

IUPAC Technical Report

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A brief guide to polymer characterization: structure (IUPAC technical report)

<https://doi.org/10.1515/pac-2022-0602>

Received June 11, 2022; accepted July 12, 2023

Abstract: To bolster the series of Brief Guides released by International Union of Pure and Applied Chemistry (IUPAC), here we introduce the first Brief Guide to Polymer Characterization. This article provides a concise overview of characterization methods for teachers, students, non-specialists, and newcomers to polymer science as well as being a useful manual for researchers and technicians. Unlike pure low molar mass chemical substances, polymers are not composed of identical molecules. The macromolecules which comprise a single polymer sample vary from one another, primarily in terms of size and shape, but often also in the arrangement or positioning of atoms within macromolecules (e.g., chain branching, isomerism, etc.). Polymer properties are often drastically different from those of other substances and their characterization relies on specialist equipment and/or common equipment used in a specialized way (e.g., particular sample preparation or data analysis). This Brief Guide focuses uniquely on the structural characterization (i.e., analyzing the molecular and multi-molecular aspects) of polymers. The complex nature of the structural variables possible in macromolecular materials often presents a challenge

Sponsoring body: IUPAC (International Union of Pure and Applied Chemistry) Polymer Division.

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with regard to the detailed structural characterization of polymers. This Brief Guide provides a useful starting point to direct the reader to the most commonly used and useful techniques to characterize these structural variables.

Keywords: Analytical chemistry; analytical techniques; macromolecules; physical chemistry; polymers; polymer characterization.

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1 Introduction

To bolster the series of brief guides released by [International Union of Pure and Applied Chemistry \(IUPAC\)](#) [1–5], here we introduce the first Brief Guide to Polymer Characterization. This article provides a concise overview of characterization methods for teachers, students, non-specialists, and newcomers to polymer science as well as being a useful manual for researchers and technicians. This guide focuses on the structural characterization (i.e., molecular and multi-molecular aspects) of **polymers** (see Fig. 1).

Through the use of a succinct table, the intention is to enable the reader to navigate from the polymer property that one wishes to measure to the technique(s) required to measure it, and vice versa. This is a starting point for the user and not a comprehensive operating manual of all of the characterization techniques that are available. Figure 1 provides an overview of polymer characterization and can be used to navigate Table 1 more easily. A glossary of acronyms and abbreviations used in the manuscript is provided at the end of the paper.

Unlike pure low **molar mass chemical substances**, polymers are not composed of identical **molecules**. The **macromolecules** which comprise a single polymer sample vary from one another, primarily in terms of size and shape, but often also in the arrangement or positioning of **atoms** within macromolecules (e.g., chain branching, **isomerism**). Polymer properties are drastically different from those of other substances and their characterization relies on specialist equipment and/or common equipment used in a specialized way (e.g., particular sample preparation or data analysis). This Brief Guide aims to provide a starting point to assist the reader to navigate some of the most useful techniques to determine the various structural **characteristics** of polymers. It is also worth noting that the guide focuses on the characterization of single (one **component**) polymers, rather than multicomponent **polymer blends**. Notably, most commercial polymers contain **additives**, which are also not discussed herein.

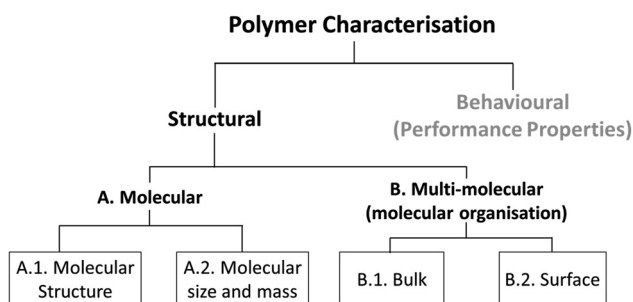


Fig. 1: Overall structure for the characterization of polymers based on the type of information sought, highlighting that this Brief Guide deals with structural characterization. This serves as a guide for this document.

Table 1: Structural features and common techniques to characterize them.

Structural feature	Experimental Techniques (listed in alphabetical order in each section)
A. Molecular	
A1. Molecular structure	
A1.1. Chemical composition	DOSY NMR (A1.5)
A1.1.1. Overall composition	Elemental analysis (A1.1.1)
A1.1.2. End groups and end group distribution	Interaction chromatography (e.g., SGIC, LCCC, TGIC, HPLC) (A1.2, A1.5)
A1.2. Sequence distribution of monomeric units	MS (MALDI-MS, ESI-MS) (A1.1, A1.1.2, A1.3)
A1.3. Chemical bonds	NMR (A1.1, A1.1.2, A1.2, A1.3, A1.4, A1.5)
A1.4. Isomerism (e.g., regioregularity, tacticity)	PES (XPS, UPS) (A1.1.1, A1.3)
A1.5. Molecular architecture (e.g., short chain branching, long chain branching)	Rheology (A1.5) SEC/GPC (A1.5) Small angle scattering (SANS/SAXS) (A1.5) Static light scattering (SLS) (A1.5) Vibrational spectroscopy (IR, Raman) (A1.3, A1.4, A1.5) Viscometry (A1.5) XAFS/XANES (A1.2) XRD (A1.4)
A2. Molecular size and mass	
A2.1. Molar mass and molar mass dispersity (\mathcal{D}_M)	Colligative properties of polymer solution (e.g., osmometry) (A2.1.1, A2.3)
A2.1.1. Number-average molar mass (M_n)	DLS (A2.4, A2.5)
A2.1.2. Mass-average molar mass (M_w, M_m)	DOSY NMR (A2.4, A2.5), End group analysis (e.g., NMR, IR, UV-Vis, titration) (A2.1.1)
A2.2. Radius of gyration	MS (MALDI-MS) (A2.1)
A2.3. Second virial coefficient (A_2)	SEC/GPC (A2.1)
A2.4. Hydrodynamic radius	SLS (A2.1.2, A2.2, A2.3)
A2.5. Diffusion coefficient	Small-angle scattering (SANS/SAXS) (A2.2, A2.3) Viscometry (A2.1)
B. Multi-molecular (molecular organization)	
B1. Bulk	
B1.1. Chemical composition	Density gradient column (B1.2)
B1.2. Density	DLS (B1.9)
B1.3. Crystal structure	DMA (B1.8)
B1.4. Degree of crystallinity	DSC (B1.4, B1.6, B1.8)
B1.5. Molecular orientation	IR (B1.1, B1.5, B1.7)
B1.6. Microphase separation (nanoscale morphology)	Laser diffraction (B1.9)
B1.7. Intra/intermolecular interactions (e.g., H-bonding)	(SS)-NMR (B1.7)
B1.8. Free volume	Polarized light microscopy (B1.3)
B1.9. Particle size, shape/morphology, and distribution	Positron annihilation spectroscopy (B1.8) Pycnometry (B1.2) SAXS (B1.5, B1.6, B1.9) SEM (B1.9) TEM (B1.6, B1.9) UV-Vis (B1.7) WAXD/WAXS/XRD (B1.3, B1.4, B1.5, B1.7)
B2. Surface	
B2.1. Chemical composition	AFM (B2.3.2)
B2.2. Molecular orientation	EDS/EDX (B2.1)
B2.3. Morphology	GI-IR (B2.2)
B2.3.1. Nanoscale	GI-SAXS/GI-WAXS (B2.2, B2.3.1)
B2.3.2. Nanoscale to microscale	IR (B2.1)
B2.3.3. Microscale	Optical microscopy (B2.3.3) PES (XPS, UPS) (B2.1, B2.3.2) Raman (B2.1) SEM/TEM (B2.3.2) TOF-SIMS (B2.1)

2 Structural characterization

The structural analysis of polymers can be further categorized into (A) the characterization of the macromolecules that make up the polymer substance, such as molar mass (averages) or chemical functionality, and (B) the analysis of multi-molecular assemblies or the effects thereof (such as **density** or **degree of crystallinity**). For the latter category, there are clearly examples where the entity to be analyzed lies within the overlap between structural and behavioral characterization. In these cases, we have attempted to place the measured characteristic and associated technique in the most commonly used and logical category. For example, if the property and/or technique are more suitable in a discussion of the structural analysis of polymers, then they are included herein. In contrast, if the property and associated technique are more appropriate for the discussion of polymer performance, then they should be dealt with separately in a more detailed discussion of the behavioral characteristics of polymers. Examples of the latter include, but are not limited to, **glass transition temperature** (T_g), **melting temperature** (T_m), and **intrinsic viscosity** ($[\eta]$), which are a direct result of polymer structure, but bear a strong influence on the behavior or performance of the polymer via the so-called structure–property relationships and are therefore more appropriately categorized as behavioral characteristics. Table 1 lists the structural features of polymers alongside techniques commonly used to characterize them.

Notably, there are several different **molar mass averages** that can be used to describe a polymer (e.g., **z-average (zentrifuge-average) molar mass**, M_z , **z+1-average molar mass**, M_{z+1} , **viscosity-average molar mass**, M_v). Here we focus on the two most commonly reported parameters (i.e., **number-average molar mass**, M_n , and **mass-average molar mass**, M_m or M_w) and the ratio between them (**molar-mass dispersity**, D_M); D_M is routinely used as a descriptor of the breadth of polymer molar mass distribution. Additionally, it should be noted that a number of the techniques used to characterize the surface of polymers can also be used to probe deeper into the sample to, for example, gain information about compositional changes going from the surface into the bulk.

It is important to appreciate that when measuring a certain molecular structural parameter (e.g., molar mass, **radius of gyration**), some techniques may only give the average of this parameter for all of the molecules in the sample, while other techniques may give an indication of the distribution with regards to the specific parameter. While, in essence, these characteristics are brought about by the analysis of all the macromolecules that comprise the polymer and hence could be thought of as multi-molecular, they are included in Section A of Table 1 because the specific properties being measured are at the molecular or submolecular scale. Moreover, as a direct consequence of polymers being comprised of a **mixture** of molecules with many different structural parameters, many characterization methods rely on a pre-analysis sorting step (**fractionation**) that is used to divide up a polymer into molecularly more uniform batches (fractions) prior to analysis. The most common pre-analysis separation steps involve **chromatography** or time-of-flight procedures (included in Table 1). Other processes, such as various types of fractionation (e.g., CEF, CRYSTAF, FFF, TREF, step crystallization), not included in Table 1, should not be overlooked as powerful tools in a polymer analyst's armory. These techniques can separate the polymer according to some inherent characteristic (e.g., molecular size, propensity to crystallize) into fractions, which, when analyzed, can provide valuable information about the distribution of that characteristic in the given polymer.

Finally, one should also note that computational modelling is a powerful theoretical tool to complement experimental characterization techniques. There are several different approaches that can be applied, such as **molecular mechanics** (MM), **molecular dynamics** (MD), and **self-consistent field theory** (SCFT), to name but a few. For example, **density functional theory** (DFT) can be applied to assign vibrational, UV–Vis, and NMR spectra, helping the interpretation of both **intramolecular** (**conformation**, **tacticity**, etc.) and **intermolecular** features (e.g., **hydrogen bonding** or other weak interactions). Computational modelling is an important pillar of analytical polymer science and, as such, is not covered in this Brief Guide and should be dealt with by a dedicated piece of work.

3 Summary

The complex nature of the structural variables possible in macromolecular materials often presents a challenge with regard to the detailed structural characterization of polymers. This Brief Guide provides a useful starting point to direct the reader to the most commonly used and useful techniques to characterize these structural variables. Common methods used to determine behavioral characteristics of polymers (such as [viscoelasticity](#), [conductivity](#), etc.) often rely on international standards and form a much larger body of work that is beyond the scope of this Brief Guide.

4 Glossary of acronyms and abbreviations

AFM	Atomic Force Microscopy
CEF	Crystallization Elution Fractionation
CRYSTAF	Crystallization Analysis Fractionation
DLS	Dynamic Light Scattering
DMA	Dynamic Mechanical Analysis
DOSY	Diffusion Ordered Spectroscopy
DSC	Differential Scanning Calorimetry
EDS/EDX	Energy-Dispersive X-ray Spectroscopy
ESI-MS	Electrospray Ionization Mass Spectrometry
FFF	Field-Flow Fractionation
GI	Grazing Incidence
GPC	Gel Permeation Chromatography
HPLC	High-Performance Liquid Chromatography
IR	Infrared Spectroscopy
LCCC	Liquid Chromatography at Critical Conditions
MALDI-MS	Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance Spectroscopy
PES	Photoelectron Spectroscopy
SANS	Small-Angle Neutron Scattering
SAXS	Small-Angle X-Ray Scattering
SEC	Size-Exclusion Chromatography
SEM	Scanning Electron Microscopy
SGIC	Solvent Gradient Interaction Chromatography
SLS	Static Light Scattering
SS	Solid State
TEM	Transmission Electron Microscopy
TGIC	Temperature Gradient Interaction Chromatography
TOF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry
TREF	Temperature Rising Elution Fractionation
UPS	Ultraviolet Photoelectron Spectroscopy
UV-Vis	Ultraviolet-Visible Spectroscopy
WAXD	Wide-Angle X-Ray Diffraction
WAXS	Wide-Angle X-Ray Scattering
XAFS	X-Ray Absorption Fine Structure
XANES	X-Ray Absorption Near Edge Structure
XPS	X-Ray Photoelectron Spectroscopy
XRD	(Fiber or Single Crystal) X-Ray Diffraction

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‡ Deceased.

Research funding: This work was prepared under project 2015-049-1-400 of IUPAC.

References

- [1] IUPAC. *Pure Appl. Chem.* **87**, 1039 (2015), <https://doi.org/10.1515/pac-2014-0718>.
- [2] IUPAC. *Pure Appl. Chem.* **92**, 527 (2020), <https://doi.org/10.1515/pac-2019-0104>.
- [3] IUPAC. *Pure Appl. Chem.* **84**, 2167 (2012), <https://doi.org/10.1351/PAC-REP-12-03-05>.
- [4] IUPAC. *Pure Appl. Chem.* **94**, 1079 (2022), <https://doi.org/10.1515/pac-2021-0115>.
- [5] IUPAC. *Pure Appl. Chem.* **87**, 71 (2015), <https://doi.org/10.1515/pac-2013-0201>.

Supplementary Material: This article contains supplementary material (<https://doi.org/10.1515/pac-2022-0602>).