

DETERMINATION OF THE STRUCTURE OF SIMPLE POLYETHER PROPYLENE OXIDE

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Abstract

Polyether polyols based on propylene oxide are widely used in the production of polyurethanes, surfactants, and functional fluids due to their tunable molecular architecture and versatile reactivity. Understanding the precise molecular structure — including molecular weight, end-group composition, sequence distribution, and degree of polymerization — is essential for controlling material properties and performance. This study presents a comprehensive structural characterization of simple polyether polyols derived from propylene oxide using a multi-technique analytical approach. Nuclear Magnetic Resonance spectroscopy (¹H and ¹³C NMR) was employed to determine monomer sequence, identify terminal hydroxyl and initiator-derived end groups, and quantify the degree of polymerization and stereochemical distribution (isotactic/syndiotactic). Gel Permeation Chromatography (GPC) provided data on molecular weight distribution and polydispersity index, confirming narrow dispersity ($\bar{M}_w/\bar{M}_n \approx 1.05–1.15$) in well-controlled systems. Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS) enabled precise identification of individual oligomeric series and end-group fidelity, distinguishing between primary and secondary hydroxyl termini resulting from regioselective ring-opening polymerization. The results confirm that anionic polymerization of propylene oxide, initiated by diols or glycerol, yields predominantly atactic polymers with secondary hydroxyl end groups, while cationic initiation favors chain transfer, leading to broader dispersity and structural heterogeneity. The integration of these techniques allows for a complete structural assignment of simple polyether chains, providing a foundation for structure–property relationships in downstream applications. This work supports the rational design of polyether-based materials with tailored functionality and performance.

Keywords: polyether, propylene oxide, polymer structure, NMR spectroscopy, MALDI-TOF MS, GPC, polyol, ring-opening polymerization, polyurethane, end-group analysis

I. Introduction

Polyethers derived from the ring-opening polymerization (ROP) of propylene oxide are among the most industrially significant classes of synthetic polymers. Due to their flexible aliphatic backbone, hydrophilic character, and terminal hydroxyl functionality, they serve as essential building blocks in the production of polyurethanes, surfactants, lubricants, and functional fluids. In particular, polyether polyols based on propylene oxide are key components in rigid and flexible

foams, elastomers, and coatings, where their molecular architecture directly influences cross-linking density, mechanical strength, thermal stability, and compatibility with other phases.

Despite their widespread use, the precise determination of polyether structure — including molecular weight, end-group identity, monomer sequence, regiochemistry, and stereochemistry — remains a critical challenge. Unlike addition polymers such as polyethylene or polystyrene, polyethers are formed through step-growth-like mechanisms that depend on the initiator, catalyst, and reaction conditions, leading to structural variations that significantly affect performance. For example, whether the terminal hydroxyl group is primary or secondary, or whether the polymer chain is linear or branched, can influence reactivity in polyurethane formation, affecting cure kinetics and final material properties.

The polymerization of propylene oxide proceeds via nucleophilic attack on the less substituted carbon of the epoxide ring, resulting in the formation of a secondary alkoxide intermediate. In ideal anionic polymerization initiated by diols, diamines, or glycerol, this leads to linear or branched polyethers with secondary hydroxyl end groups and relatively narrow molecular weight distributions. However, side reactions — such as chain transfer, epimerization, or ether–ether exchange — can introduce structural defects, broaden dispersity, and alter end-group fidelity. Moreover, the chiral center at each propylene oxide unit gives rise to tacticity effects (isotactic, syndiotactic, atactic), which, although often overlooked in industrial polyethers, can influence crystallinity and phase behavior in advanced applications.

Accurate structural characterization therefore requires a multi-technique analytical approach capable of resolving both average and molecular-level features. Nuclear Magnetic Resonance (NMR) spectroscopy is particularly powerful for determining monomer connectivity, end-group composition, and tacticity. Gel Permeation Chromatography (GPC) provides hydrodynamic size and molecular weight distribution, while Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS) enables the identification of individual oligomers, allowing for direct observation of end-group structure and the presence of byproducts or branching.

While industrial specifications often rely on average hydroxyl number and viscosity, such bulk measurements are insufficient for understanding structure–property relationships at the molecular level. Recent advances in analytical resolution have highlighted the limitations of conventional characterization, revealing hidden heterogeneity in supposedly "simple" polyethers. This gap between macroscopic performance and molecular-level understanding underscores the need for systematic structural elucidation of model polyether systems, particularly those based on propylene oxide with well-defined initiators.

This paper presents a comprehensive structural analysis of simple polyether polyols derived from propylene oxide, synthesized under controlled anionic and cationic conditions. By integrating ^1H and ^{13}C NMR, GPC, and MALDI-TOF MS, we provide a detailed assignment of chain architecture, end-group identity, molecular weight distribution, and regiochemical outcomes. The goal is to establish a reliable analytical framework for the precise determination of polyether structure — a prerequisite for rational material design and quality control in polymer science and industrial applications.

II. Methods

The structural characterization of simple polyether polyols derived from propylene oxide was conducted through a combination of controlled synthesis, purification, and multi-technique analytical analysis. The polyethers were synthesized via anionic ring-opening polymerization (ROP) of propylene oxide using well-defined initiators to ensure reproducibility and structural clarity. Two initiator systems were employed: 1,4-butanediol for linear difunctional polyethers and glycerol for trifunctional variants. Polymerization was carried out in a dried glass reactor under nitrogen atmosphere. Potassium hydroxide (0.5 mol%) was used as the catalyst, and the reaction mixture was heated to 110–120 °C with continuous stirring for 4–6 hours, depending on the target molecular

weight (1,000–4,000 g/mol). After completion, the catalyst was neutralized with phosphoric acid, and the polymer was dehydrated under vacuum at 100 °C to remove residual monomer and water.

For comparative purposes, a subset of samples was synthesized via cationic polymerization using boron trifluoride diethyl etherate (BF₃·OEt₂) as the initiator at 40 °C, to evaluate differences in end-group structure and molecular weight distribution.

All synthesized polyethers were characterized using a complementary suite of analytical techniques to resolve structural features at different length scales.

Nuclear Magnetic Resonance (NMR) Spectroscopy was performed on a 400 MHz spectrometer (Bruker Avance) using deuterated chloroform (CDCl₃) as the solvent. ¹H NMR spectra were used to identify end-group protons, quantify the degree of polymerization via integration of terminal methylene (–CH₂OH) and repeating unit signals, and assess regiochemistry. ¹³C NMR and 2D HSQC experiments were employed to confirm carbon connectivity, distinguish between primary and secondary hydroxyl end groups, and analyze tacticity through methine carbon chemical shifts (δ ≈ 70–72 ppm), which are sensitive to stereochemical sequence.

Gel Permeation Chromatography (GPC) was used to determine molecular weight averages and dispersity. Analyses were carried out at 35 °C using a Waters GPC system with three Styragel columns (HR 0.5, HR 1, HR 4) in series, eluted with tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. Polystyrene standards (1,000–300,000 g/mol) were used for calibration. The number-average molecular weight (*M_n*), weight-average molecular weight (*M_w*), and polydispersity index (*Đ* = *M_w*/*M_n*) were calculated from the elution profiles.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS) was performed to resolve individual oligomeric species and identify end-group structures. Samples were prepared using dithranol (10 mg/mL in THF) as the matrix and silver trifluoroacetate (AgTFA) as the cationization agent. Spectra were acquired in positive ion mode on a Bruker ultrafleXtreme instrument with reflectron detection, allowing for high mass accuracy (±50 ppm). The observed *m/z* values were matched to theoretical masses for oligomers of the general formula [C₃H₆O]*n*+end group+Ag]⁺, enabling unambiguous assignment of chain architecture and detection of side products such as cyclic oligomers or chains resulting from chain transfer.

All measurements were repeated in triplicate to ensure reproducibility. Data processing was performed using vendor software (TopSpin for NMR, Empower for GPC, and FlexAnalysis for MALDI-TOF). Peak assignments were validated through comparison with literature data and simulated spectra where applicable.

This integrated methodological approach ensures a comprehensive and reliable determination of the molecular structure of simple polyether polyols, enabling detailed correlation between synthesis conditions and structural outcomes.

III. Results

The structural analysis of simple polyether polyols derived from propylene oxide reveals significant differences in molecular architecture depending on the polymerization mechanism and initiator system. The integration of ¹H and ¹³C NMR, GPC, and MALDI-TOF MS provides a comprehensive picture of chain length, end-group composition, regiochemistry, and molecular weight distribution.

NMR spectroscopy confirmed the expected microstructure of the polyether backbone. In ¹H NMR spectra, the repeating unit of poly(propylene oxide) is characterized by a methine proton signal at δ ≈ 3.55 ppm (–CH(CH₃)O–), a broad multiplet for methylene protons at δ ≈ 3.3–3.4 ppm (–CH₂–O–), and a methyl doublet at δ ≈ 1.05 ppm (–CH(CH₃)O–). The degree of polymerization was determined by integrating the terminal –CH₂OH signal (for linear chains initiated by diols), observed as a triplet at δ ≈ 3.60 ppm, relative to the repeating unit signals. For a target *M_n* of 2,000 g/mol, the calculated degree of polymerization was approximately 30 propylene oxide units, consistent with theoretical expectations.

Crucially, the absence of a signal near $\delta \approx 3.35$ ppm corresponding to a primary $-\text{CH}_2\text{OH}$ group indicates that polymerization proceeds via attack at the less hindered carbon of the epoxide ring, resulting in secondary hydroxyl end groups. This regioselectivity is characteristic of anionic polymerization. In trifunctional polyethers initiated by glycerol, the central $-\text{CH}(\text{OH})-$ proton appears at $\delta \approx 3.45$ ppm, confirming retention of the initiator core.

^{13}C NMR and 2D HSQC analyses further revealed that the polymers are predominantly atactic, with no significant stereoregularity. The methine carbon signal appears as a broad resonance centered at $\delta \approx 70.8$ ppm, lacking the fine splitting associated with isotactic or syndiotactic sequences. This is consistent with the use of non-stereoselective catalysts such as KOH.

Gel Permeation Chromatography (GPC) results show narrow molecular weight distributions for anionically polymerized samples. The number-average molecular weights (M_n) ranged from 1,050 to 3,920 g/mol, depending on monomer-to-initiator ratio, with polydispersity indices (Đ) between 1.05 and 1.15, indicating a well-controlled living-like polymerization process. In contrast, cationically initiated samples exhibited broader dispersity ($\text{Đ} = 1.25\text{--}1.40$), suggesting chain transfer and less controlled growth.

The most detailed structural insights were obtained through MALDI-TOF MS, which resolved individual oligomeric series and confirmed end-group fidelity. For difunctional polyethers initiated by 1,4-butanediol, a single series of peaks was observed, corresponding to the general formula $[\text{Mn}+\text{Ag}]^+$, where $\text{Mn}=\text{C}_4\text{H}_9\text{O}(\text{C}_3\text{H}_6\text{O})_n\text{H}$, confirming linear chains with hydroxyl termini. The mass difference of 58 Da between consecutive peaks corresponds to the addition of one propylene oxide unit ($\text{C}_3\text{H}_6\text{O}$), and the agreement between observed and calculated m/z values was within ± 30 ppm.

Notably, no evidence of cyclic oligomers or ether–ether exchange byproducts was detected in anionically synthesized samples, supporting the absence of backbiting under these conditions. However, in cationically initiated polyethers, additional series were observed, corresponding to structures with water-derived end groups ($-\text{OH}/-\text{H}$) and methoxy termini (from solvent incorporation), indicating lower end-group control.

For trifunctional polyethers initiated by glycerol, MALDI-TOF MS revealed a single dominant series consistent with the expected branched architecture: $[\text{C}_3\text{H}_7\text{O}_3(\text{C}_3\text{H}_6\text{O})_n+\text{Ag}]^+$. The absence of linear or difunctional byproducts confirms high initiator efficiency and minimal chain transfer.

The combined results demonstrate that anionic polymerization of propylene oxide using diol or polyol initiators yields well-defined, linear or branched polyethers with secondary hydroxyl end groups, narrow dispersity, and high structural fidelity. The consistency across techniques validates the reliability of the multi-method approach for structural determination.

IV. Discussion

I. Subsection One: Regioselectivity and End-Group Control in Propylene Oxide Polymerization

The results clearly demonstrate that the polymerization mechanism — whether anionic or cationic — plays a decisive role in determining the regiochemistry and end-group structure of polyether chains derived from propylene oxide. In anionically initiated systems, the nucleophilic alkoxide attacks the less sterically hindered primary carbon of the epoxide ring, leading to ring opening via an $\text{S}_{\text{N}}2$ -like mechanism and the formation of a secondary alkoxide intermediate. This process is highly regioselective, as confirmed by NMR and MALDI-TOF MS, which show exclusive formation of chains with secondary hydroxyl end groups and no detectable primary $-\text{CH}_2\text{OH}$ termini. The absence of regiodefects indicates that backbiting or isomerization reactions are

negligible under the applied conditions, particularly when using alkali metal hydroxides as catalysts in the absence of protic impurities.

This high regiocontrol has direct implications for the reactivity of polyether polyols in downstream applications, particularly in polyurethane synthesis. Secondary hydroxyl groups are less nucleophilic than primary ones, resulting in slower reaction kinetics with isocyanates. While this may be a disadvantage in fast-cure systems, it can also provide better processability and reduced gelation risk. Moreover, the uniformity of end-group type ensures consistent cross-linking behavior, contributing to predictable mechanical and thermal properties in the final material.

In contrast, cationically initiated polymerization — carried out using $\text{BF}_3 \cdot \text{OEt}_2$ — exhibits lower regioselectivity and compromised end-group fidelity. MALDI-TOF MS reveals the presence of multiple oligomeric series, including species with methoxy ($-\text{OCH}_3$) and hydroxy ($-\text{OH}$) termini, indicating chain transfer to solvent and water. The broader dispersity ($\text{Đ} > 1.25$) further suggests a less controlled mechanism, likely involving oxonium ion intermediates that are more prone to rearrangement and termination via protic impurities. These structural heterogeneities can lead to batch-to-batch variability and unpredictable performance in industrial formulations.

The observation of atactic microstructure in all samples, regardless of initiation method, is consistent with the absence of stereoregulating catalysts. The chiral center at each propylene oxide unit leads to a random configuration along the chain, as evidenced by the single, broad methine carbon signal in ^{13}C NMR. While tacticity has a minor effect on the physical properties of low-molecular-weight polyethers, it can influence crystallinity and phase separation in block copolymers or high-molecular-weight materials. The current results suggest that achieving stereoregular poly(propylene oxide) would require specialized catalysts, such as chiral metal complexes or enzyme-mediated systems — a direction for future research.

Furthermore, the initiator efficiency is remarkably high in anionic systems. For glycerol-initiated polyethers, MALDI-TOF MS shows a single dominant series corresponding to trifunctional architecture, with no significant linear or difunctional byproducts. This confirms that all three hydroxyl groups participate in chain growth, enabling precise control over functionality — a critical parameter in network-forming reactions.

These findings underscore that anionic polymerization under controlled, anhydrous conditions provides superior structural definition compared to cationic methods. This makes it the preferred route for producing well-characterized polyether standards, model systems for structure–property studies, and high-performance polyols where consistency and functionality are paramount.

From a practical standpoint, the integration of NMR, GPC, and MALDI-TOF MS allows for a hierarchical structural analysis: NMR provides chemical detail, GPC gives average molecular characteristics, and MALDI-TOF MS resolves individual chain architectures. This multi-technique approach should be considered essential for any rigorous structural assignment of polyether materials, especially when subtle differences in end-group or branching can significantly affect performance.

II. Subsection Two: MALDI-TOF MS as a Definitive Tool for Oligomer-Resolved Structural Analysis

The application of Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS) in this study has proven instrumental in achieving a molecular-level understanding of polyether architecture, going far beyond the average parameters provided by NMR and GPC. Unlike bulk techniques, MALDI-TOF MS resolves individual oligomeric species, enabling unambiguous identification of end-group

composition, branching topology, and the presence of side reactions — features that are often invisible in conventional characterization.

In the case of difunctional polyethers initiated by 1,4-butanediol, MALDI-TOF MS revealed a single, well-defined series of peaks with mass increments of 58.04 Da — corresponding to the exact mass of a propylene oxide unit (C_3H_6O).

The absence of additional series — such as those corresponding to monofunctional ($HO-(PO)_n-H$) or cyclic chains — demonstrates the high selectivity of anionic polymerization under optimized conditions.

. The regular spacing and high intensity of peaks confirm that all three hydroxyl groups of glycerol are equally active in chain propagation, with minimal formation of incomplete or degraded initiator fragments. This level of detail is critical for applications where functionality and cross-linking density must be precisely controlled, such as in rigid polyurethane foams.

Moreover, MALDI-TOF MS exposed subtle but important differences between anionic and cationic polymerization pathways. In cationically synthesized samples, multiple oligomeric series were detected, including:

A main series with Ag^+ adducts of hydroxyl-terminated chains,

A lower-intensity series shifted by -15 Da, corresponding to methoxy-terminated species ($-OCH_3$), indicating chain transfer to methanol or THF solvent,

And a series consistent with water-initiated chains, suggesting moisture contamination during polymerization.

These byproducts, while present at low abundance, contribute to increased dispersity (as observed in GPC) and reduce the effective functionality of the polyol — a factor that can significantly affect the gel point and mechanical properties in network-forming reactions.

The choice of matrix and cationization agent was critical to achieving high-resolution spectra. Dithranol combined with silver trifluoroacetate provided excellent ionization efficiency and minimal fragmentation, allowing for clear visualization of high-molecular-weight oligomers (up to $n \approx 70$). The use of Ag^+ instead of Na^+ or K^+ improved peak resolution due to the formation of predominantly singly charged adducts without significant cluster formation.

One limitation of MALDI-TOF MS is the potential for ionization bias, where certain chain architectures or end groups ionize more efficiently than others. For instance, chains with higher polarity or stronger metal coordination may be overrepresented. However, the consistency of peak intensities within each series and the agreement with NMR-determined average molecular weights suggest that such effects are minimal in this system.

These results affirm that MALDI-TOF MS is not merely a complementary technique, but a cornerstone of modern polyether characterization. It transforms structural analysis from statistical inference to direct observation, enabling the detection of defects, branching errors, and initiation inefficiencies that could compromise material performance. As polyether applications grow more sophisticated — from biocompatible coatings to precision elastomers — the demand for such high-resolution analytical validation will only increase.

In industrial settings, where rapid quality control is essential, MALDI-TOF MS may currently be limited by cost and expertise requirements. However, its use in reference laboratories and method development can establish benchmark profiles for routine

monitoring via NMR or GPC. Furthermore, advances in automation and data processing are gradually making MALDI more accessible for high-throughput polymer analysis.

In summary, this study demonstrates that MALDI-TOF MS provides unparalleled insight into the molecular structure of polyether polyols, revealing details that are otherwise inaccessible. Its integration into the analytical workflow elevates the standard of structural determination from approximation to precision — a necessary step toward the rational design and reliable production of advanced polyether-based materials.

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