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High-Performance Liquid Chromatography of Poly(tetramethylene ether) Glycols

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ABSTRACT: A high-performance liquid chromatographic method for the analysis of poly(tetramethylene ether) glycols has been developed. In contrast to gel permeation chromatography, the new technique allows efficient separation of these polyethers into individual oligomers and thus affords more information about the polymer. Liquid chromatograms are compared with gel permeation chromatograms, and the advantages and limitations of the new technique are discussed.

Introduction

The most important criteria that physically characterize a linear polymer are molecular weight and molecular weight distribution. Number-average molecular weight M_n of poly(tetramethylene ether) glycol (PTMEG) is most accurately determined by titration (acetic anhydride or phthalic anhydride method)[3] or by spectroscopic methods (calibrated IR scans, end-group determination by NMR, etc.).[4] Weight-average molecular weight M_w and polydispersity M_w/M_n are less easily determined, and the latter is frequently approximated by an empirical viscosity ratio M_{wv}/M_n, determined from polymer bulk viscosity at a specified temperature.[5]

The weight-average molecular weight M_w is usually measured by gel permeation chromatography (GPC), which partially fractionates the polymer sample by retaining the shorter chains longer in the porous column packing and allowing the longer chains to pass through the column faster. The resulting chromatogram is a plot of polymer concentration in the eluant vs. elution time, with the highest molecular weight fractions recorded first. After calibration with samples of known molecular weights, GPC elution time can be converted to molecular weight and is generally plotted on a log scale. Figure 1 shows typical GPC scans of commercial poly(tetramethylene ether) glycols of number-average molecular weights 1000 and 2000. The weight-average molecular weights of these samples, calculated from the GPC data, were 1720 and 3420, respectively.

The newer, high-efficiency μ-Styragel column packings improve fractionation to a point where the individual oligomer fractions are partially separated, particulalrly when several columns are used in series (Figure 2). Complete separation of some fractions on a vinyl acetate gel has been described[6] and separation of all fractions can, in principle, be achieved by GPC using extremely long columns and consequently long elution times.[7] However, we were looking for a more efficient method of separating PTMEG into its individual oligomers, on both an analytical and a preparative scale.

Adsorption chromatography on silica gel columns had been tried earlier, and although some molecular weight

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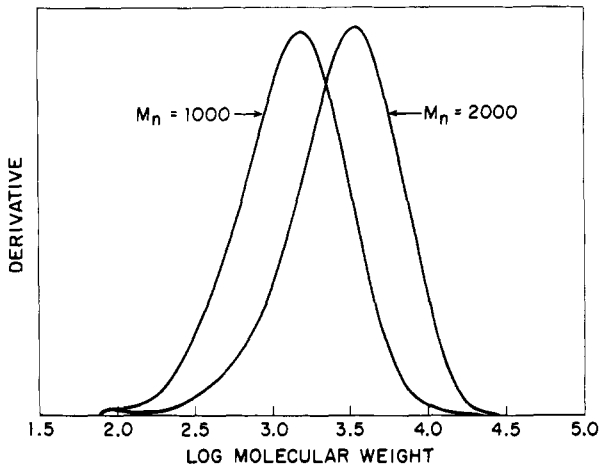


Figure 1. Gel permeation chromatograms of poly(tetramethylene ether) glycols of molecular weights M_n = 1000 and 2000.

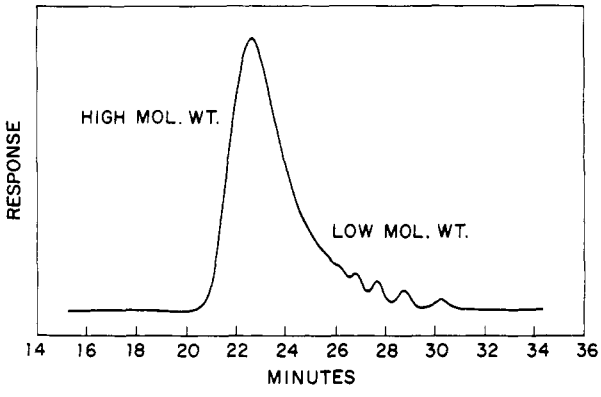


Figure 2. Size exclusion chromatogram of a poly(tetramethylene ether) glycol of molecular weight M_n = 850.

fractionation was observed, no separation of individual fractions was achieved.[8] High-performance liquid chromatography (HPLC) seemed to be the method of choice since good separation of molecular weight fractions had been obtained with other types of polymers.[9] After some initial problems, a method has now been defined that separates poly(tetramethylene ethers) quantitatively into individual oligomers on a single short HPLC column.

This paper describes the results obtained by this new technique, which may be applicable to a wide variety of other polyethers.[10]

Experimental Section

Dry tetrahydrofuran stored over metallic sodium was used as the monomer. Trifluoromethanesulfonic acid was distilled under N_2 at atmospheric pressure prior to use (bp 160 °C). All other reagents or solvents are commerically available in reagent grade and were used without further purification.

Poly(tetramethylene ethers) were prepared by mixing THF (100 g) with CF_3SO_3H (1.5 g) and $(CH_3CO)_2O$ (8 g) in a polymerization flask equipped with a mechanical stirrer, nitrogen inlet, and thermometer. After 3 h at 50 °C under dry N_2, the polymerization was quenched with H_2O and the strong acid initiator removed by passing the solution over a column of basic ion exchange resin Amberlite IRA-68. After hydrolysis of the acetate end groups in excess methanol, the solvent was removed by distillation, and the polymer was dried for 2 h at 120 °C (1 mm): yield 48 g; M_n = 1060.

Commercial poly(tetramethylene ethers) were samples of Teracol Polyether Glycol (Du Pont).

The phenylurethane derivatives of the polyether glycols were prepared by dissolving 2 g of the PTMEG in 4 g of THF and adding a stoichiometric amount + 20% excess of phenyl isocyanate. The sample was thoroughly mixed and 1 drop of dibutyltin dilaurate catalyst was added. The sample mixture was subsequently kept at 65 °C for 1 h. Unreacted phenyl isocyanate was destroyed by addition of MeOH and the sample was finally dried at 10 mm in a rotating evaporator on a steam bath.

For HPLC, the PTMEG diurethane was dissolved in MeOH, and a 0.5% solution in MeOH/H_2O (85/15) was prepared. Fifty microliters of this solution was injected into a Du Pont Model 850 liquid chromatograph equipped with a 25-cm Zorbax C8 column. Operating conditions were as follows: column temperature, 35 °C; column pressure, 12 bar; flow rate, 2 mL/min; carrier A, 85% CH_3OH, 15% H_2O; carrier B, 100% CH_3OH; linear gradient, 0–50% B in 15 min, 50–100% B in 50 min; detector, UV (230 nm). Base lines and peak areas were calculated on the Du Pont PDP-10 ATS system.

Formation of double peaks in the chromatogram indicates the presence of mono- and diurethanes, i.e., incomplete reaction with phenyl isocyanate. In this case, more reagent or longer reaction times have to be used to ensure complete conversion.

Gas chromatograms were obtained on a Varian Aerograph Series 2700 model with flame ionization detectors. Sixty-centimeter columns packed with 10% SE-30 on Chromosorb W-HP were used. Injection port and detector temperatures were maintained at 280 °C. Column temperature was programmed at 20 °C/min from 100 to 275 °C and maintained at 275 °C as described earlier.[11] The internal standard was 2,6-di-*tert*-butyl-4-methylphenol (BHT). Samples of PTMEG in MeOH were injected directly into the glass-lined injection port.

Gel permeation chromatograms were obtained on a Waters Associates Model 6000, equipped with a Model 401 refractive index detector. The most suitable columns were found to be μ-Styragel 100-Å columns. For the size exclusion chromatogram (Figure 2), four 100-Å columns and two 500-Å columns were used in series. THF was used as the solvent and the column was calibrated with PTMEG samples of known molecular weight.

Results and Discussion

Fractionation of polymers by HPLC has been used successfully for some time, and we tried to adopt this method to the analysis of poly(tetramethylene ether) glycols. An isocratic technique gave encouraging initial results, but it soon became clear that elution with a solvent gradient system would be necessary in order to elute the high molecular weight fractions in a reasonable time.

In a solvent gradient technique, however, the usual refractive index detector responds not only to polymer concentrations but also to solvent changes. A UV detector was therefore chosen as a suitable detector that would not respond to compositional changes of UV-transparent solvent systems. Since PTMEG is also UV transparent, UV-detectable end groups have to be attached, e.g., benzoates or carbamates. Reaction of phenyl isocyanate to form carbamates was selected because of the simplicity of the procedure and because the product workup does not require a washing step, which might change the polymer distribution by partial extraction of the more hydrophilic oligomers. The PTMEG dicarbamates (bis(phenylurethanes)) are soluble in methanol, but have very low solubility in water, and by a suitable choice of a solvent gradient, the individual polymer fractions can be separated into a pattern of nearly equidistant oligomer peaks on a very short (25 cm) column. This is illustrated in Figure 3, which is a reverse-phase HPLC scan of the diurethane of a PTMEG of molecular weight 1060, obtained by polymerization of THF with a $CF_3SO_3H/(CH_3CO)_2O$ catalyst system. In such a system, the carboxylic anhydride participates in the initiation step[12] and thus acts as a molecular weight controlling agent. In its absence, only very long chains and macrocyclic oligomers are normally obtained.[13] Acetic anhydride also acts as a chain-transfer agent, as shown in Scheme I. Termination occurs by acetic acid attack on the oxonium ion with regeneration of the strong acid initiator. After hydrolysis, the PTMEG glycols

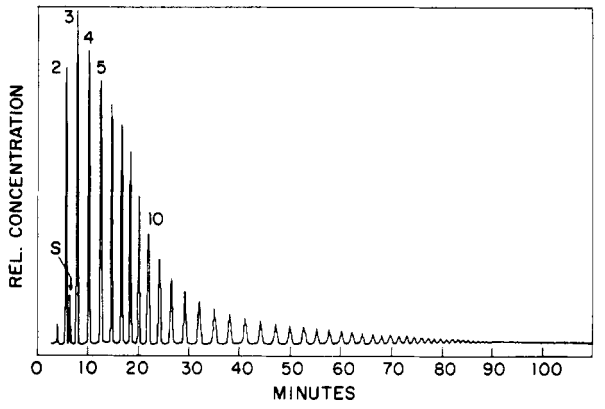
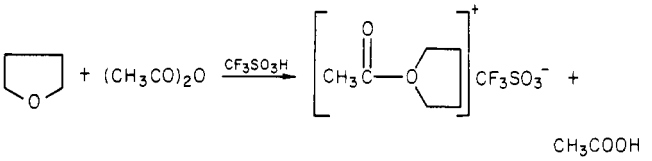


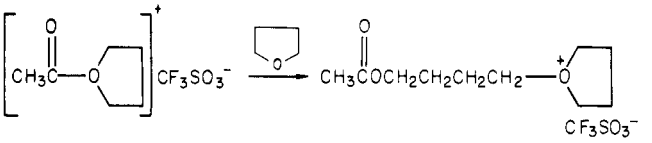
Figure 3. High-performance liquid chromatogram of a poly(tetramethylene ether) glycol dicarbamate of molecular weight M_n = 1060 and M_w = 1910. S indicates the elution time standard and 2, 3, 4, etc. are the degrees of polymerization.

Scheme I

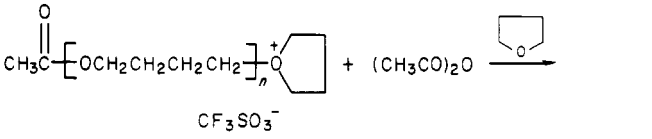
Initiation

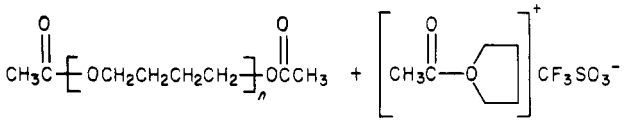


Propagation

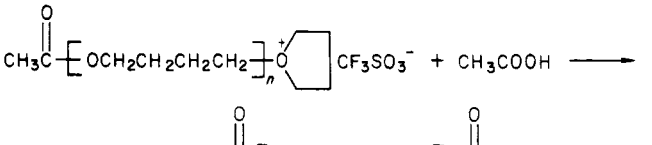


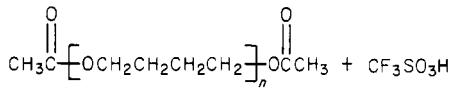
Chain Transfer



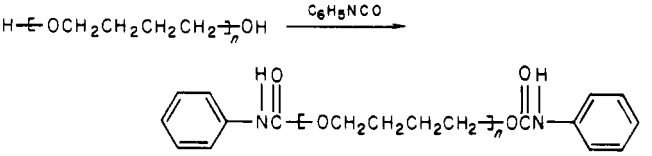


Termination





were converted to the corresponding dicarbamates for liquid chromatography:



In contrast to gel permeation or size exclusion methods where the high molecular weight fractions reach the detector first, low molecular weight oligomers are eluted from the HPLC column first. This provided a convenient way to identify the individual fractions in Figure 3 by comparing the HPLC scans of low molecular weight oligomers

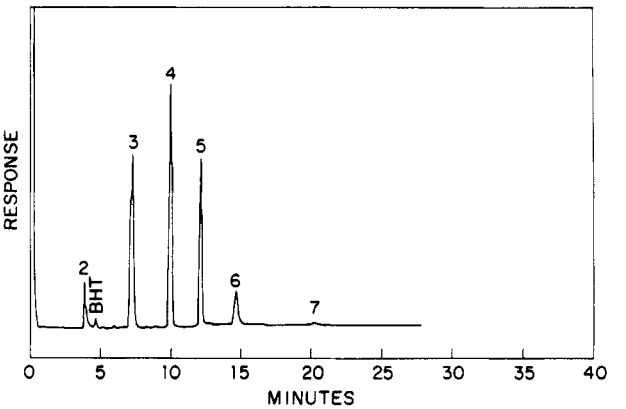


Figure 4. Gas chromatogram of a water-soluble fraction of poly(tetramethylene ether) glycol, M_n = 300.

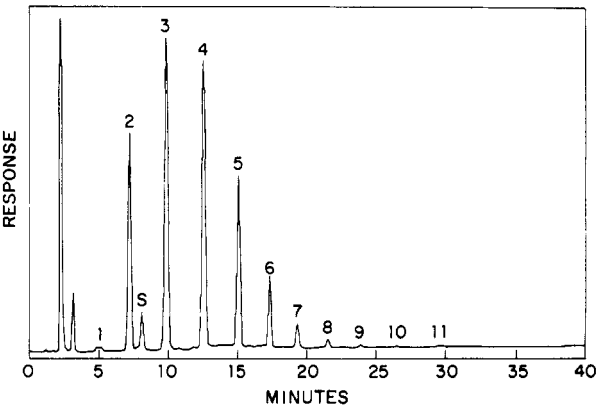


Figure 5. High-performance liquid chromatogram of the water-soluble PTMEG fraction (M_n = 300) shown in Figure 4. S is the elution time standard.

Table I
Oligomer Ratios in a Water-Soluble PTMEG Fraction[a]

oligomer	GC areas	HPLC areas
2 (dimer)	10.0	10.0
3	50.0	17.0
4	56.8	17.9
5	34.3	10.1
6	13.2	4.8
7	1.6	1.1
8		0.4
9		0.2
10		0.1

[a] Areas normalized for the dimer.

with the corresponding GC peaks that had been identified earlier by chemical ionization mass spectroscopy.[11]

In Figure 4, a gas chromatogram of the water-soluble fraction extracted from a PTMEG of molecular weight 650 is shown. The lowest oligomer peak is the dimer and the highest, obtained after a 30-min run, is the heptamer, as confirmed by mass spectroscopy. The corresponding HPLC scan is shown in Figure 5. The lowest major oligomer peak is again the dimer, although a small concentration of monomer (butanediol) is also visible. There are more long-chain oligomers detected by HPLC than by GC. The highest oligomer found was the undecamer, clearly visible at higher detector sensitivity.

The first two peaks in Figure 5 are phenyl isocyanate side products, phenylmethylurethane and triphenyl isocyanurate. The peak labeled S (elution time standard) is due to triphenylbiuret. Di-*tert*-butylhydroxytoluene (BHT), the internal standard in the gas chromatograms, is eluted with the octamer under these HPLC conditions.

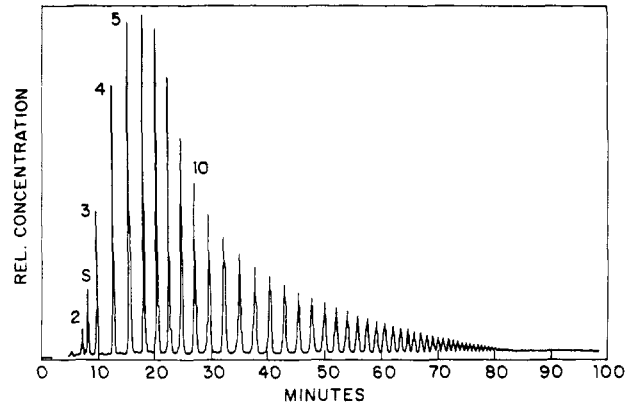


Figure 6. High-performance liquid chromatogram of a commercial poly(tetramethylene ether) glycol of molecular weight M_n = 1000. S is the elution time standard and 2, 3, 4, etc. are the degrees of polymerization.

The relative retention times of the bis(phenylurethanes) of butanediol and butanediol dimer were known from HPLC scans of the pure compounds, and the molecular weight and degrees of polymerization of all the polymer fractions could thus be assigned. The normalized concentrations of the oligomers in terms of peak areas are given in Table I.

The areas or area ratios (detector response) in both types of chromatograms show a similar trend, but the data are not directly comparable since in one case (HPLC) we measure end groups of a PTMEG derivative and the response is proportional to the number of chains and in the other case (GC) we measure an ionization current that is proportional to the weight of the chains and a changing response factor. (Fractions 8–11 were not recorded by GC because of very long retention times.)

In contrast to gel permeation chromatography, no calibration samples are necessary in this HPLC technique, and molecular weight and molecular weight distribution of the polymer can be calculated directly from the peak areas. The molecular weight of the low molecular weight oligomer fraction shown in Figure 5 and Table I was thus calculated to be 293. The molecular weight obtained by NMR spectroscopy of the diacetate was found to be 285, in very good agreement.

The number-average molecular weight of the polymer shown in Figure 3, calculated from HPLC data, was M_n = 1060, in excellent agreement with the molecular weight obtained by titration. The weight-average molecular weight was M_w = 1910 and the polydispersity therefore M_w/M_n = 1.80.

The relative concentrations of the different oligomers further allow conclusions about the polymerization mechanism. The fact that dimer is present in lower concentration than expected (Figure 3) indicates that a dimer complex may actually be involved in the initiation step, similar to the one proposed for initiation by CF_3SO_3H alone.[13]

In contrast to the PTMEG sample discussed above, a chromatogram of a commercial PTMEG of molecular weight 1000 is shown in Figure 6. Chains up to a degree of polymerization of 66, which corresponds to a PTMEG molecular weight of 4770, are separated into individual peaks. The predominant oligomer in terms of numbers of molecules is the pentamer, corresponding to a molecular weight of 378. The predominant oligomer in terms of weight is the decamer, corresponding to a molecular weight of 728. The number-average molecular weight of this sample calculated from HPLC data is 992. The molecular weight obtained by end-group titration is 1010, in good agreement. The calculated weight-average molecular weight of this sample was 1669, the z-average molecular weight was 1977, and the corresponding ratios were therefore M_w/M_n = 1.68 and M_z/M_n = 1.99.

Conclusions

Liquid chromatography is an excellent method to study the polydispersity of poly(tetramethylene ethers) and, with slight modifications, may be applicable to other polyethers as well. It is particularly useful to study the lower molecular weight fractions, whereas gel permeation chromatography is better suited for the higher fractions. Both methods thus complement each other, although HPLC, where applicable, affords more information about sample composition and may allow conclusions about the polymerization mechanism.

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