



Quantitative NMR Analysis of PTMEG compounds

Gilhoon Kim, Hoshik Won*

Department of Applied Chemistry, Hanyang University, 55, Hanyang Daehak-Ro, Sangrok-Gu, Ansan 426-791, Korea

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Abstract PTMEG(Polytetramethylene ether glycol) is a polymer compound widely used as a wide range of applications in the textile industry. PTMEG substance carrying various 1,800~2,000 molecular weight are mainly used as the raw material of the spandex production.

Molecular weight and degree of polymerization value for 4 different PTMEG samples under pilot plant scale synthetic process were determined by a new quantitative NMR method. In NMR experiments, *p*-toluenesulfonic acid(TSOH) was used for external standard material of PTMEG quantitative analysis. We were measuring The concentration of the primary standard TSOH was measured by UV/Vis spectroscopy. By using NMR peak assignments and the integral values of designated proton NMR peaks, We were able to measure the % composition of the synthetic PTMEG polymers, concentrations, molecular weight and the degree of polymerization that show the synthetic process of each manufacturing pilot plant. By utilizing a newly developed quantitative NMR method were able to obtain the molecular weight of PTMEG samples within 0.08 error % range.

Keywords. PTMEG, NMR, Quantitative analysis, Degree of polymerization

Introduction

Nuclear magnetic resonance(NMR) spectroscopy techniques provide various high performance analytical tools for quantitative analysis as well as the structure determination of molecules. Molecular structure determination is usually made on the basis of the geometrical information from coupling constant(J) and interatomic distance information from nuclear overhauser effects(NOE).¹ ¹H-NMR spectroscopy as an analytical tool for quantitative analysis was first reported by Jungnickel and Forbes² in 1963. In the past three decades, there has been growing interest in quantitative NMR for the absolute quantitation of active drugs and their purity in various formulations.³ One of the major advantages of quantitative NMR analysis is that it can be applied in the quantitative estimation of purity of compounds without using any specific reference standard. We developed a new quantitative NMR method providing the determination of the concentration out of mixture compounds, and of the degree of polymerization by using peak integration in combination with external standards in this study.

Polytetramethylene ether glycol (PTMEG) also called polytetrahydrofuran, is a chemical compound with formula HO-(-(CH₂)₄O)-_n-H, linear form polyether glycol carrying the hydroxyl(OH) end groups. Polytetrahydrofuran is commonly prepared by ac-

* Address correspondence to: Hoshik Won, Department of Applied Chemistry, Hanyang University ERICA, 55, Hanyang Deahak-Ro, Sangrok-Gu, Ansan, 426-791, Korea, Tel : 031-400-5497, E-mail: hswon@hanyang.ac.kr

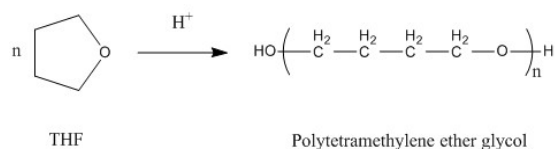


Figure 1. Synthetic process of polytetramethylene ether glycol (PTMEG)

acid-catalyzed ring opening polymerization of tetrahydrofuran as shown in Figure 1.

Synthetic PTMEG is widely used as a raw material in the textile industry applications depending on its molecular weight. PTMEGs are commercially available as polymers of low average molecular weights in the range of 250 and 3000 daltons. PTMEG having the average molecular weight of 1,800~2,000 daltons is mainly used as the raw material of the spandex. So, there are many attempts to macroscale synthesis in industry. Other PTMEGs with different molecular weight are widely used in the production of the elastomeric copolymer such as polyurethane production. PTMEGs for spandex material were obtained by using the synthetic process because sale product is expensive.

In this study, we designed a new NMR quantitative NMR method measuring molecular weight and degree of polymerization value of 4 synthetic PTMEG polymer samples for the material of spandex. By using the chemical shift and the integration value of the ^1H -NMR spectrums in combination with external standard *p*-toluenesulfonic acid. Systematic approach was developed for the determination of molecular weight, and for the degree of polymerization of PTMEG with quantitative assessments.

Experimental Methods

Materials- 4 different synthetic raw PTMEG polymer materials used for commercial spandex synthesis were supplied from H-company. The standard PTMEG (m.w:2,000) sample for comparison were purchased from Sigma Aldrich.

In NMR quantitative analysis of synthetic PTMEG, *p*-toluenesulfonic acid (TSOH) is used as a primary

external standard material, and the concentration of this TSOH was determined by using UV-Vis spectroscopy. NMR solvents were purchased from Cambridge isotope laboratory.

UV-Vis Spectroscopic measurements- Concentration of TSOH standard solution was measured by measuring absorbance with UV-Vis spectroscopy.

UV-Vis spectra were measured in 220nm-400nm wavelength range by utilizing SINCO UV-Vis spectrometer. Beer-Lambert law was used for calculate the concentration of the standard materials.

T_1 relaxation time measurement- To measure T_1 of PTMEG sample, a 180° pulse($28\mu\text{s}$) is first applied to the sample so that the *z*-component of the total magnetization vector is rotated onto the *xy*-plane, which induces a free induction decay. Then another 90° pulse($14\mu\text{s}$) is applied after a certain time τ to again rotate the magnetization that decayed back to the *z*-axis into the *xy*-plane, where the precession of the magnetic moment becomes measurable. The 90° pulse can be repeated in series to obtain a clear signal.⁵ 10 array experiments starting with initial τ ($0.0625\mu\text{s}$) and final τ (32s) with $0.6931\mu\text{s}$ increment were carried out.

^1H NMR experiment- All homo-nuclear ^1H -NMR measurements were obtained by using Varian 500Mhz FT-NMR spectrometer. NMR spectral data were collected with following conditions: TSOH in D_2O , $T=25^\circ\text{C}$, external reference sample was prepared each in $100\mu\text{l}$ 3mm external tube.

PTMEG samples were dissolved in CDCl_3 $500\mu\text{l}$ in 5mm NMR tube. ^1H -NMR chemical shifts were referenced to internal CDCl_3 (7.24ppm), and water peak was suppressed by presaturation. The NMR data were processed and analyzed by using VNMR, NMR Pipe software and visualized using NMRViewJ for windows.

Results

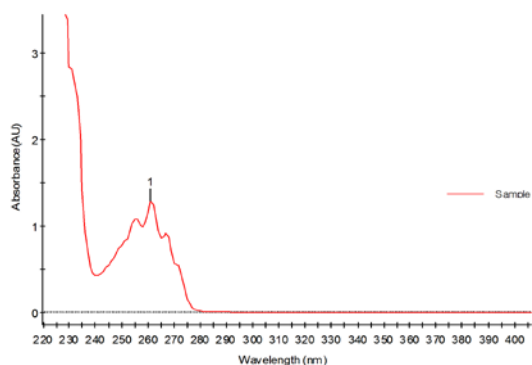


Figure 2. UV-Vis absorption spectra of TSOH

UV-Vis Analysis & Calculating Concentrations- In spectra, characteristic absorption peaks of the TSOH at 261.2nm ($\lambda_{\max}=1.2968\text{AU}$) due to the attribution of $\pi \rightarrow \pi^*$ transition from the conjugation of aromatic ring as shown in Figure 2. By applying the Beer-Lambert law (path length = 1cm), the concentration of TSOH was calculate to 22.15mM.

Measurement of T_1 relaxation- Most of polymer such as PTMEG has different hydrogen nuclei relaxation time because of location within the long-chain and terminal chains. Thus, sufficiently given d_1 relaxation time can reduce the experimental error.

Macroscopic magnetization is sum of each spinmagnetic field, so high-quality spectrum can be obtained

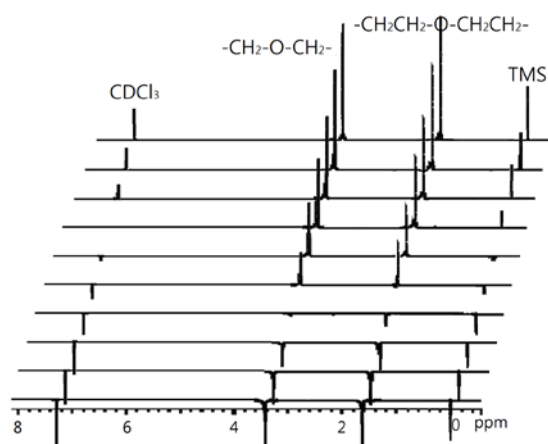


Figure 3. T_1 measurement stack plot of PTMEG standard sample (array size:10, first value:0.0625 μs , last value:32s, increment:0.6931 μs)

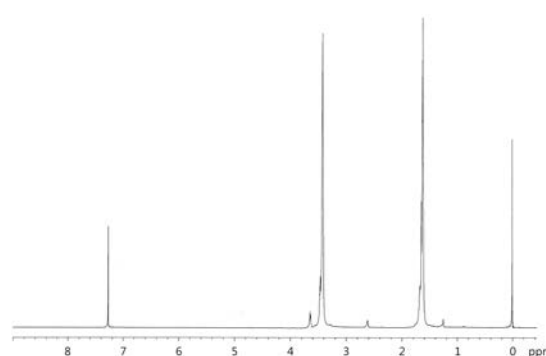


Figure 4. $^1\text{H-NMR}$ spectrum of standard PTMEG sample

when sufficient relaxation delay d_1 is equal to or greater than the $5T_1$. In τ array experiment (inversion recovery experiment), T_1 time measurement of standard PTMEG sample was measured to be 20sec as shown in Figure 3. All subsequent experiments in the $d_1 \geq 5T_1$ 120s were performed.

$^1\text{H-NMR}$ spectra assignment- $^1\text{H-NMR}$ spectrum of standard PTMEG is shown in Figure 4, and summarized in Table 1, respectively. The chemical shifts of terminal OH at 2.65ppm, terminal methylene CH_2 at 3.65ppm, CH_2 near oxygen in long-chain at 3.45ppm, normal methylene at 1.65ppm were observed, respectively.

Table 1. Structure and $^1\text{H-NMR}$ chemical shift of PTMEG

Component	Chemical structure	Chemical Shift (ppm)
THF	$-\text{CH}_2-\text{O}-\text{CH}_2-$	3.75 (CH_2 near Oxygen)
	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-$	1.9 (Methylene)
PTMEG	$-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$	3.65 (Terminal CH_2)
	$-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$	3.45 (CH_2 near Oxygen)
	$-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$	2.65 (Terminal OH)
	$-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$	1.65 (Methylene)
n-Octane	$-\text{CH}_2-\text{CH}_2-$	1.3 (Methylene)
	$-\text{CH}_2-\text{CH}_3$	0.9 (Terminal methyl)

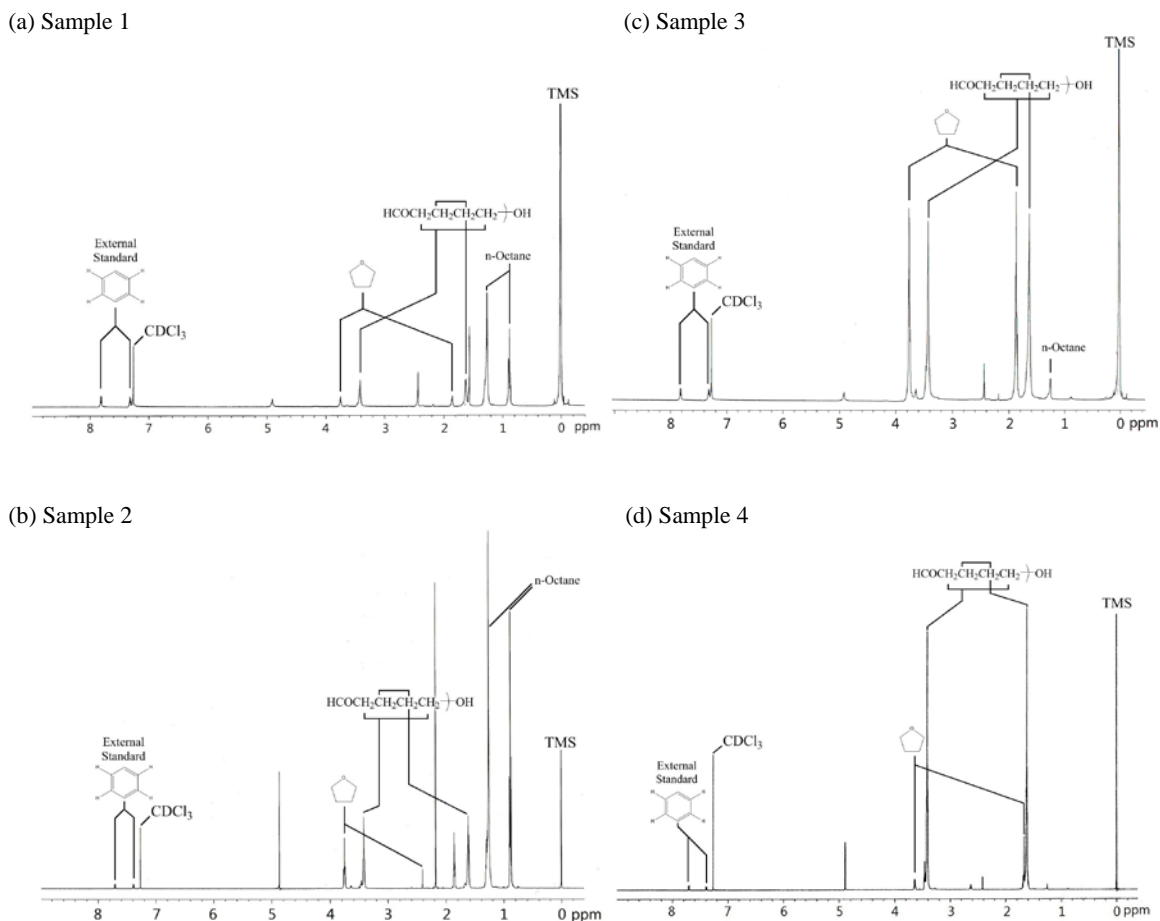


Figure 5. $^1\text{H-NMR}$ spectrum of synthetic PTMEG samples and external standard TSOH

As shown in Figure 5, all samples included NMR peaks originated from PTMEG, THF, n-Octane, and external standard TSOH are summarized in Table 2.

Table 2. Integral values of synthetic PTMEG samples

Name	PTMEG	THF	n-Octane
Sample1	3.59	0.98 0.99	15.49 7.01
Sample2	23.59	1.00 0.94	108.60 53.55
Sample3	29.49	21.78 22.66	35.40 2.32
Sample4	23.74	1.00	27.42

Calculating the % component of synthetic PTMEG- By using the integral value from $^1\text{H-NMR}$ spectrum can be determined the composition of each % PTMEG compound. The integrated value is proportional to the concentration of the TSOH standard material. Thus, the concentration of each component can be obtained by comparison with that of standard. In the case of sample 1, integral value of 3.75ppm (CH_2 near Oxygen) and 1.83ppm(CH_2) of THF and 3.45 ppm(CH_2 near Oxygen) PTMEG, 0.9ppm(CH_3) and 1.3ppm(CH_2) of n-Octane were substitute to calculate the concentration shown in Table 3.

In the same way, the analysis of % composition by using the integration value of the other samples were obtained and summarized in Table 4.

Table 3. Calculation and result of Sample 1.

Sample 1	Conc. of TSOH	Integral Value	M	mole
THF	22.16 mM	1.97	0.04365	2.1827×10^{-5}
PTMEG		7.18	0.15910	7.9554×10^{-5}
n-Octane		20.16	0.44681	2.2341×10^{-4}

* Concentration

1: 22.16mM = (0.98+0.99) : [THF] → 0.04365 M

1: 22.16mM = (3.59 × 2) : [PTMEG] → 0.15910 M

1: 22.16mM = 15.49+(7.01/3×2) : [n-Octane] → 0.44681 M

* Number of moles

0.04365 M : 1L = x : 500 μ l → 2.1827×10^{-5} mole(THF)

0.15910 M : 1L = y : 500 μ l → 7.9554×10^{-5} mole(PTMEG)

0.44681 M : 1L = z : 500 μ l → 2.2341×10^{-4} mole(n-Octane)

* % composition

$(2.1827 \times 10^{-5} / 3.2479 \times 10^{-4}) \times 100 = 6.72\% \rightarrow$ % of THF

$(7.9554 \times 10^{-5} / 3.2479 \times 10^{-4}) \times 100 = 24.49\% \rightarrow$ % of PTMEG

$(2.2341 \times 10^{-4} / 3.2479 \times 10^{-4}) \times 100 = 68.79\% \rightarrow$ % of n-Octane

Table 4. % Composition of synthetic PTMEG samples.

Name	PTMEG	THF	n-Octane
Sample 1	24.49%	6.72%	68.79%
Sample 2	23.66%	12.84%	63.41%
Sample 3	55.24%	42.59%	-
Sample 4	99.96%	-	-

Determination the degree of polymerization and molecular weight- The degree of polymerization was determined by obtaining iterative number(n) of monomer and the molecular weight was also determined by using the chemical shift and the integrated value of NMR peaks originated from PTMEG polymer. Integrals of HOCH₂-(-CH₂-O-CH₂-) peak (number of H) and monomer repeating unit n value has a definite correlation. This correlation may be gathered from the structure of the PTMEG. During the processing, the value of the terminal CH₂-peak (HOCH₂-) in 3.65 ppm were fixed to 1 as reference to obtain a integral value of the peak CH₂-(-CH₂OCH₂-) in 3.45 ppm within the inner chain. So repeating unit of monomer is given to following rela-

tionship.

$$n = \text{Integral value of } (-\text{CH}_2\text{-O-CH}_2\text{-}) \text{ peak} + 1$$

Since the molecular weight of the PTMEG monomer is give to 72, so the molecular weight can be obtained by substituting the n value from the following formula,

$$\text{Molecular weight of PTMEG} = (n \text{ value} \times 72) + 18$$

where 72 is the molecular weight of the repeating unit, 18 is the molecular weight of the part that is not repeated in the molecular structure(sum of the terminal CH and O). Monomer repeat unit n value and molecular weight of sample and error rate from comparison with Aldrich PTMEG standard sample were summarized in Table 5.

Table 5. Degree of polymerization and molecular weight of synthetic PTMEG samples

Name	n value	Molecular Weight	Error rate
PTMEG (Aldrich)	27.40	1990.80	0.46% (M.w : 2,000)
Sample 1	24.50	1782.00	1.00% (M.w : 1,800)
Sample 2	24.59	1788.48	0.64 (M.w : 1,800)
Sample 3	24.49	1781.28	1.04% (M.w : 1,800)
Sample 4	24.73	1798.56	0.08% (M.w : 1,800)

Discussion

By using NMR peak assignment, integration for designated peaks of PTMEG and external standard TSOH, we were able to provide new quantitative NMR method. In this study, % composition and degree of polymerization value of the synthetic PTMEG samples were determined from external standard TSOH integral value. The repeating unit of monomer was 25, and molecular weight error rate of PTMEG polymer was observed at least 0.08% (Sam-

ple 4) from maximum 1.04% (Sample 3). The new quantitative analysis of commercial polymer synthesis. NMR method can be applied for studying the quanti-

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