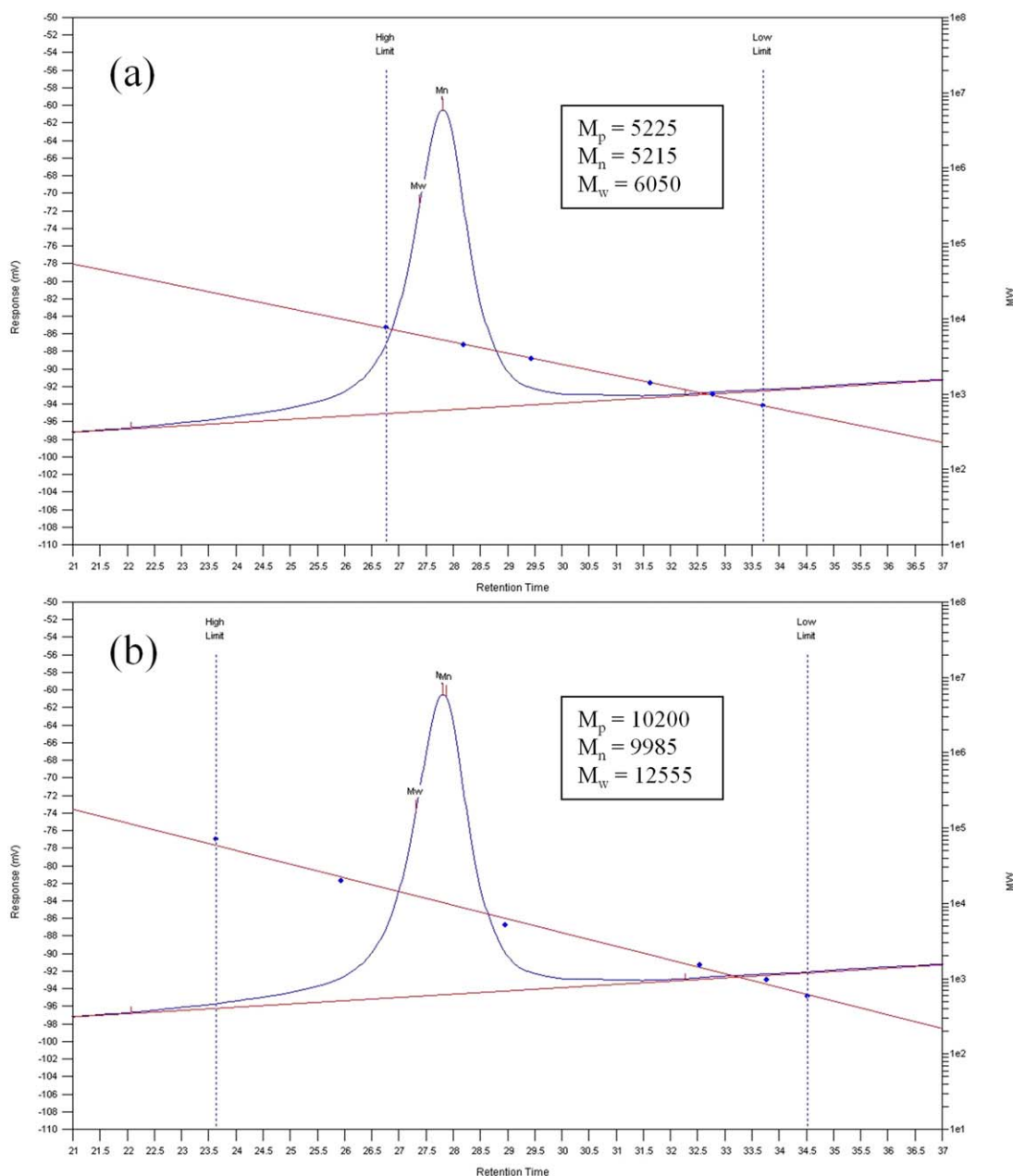


Figure 3. GPC chromatograms of Acclaim[®] 6300N polyol using (a) polyether polyol calibration and (b) PS calibration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

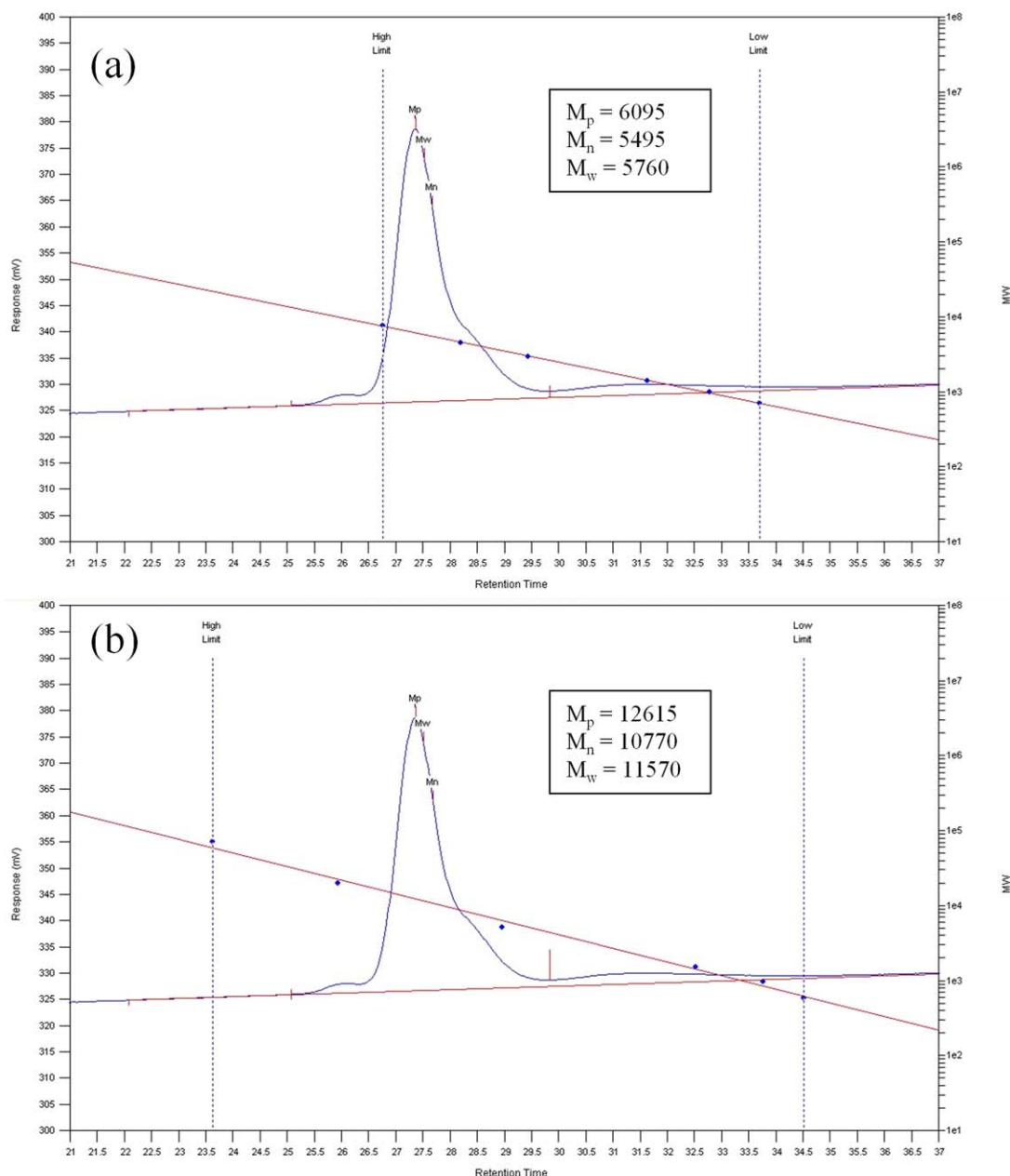


Figure 4. GPC chromatograms of Poly-C[®] 85-29 polyol using (a) polyether polyol calibration and (b) PS calibration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Analytical reagent-grade tetrahydrofuran (THF), stabilised with 0.025% butylated hydroxyl toluene, was purchased from Fischer Chemical (China).

Preparation of Standards and Samples

The polyether polyols and PS standards were dissolved in THF to give an accurate concentration of 2 mg mL⁻¹. The solutions were prepared at least one hour prior to the GPC analysis.

Methods

An integrated GPC system (PL-GPC 50 Plus, Polymer Laboratories Ltd, UK) with a differential refractive index (DRI) detector was used for the determination of MW and MWD. A set of

four Phenogel columns (5 μm particle size and porosities of 50, 100, 1000, and 10,000 Å) from Phenomenex (Torrance, CA), covering a MW range of 10²–10⁶ Da, was used for a separation. THF was used as the eluent at a flow rate of 1 mL min⁻¹. The columns and detectors were thermostated at 30°C. This set-up with four Phenogel columns attached in series was similar to the set-up reported by Kansas Polymer Research Centre, US.^{11–21}

The column calibration data were generated using Cirrus software. The calibration curves were fitted to polynomial of order 1. Linear correlation coefficients (*r*) and coefficients of determination (*r*²) of the constructed calibration curves were calculated.

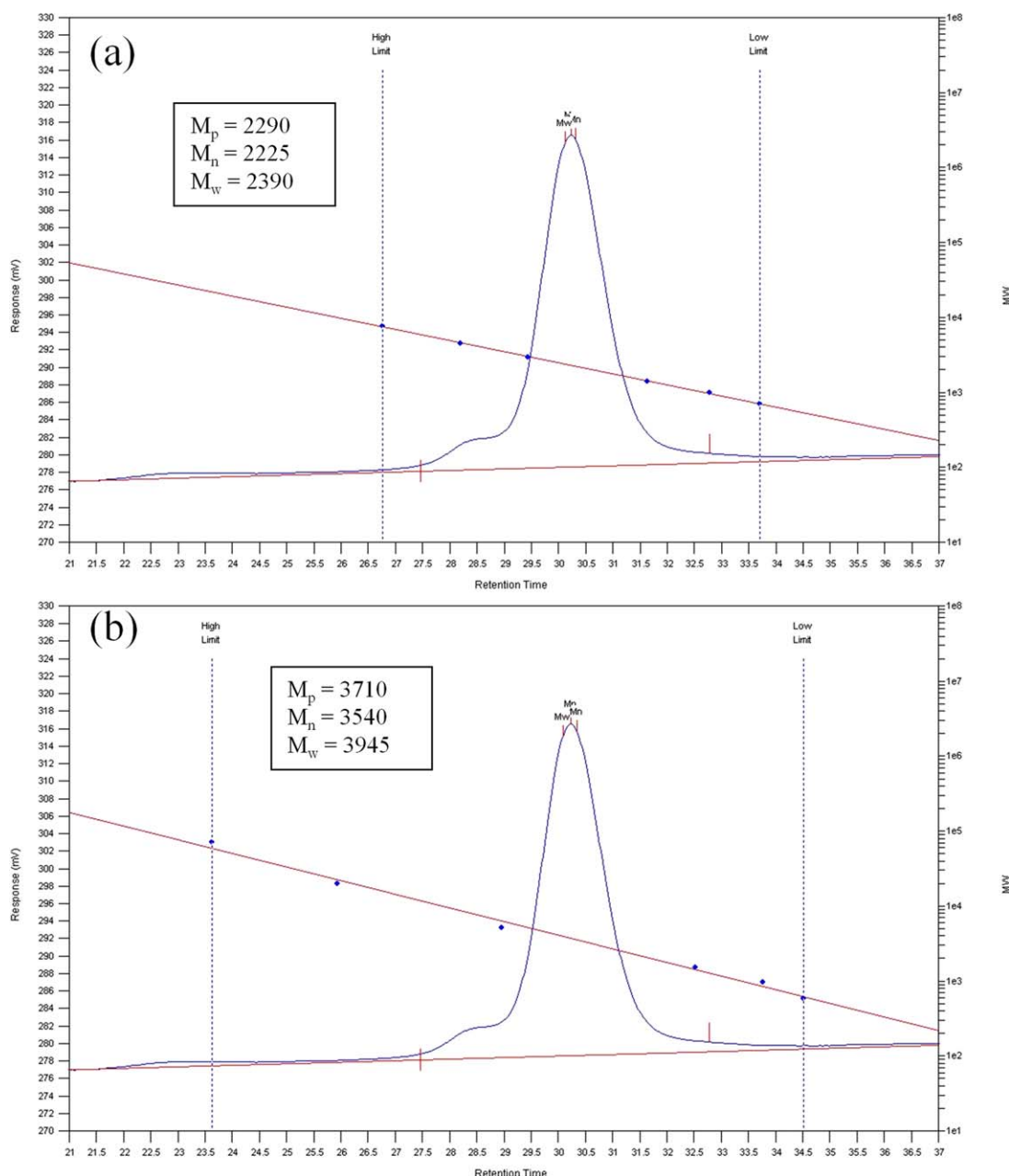


Figure 5. GPC chromatograms of Acclaim® 2220N polyol using (a) polyether polyol calibration and (b) PS calibration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

GPC calculations were performed using area integration method. MW average values (M_p , M_n and M_w) and PD of each sample were obtained through narrow-MWD standard calibration by application of GPC-Cirrus software (Agilent). They are defined as follow, where W_i is the weight of molecules having molecular weight M_i .³³

$$M_n = \frac{\sum_i W_i}{\sum_i W_i / M_i} \quad M_w = \frac{\sum_i W_i M_i}{\sum_i W_i} \quad PD = \frac{M_w}{M_n} \quad (1)$$

The GPC calibration curves were constructed with selected polyether polyols as calibration standards and also with six PS standards (Tables I and II). Subsequently, the MWs of 10 polyether polyols were determined by GPC using the polyether poly-

ols calibration curve and were compared against MWs obtained by GPC using the PS calibration curve.

RESULTS AND DISCUSSION

Polyether Polyols as Calibration Standards

Six commercial polyether polyols with known MW ranging from 700 to 8000 Da were used to construct the calibration curve. The polyether polyols used for the calibration curves were Acclaim® and Poly-G® polyether polyols with analytically determined hydroxyl value and stoichiometrically defined functionality (Tables I and III). Equivalent weight and theoretical MW were calculated using eqs. (2) and (3), respectively.³

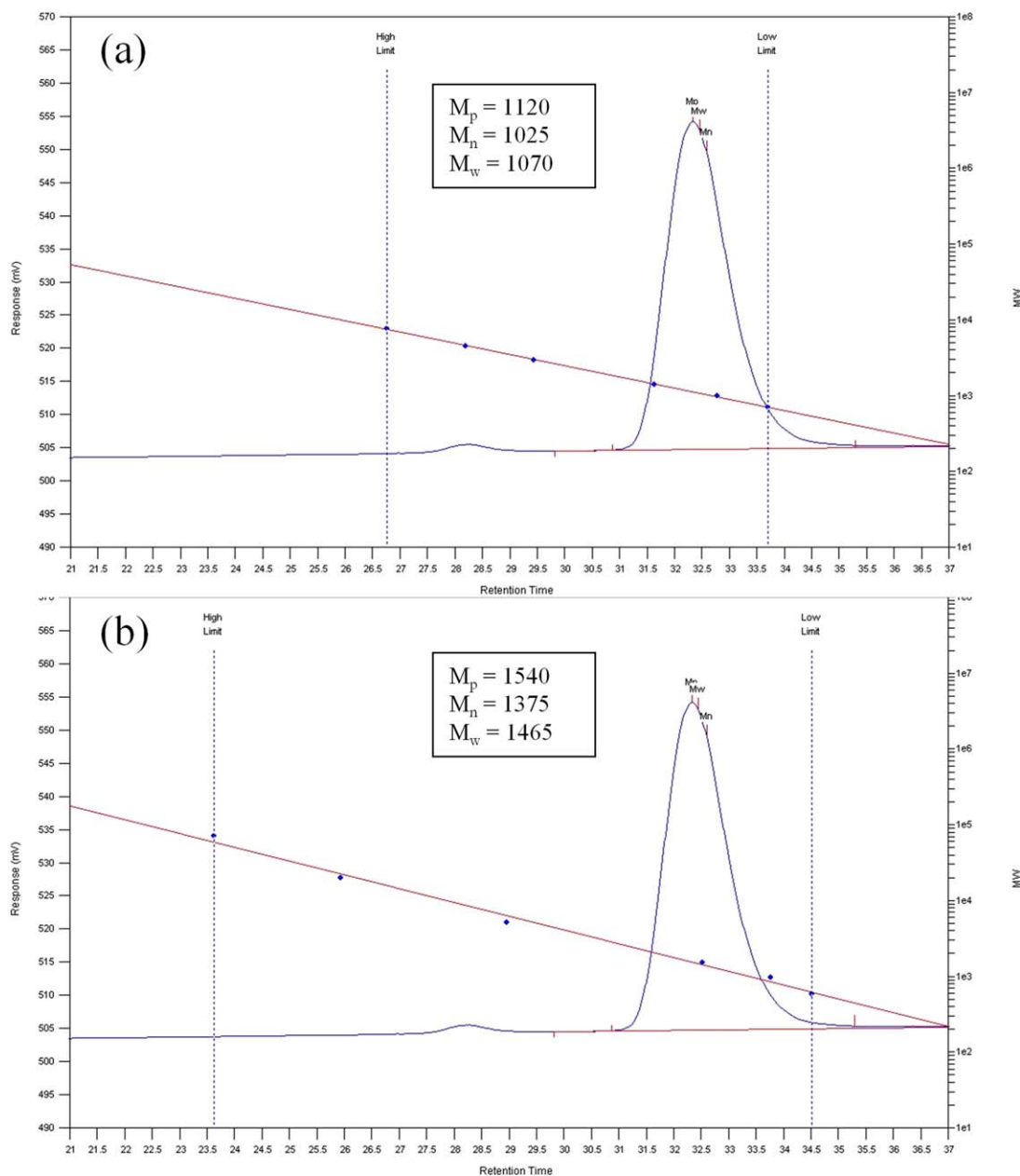


Figure 6. GPC chromatograms of Lumulse[®] POE 26 polyol using (a) polyether polyol calibration and (b) PS calibration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\text{Equivalent Weight} = \frac{56100}{\text{Hydroxyl Number}} \quad (2)$$

where hydroxyl number is expressed as mg KOH g⁻¹ and 56,100 is the equivalent weight of KOH in mg.

$$\text{Theoretical MW} = \text{Theoretical functionality} \times \text{Equivalent weight} \quad (3)$$

The six commercial polyether polyols selected as calibration standards exhibited low PD (close to 1) when analyzed with GPC using PS calibration (Table IV). Hence, they can be used as narrow standards for the construction of calibration curves. However, the MWs (M_p , M_n and M_w) of these selected poly-

ether polyols obtained with GPC using PS calibration were not comparable to the theoretical values.

Low molecular weight propylene oxide-based polyether polyols have almost ideal PD index of 1, which is a result of the reaction mechanism of propoxylation.³ At low MWs, polyether polyols typically have low unsaturation and formation of monols, and therefore their actual functionalities are close to their theoretical stoichiometrically defined functionalities.^{3,35–38}

Acclaim[®] polyether polyols, i.e., Acclaim[®] 8200N and Acclaim[®] 3300N, are produced with a patented organo-metallic propoxylation catalyst which enables commercial production of high MW polyether polyols with low unsaturation. Actual functionalities of

these polyols are close to their theoretical stoichiometrically defined functionalities.^{3,35–38}

Good linearity with a correlation coefficient (r) of -0.9996 was observed for the calibration curve constructed using a series of six commercial polyether polyols (Table I and Figure 1). Calibration curve constructed using a series of six standard PS also showed good linearity with a correlation coefficient (r) of -0.9964 (Table II and Figure 2).

MW Determination of Commercial Polyols

Commercial polyether polyols were analyzed by GPC using polyether polyol and PS calibration curves and the MWs obtained are listed in Table V. The GPC chromatograms obtained using the two different calibration curves for Acclaim[®] 6300N, Poly-G[®] 85-29, Acclaim[®] 2220N, and Lumulse[®] POE 26 polyether polyols are shown in Figures 3–6, respectively.

The GPC analysis results show that the MWs (M_p , M_n , and M_w) of the polyether polyols obtained using polyether polyols calibration curves are closer to the theoretical values than the ones obtained using PS calibration standards. This was especially evident for polyether polyols with higher MWs. For Acclaim[®] 6300, the MWs determined via GPC with polyether polyols calibration were lower but very close to the theoretical MW of 6188, whereas the MWs determined via GPC with PS calibration were 1.6–2.0 times higher than the theoretical MW value (Table V and Figure 3). For Poly-G[®] 85-29, the MWs determined via GPC with polyether polyols calibration were also very close to the theoretical MW of 6011, whereas the MWs determined via GPC with PS calibration were 1.8–2.0 times higher than the theoretical MW value (Table V and Figure 4).

As MWs of polyether polyols decreased, the MWs determined via GPC with PS calibration were found to be approaching the expected theoretical MWs. For Acclaim[®] 2220N, the MWs determined via GPC with PS calibration were 1.5–1.7 times higher than the theoretical MW value of 2299 (Table V and Figure 5) and for Lumulse[®] POE 26, the MWs determined via GPC with PS calibration were 1.1–1.2 times higher than the theoretical MW value of 1299 (Table V and Figure 6).

However, across all MWs, the MWs of polyether polyols determined via GPC with polyether polyols calibration were closer to the theoretical values than the MWs determined via GPC with PS calibration. Moreover, the PDs obtained using polyether polyols calibration were closer to 1 than the PDs obtained using PS calibration (Table V). These outcomes were expected since the polyether polyol samples were analyzed against calibration standards having similar chemical composition and solubility in THF, which leads to comparable separation in GPC.

CONCLUSIONS

Polyether polyols with theoretical molecular weights (MWs) calculated from well-defined hydroxyl values and stoichiometrically defined functionalities were used as calibration standards to determine the MWs of commercial polyether polyols. Polyether polyols selected as calibration standards exhibited low PD values in GPC analysis with PS standards, which makes them suitable as calibration standards. Calibration curve with good

linearity ($r = -0.9996$) was obtained with polyether polyols as calibration standards. The MWs of commercial polyether polyols obtained with GPC calibrated against polyether polyols were closer to the theoretical values than the MWs obtained via GPC calibrated against PS standards. Therefore, the results indicate that GPC with polyether polyols calibration offers a more reliable determination of MWs of polyether polyols compared to the conventional PS standards. The use of polyether polyols as calibration standards in GPC analysis could be extended to the MWs determination of natural oil-based polyols, e.g., palm oil-based polyols, which is the subject of our ongoing study.

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REFERENCES

- Oertel, G. *Polyurethane Handbook*; Hanser: Munich, Germany, **1985**.
- Saunders, J. H.; Kurt, C. F. *Polyurethanes: Chemistry and Technology*; Interscience Publisher: New York, **1962**.
- Ionescu, M. *Chemistry and Technology of Polyols for Polyurethanes*; Rapra Technology Limited: Shawbury, UK, **2005**.
- Herrington, R.; Hock, K. *Flexible Polyurethane Foams*; Dow Chemical Company: Midland, **1997**.
- 2014 End-Use Market Survey for Polyurethanes Industry in the United States, Canada and Mexico; American Chemistry Council: Washington, **2015**.
- Kostanski, L. K.; Keller, D. M.; Hamielec, A. E. *J. Biochem. Biophys. Methods* **2004**, *58*, 159.
- Styring, M. G.; Hamielec, A. E.; *Determination of Molecular Weight*; Cooper, R. Ed.; Wiley: New York, **1989**; p 263.
- Sommers, C. D.; Ye, H.; Kolinski, R. E.; Nasr, M.; Buhse, L. E.; Al-Hakim, A.; Keire, D. A. *Anal. Bioanal. Chem.* **2011**, *401*, 2445.
- Beirne, J.; Truchan, H.; Rao, L. *Anal. Bioanal. Chem.* **2011**, *399*, 717.
- Holding, S. *Chromatogr. Today* **2011**, *4*, 4.
- Ionescu, M.; Sinharoy, S.; Petrović, Z. S. *J. Polym. Environ.* **2009**, *17*, 123.
- Ionescu, M.; Petrović, Z. S.; Wan, X. *J. Polym. Environ.* **2007**, *15*, 237.
- Petrović, Z. S.; Wan, X.; Bilic, O.; Zlatanić, A.; Hong, J.; Javni, I.; Ionescu, M.; Milić, J.; Degruson, D. *J. Am. Oil Chem. Soc.* **2013**, *90*, 1073.
- Ionescu, M.; Petrović, Z. S. *J. Cell. Plast.* **2010**, *46*, 223.

15. Petrović, Z. S.; Cvetković, I.; Hong, D. P.; Wan, X.; Zhang, W.; Abraham, T. W.; Malsam, J. *Eur. J. Lipid Sci. Technol.* **2010**, *112*, 97.
16. Ionescu, M.; Ji, Y.; Shirley, W. M.; Petrović, Z. S.; In Renewable and Sustainable Polymers; Payne, G., Smith, P., Eds.; ACS Symposium Series 1063; American Chemical Society: Washington, DC, **2011**, p 73.
17. Petrović, Z. S.; Cvetković, I. *Contemporary Mater.* **2012**, III-1, 63.
18. Ionescu, M.; Wan, X.; Bilić, N.; Petrović, Z. S. *J. Polym. Environ.* **2012**, *20*, 647.
19. Petrović, Z. S.; Cvetković, I.; Milić, J.; Hong, D. P.; Javni, I. *J. Appl. Polym. Sci.* **2012**, *125*, 2920.
20. Luo, Q.; Liu, M.; Xu, Y.; Ionescu, M.; Petrović, Z. S. *Macromolecules* **2011**, *44*, 7149.
21. Hong, J.; Luo, Q.; Wan, X.; Petrović, Z. S.; Shah, B. K. *Bio-macromolecules* **2012**, *13*, 261.
22. Pawlik, H.; Prociak, A. *J. Polym. Environ.* **2012**, *20*, 438.
23. Dworakowska, S.; Bogdal, D.; Prociak, A. *Polymers* **2012**, *4*, 1462.
24. Sabani, S.; Onen, A. H.; Gungor, A. *J. Coat. Technol. Res.* **2012**, *9*, 703.
25. Bagdi, K. Role of Interactions on the Structure and Properties of Segmented Polyurethane Elastomers. Ph.D. Thesis, Budapest University of Technology and Economics: Budapest, Hungary, **2010**.
26. Lorenz, K.; Hofmann, J.; Zwick, H.; Steinlein, C.; Browne, E. US 20140142344 A1, **2014**.
27. John, J.; Bhattacharya, M.; Turner, R. B. *J. Appl. Polym. Sci.* **2002**, *86*, 3097.
28. Mateos, E.; Cebolla, V. L.; Membrado, L.; Piera, E.; Caballero, M. A. *J. Chromatogr. Sci.* **2007**, *45*, 524.
29. Khoon, P. A.; Choy, S. L.; Sit, F. C.; Cheng, H. C. *J. Appl. Polym. Sci.* **2014**, *131*, 39967.
30. Fan, W.; Fan, X.; Tian, W.; Zhu, X.; Zhang, W. *Polym. Test.* **2014**, *40*, 116.
31. Caillol, S.; Desroches, M.; Boutevin, G.; Loubat, C.; Auvergne, R.; Boutevin, B. *Eur. J. Lipid Sci. Technol.* **2012**, *114*, 1447.
32. Shutov, P. L.; Jimenez, J.; Van Der, W. H. R.; Casati, F. WO2011137011 A1, **2011**.
33. Shutov, P. L.; Van Der, W. H. R.; Masy, J.; Babb, D. A. U.S. Patent 20140018459, **2014**.
34. Yau, W. W.; Kirkland, J. J.; Bly, D. D. In Modern Size-Exclusion Liquid Chromatography; Wiley-Interscience: New York, **1979**.
35. Dow Polyurethanes—Flexible Foams, 2nd ed. Herrington, R., Eds.; DOW Chemical Company: Midland, **1997**.
36. Barksby, N.; Allen, G. L. In Low Monol Polyols and Their Effects in Urethane Systems, Proceedings of the Polyurethane World Congress, Vancouver, Canada, October 10–13, 1993; Technomic: Lancaster, **1993**.
37. Smith, C. P.; Reisch, J. W.; O'Conner, J. M. In Thermoplastic Polyurethane Elastomer Made from High Molecular Weight POLY-L Polyols, Proceedings of the Polyurethane World Congress, Nice, France, September 24–26, 1991; Technomic: Lancaster, **1991**.
38. Reisch, J. W.; Capone, D. M. In Polyurethane Sealants and Cast Elastomers with Superior Physical Properties, Proceedings of the Polyurethane World Congress, Orlando, U. S., September 30–October 3, 1990; Technomic: Lancaster, **1990**.