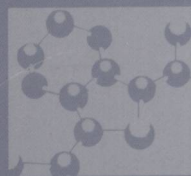# Characterization and Analysis *of* Polymers

CHARACTERIZATION ANALYSIS OF POLYMERS

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CHARACTERIZATION ANALYSIS OF POLYMERS

CHARACTERIZATION ANALYSIS OF POLYMERS
EDITORIAL STAFF

PREFACE

Owing to their versatility and wide range of applications, polymeric materials are of great commercial importance. The physical and chemical properties of polymeric materials influence their processing and use, so their polymerization and processing have to be carefully controlled, and the nature of the polymer determined and monitored to ensure that the final products are of the desirable properties.

Characterization and Analysis of Polymers provides comprehensive, up-to-date information on methods used to characterize physical and chemical properties of polymers including molecular structure, molar mass and molar mass distribution, morphology and mechanical properties. Among the methods discussed are mass spectrometry, atomic force microscopy, chromatographic methods, laser light scattering, nuclear magnetic resonance and thermal analysis. Containing carefully selected reprints from the third edition of Wiley's renowned *Encyclopedia of Polymer Science and Technology*, this reference features the same breadth and quality of coverage and clarity of presentation found in the original.

Written by prominent scholars from around the world, **Characterization and Analysis of Polymers** offers 26 self-contained articles focusing on the theoretical and applied aspects of important methods and techniques. This reliable reference will be of particular interest to polymers and materials scientists, chemists, chemical engineers, process engineers, students, researchers and educators in related fields and consultants and suppliers in the plastic and related industries.

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INTRODUCTION

CHARACTERIZATION OF POLYMERS

Introduction

Over the last 50 years, systematic investigation has established a number of structure–property relationships for polymeric materials, which allow prediction of their physical properties from a knowledge of the chemical structure of the repeat units and molar mass of the material. All polymeric materials can be divided into a series of subclasses, reflecting either their method of synthesis or some particular characteristic of the material. Using this classification, it is possible to quickly identify how the material will respond to external factors such as change of temperature, pressure, stress, impact, etc.

The term *polymer* (*poly*–many, and monomer–low molar mass unit) reflects the simplicity of the high molecular weight macromolecular structure. *Natural polymers*, although they may have complex sequences of repeat units, can exhibit physical properties that obey the same physical laws as their equivalent *synthetic polymers*. The increased use of polymers in everyday life has come with the discovery of simple synthetic routes to the raw materials and the ability to tailor their physical properties to particular applications. Despite the wide range of methods available for their synthesis, the physical characteristics of many polymers can be predicted by recognizing certain generic features in their structure.

Many polymers are created from the reaction of monomers that contain an unsaturated carbon (ene/vinyl) bond. For example, polyethylene $[-(CH_2=CH_2)_n-]$, where n is the degree of polymerization and indicates the number of the repeat units in the chain. Synthesis of the polymer can be achieved using either free-radical processes, ionic (anionic or cationic initiation), or using a coordination polymerization route that uses an *addition reaction*. These synthetic routes produce macromolecular chains that have similar chain lengths and well-defined physical properties. Polymers with heteroatoms in the polymer backbone are frequently produced by a step-growth method that may either involve ring opening or elimination of a low molecular weight molecular species; eg, poly(ethylene oxide) produced by ring opening of ethylene oxide and poly(ethylene adipate) produced by the condensation of ethylene diol and adipic acid with the

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HOMOPOLYMER CLASSIFICATION
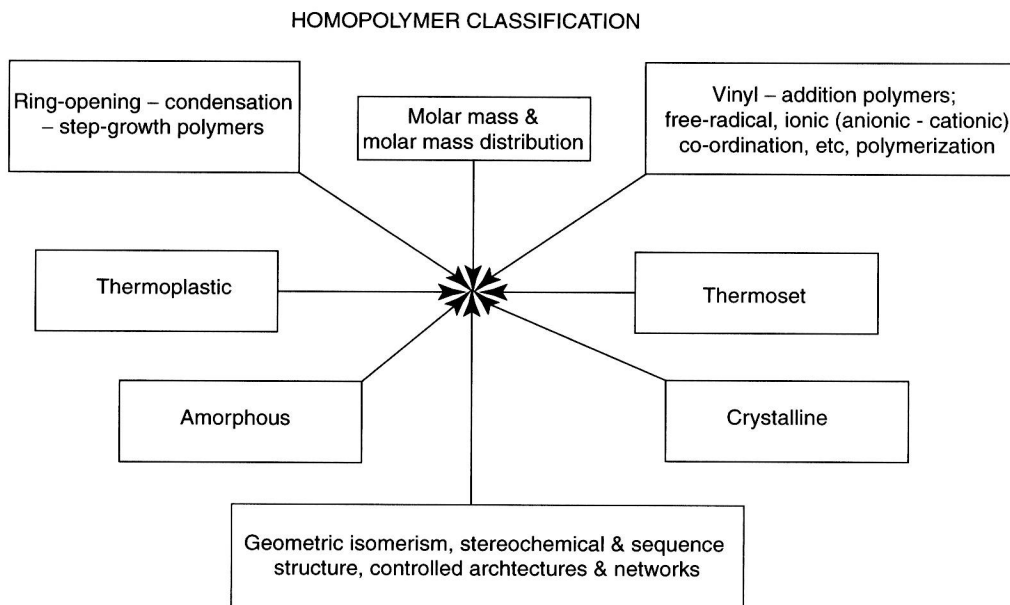
Fig. 1.   Classification of homopolymer types.

elimination of a molecule of water. *Step-growth* methods produce materials with a broad spread of lengths, and consequently a range of physical properties. The distribution of chain lengths is reflected in a range in the physical properties.

Knowledge of the chemical structure of the monomer and the distribution of chain lengths allows prediction of the method used for the production of that polymer. If the monomer is effectively difunctional, then the polymer will have a linear backbone structure and is a *thermoplastic*. Such polymers can be heated to an elevated temperature and shaped. If the monomer has functionality greater than two, then a cross-linked three-dimensional matrix can be created and the material is a *thermoset*, which cannot be reshaped by heating to an elevated temperature. Thermoplastics and Thermosets can be created using similar chemistry, the only difference being the number of functions associated with the primary monomer unit.

The chemical structure of the repeat unit has a dominant effect on the ability of the polymer chains to pack together to form an ordered structure. If there is either a high level of symmetry or relative simplicity of the polymer backbone, then packing is encouraged and a *crystalline* structure generated. If the monomer structure is asymmetric and/or contains bulky pendant groups, packing may be inhibited and the solid structure is disordered and *amorphous*. Being able to differentiate between these different types of organization can help with prediction of the physical properties of the solid.

A useful classification of the polymers is presented in Figure 1.

Blending together two different types of compatible polymer material will create physical properties that are different from those of the individual

materials (see POLYMER BLENDS). Polymeric materials may be formed using more than one repeat unit, and these are classified as *copolymers*. In real polymeric materials, there may be present a range of Additives (qv): Plasticizers (qv), Antioxidants (qv), processing aids, Fillers (qv), Reinforcement (qv), antistatic modifiers, pigments, dyes, etc. These additives will influence the physical properties of the material, and understanding their influence is critical to understanding the properties of the material.

The questions that need to be asked in order to fully characterize a polymeric material include the following:

(1) What is the chemical structure of the repeat units from which the polymer is constructed? Does the polymer have a specific geometrical isomeric structure, particular sequence or branched-chain structures?
(2) Is the sample a thermoplastic or a thermoset?
(3) What is the average length of the polymer chains present? Are these chains of the same length or is there a broad distribution of lengths present?
(4) Is the solid a crystalline or an amorphous material?

In addition, knowledge of a number of physical properties is required to determine whether the polymer is suitable for a particular application.

Sample Preparation

All methods used by organic chemists for the determination of molecular structure are appropriate for the characterization of polymers. However, the simple analysis may not be able to differentiate between a homopolymer, a copolymer, or a blend of polymers. Even with a homopolymer, such as a commercial polypropylene, the solid may contain varying amounts of polymers with different molar masses and stereochemical and block sequence structure. Therefore it is desirable to be able to dissolve the polymer in selective solvents and extract species on the basis of solubility.

To obtain an unambiguous characterization of a particular material, it is often essential to fractionate a material (1–3). Synthetic polymers are rarely homogeneous chemical species, but have multivariate distributions in molecular weight, chemical composition, chain architecture, and functionality (4). For a precise characterization of a synthetic polymer, all the distributions need to be determined, which is a difficult, if not virtually impossible, task. Traditionally, fractionation has allowed separation of polymers on the basis of molecular mass or chemical composition (2). With proper techniques it is often possible to separate and characterize complex homo- and copolymer species on the basis of chemical heterogeneity and molar mass.

Separation by Solubility. Fractionation of a polymer has traditionally been based on solubility using precipitation, fractional dissolution (extraction), coacervate extraction, thin-layer chromatography, counter current distribution, and turbidimetry (5).

Two methods have been developed that are in common usage and aid the fractionation of polymer materials. These are temperature rising elution fractionation (TREF) (6–8) and Field Flow Fractionation (FFF) (9).

TREF was developed to separate semicrystalline polymers according to differences in molecular structure or composition that influence the crystallinity and solubility. TREF can be divided into crystallization and elution stages. In the crystallization stage, the polymer is dissolved in a good solvent, and then allowed to crystallize under controlled conditions by slowly decreasing the temperature. Crystallization may take place on an inert support or the support may be added later. In the elution step, solvent is pumped through a column packed with the polymer-support mixture, while the temperature is increased. Polymer elutes in the reverse order that it was crystallized, with less crystalline material eluting at lower temperatures followed by more crystalline polymer at higher temperatures and has been used for polyalkenes (6,8). In preparative TREF (P-TREF) polymer fractions are collected at predetermined but different elution temperature intervals from those used in the crystallization (8). Critical, isobaric temperature rising elution fractionation (CITREF) is carried out using supercritical fluids, such as propylene and propane, in a column containing a high surface area stainless steel mesh packing in a manner analogous to P-TREF (10,11).

FFF is based on the simultaneous action of the effect of field forces and the carrier liquid flow on the fractionated species inside a belt-shaped fractionation channel (9,12). FFF is used to fractionate polymers or mixtures. Separation is based on the use of intensive properties, such as chemical composition and structure of the polymer chains, electrical charge, density, etc. Separation is influenced by application of a temperature gradient (ThFFF) (13) or an electrical field (EFFF) (14), and separation is aided by flow. In ThFFF, a temperature difference between the walls of the channel produces a flux, known as the Soret effect, usually towards the cold wall. In the EFFF, an electric potential across the channel generates a transverse flux of charged macromolecules or particles (14). In preparative FFF, a lower dilution of the separated species during the elution occurs as compared with flow FFF, due to partial depletion of the liquid due to the cross-flow. Two-dimensional thermal field-flow fractionation (2D-ThFFF) is devised for continuous fractionation of macromolecules (15). The sample introduced into a disc-shaped channel undergoes radial and tangential flow. Random copolymers of styrene and acrylonitrile (SAN) in toluene have been fractionated. (16). Polymer Brushes (qv) with poly(methyl methacrylate) (PMMA) backbone and polystyrene side chains have been separated using continuous counter-current extraction (17). FFF is applicable for the separation of polymers with molar mass in the range 10^3–10^8 and variants include sedimentation as an applied field (18–20). For small-scale analysis, components are sometimes quickly and conveniently separated by thin-layer chromatography (TLC), (21).

Molecular Size.   Separation of soluble macromolecules can be achieved in size-exclusion chromatography (SEC) or gel-permeation chromatography (GPC) as a consequence of the differential permeation of the molecules into the porous solid column packing. Small molecules will penetrate more effectively and are eluted last from the column; the large species are eluted first. The separation is based on the size of the polymer molecule in solution—*hydrodynamic volume* that is directly related to molar mass of the polymer molecule. Since the

hydrodynamic volume takes into account the polymer–solvent interactions, it is possible to create a universal calibration that takes into account variations in size due to change in polymer–solvent interaction. Care must be taken to ensure that size exclusion is the only separation mechanism operating in the column and to avoid errors arising because of Adsorption (qv) and aggregation (22). The SEC/GPC technique is used for the determination of the molar mass relative to some calibration standards, but can also be used for the separation of the mixtures into narrow molar mass fractions.

Molecular Structure Characterization

The first step in any analysis is determination of the elemental composition of the polymer. Combustion analysis can establish the presence of carbon, hydrogen, halogen, sulfur, and the Kjeldahl oxidation for nitrogen and, occasionally, phosphorus. The structure of the polymer will then usually be determined by a combination of spectroscopic and mass spectroscopic analysis of degradation products.

Infrared and Raman Spectroscopy. Identification of the type of functional groups present in a polymer is effectively achieved by infrared and Raman analysis (23–28). The spectroscopic selection rules for infrared and Raman activity are respectively a dipole moment or polarizability change during interaction of electromagnetic radiation with the atomic grouping (see VIBRATIONAL SPECTROSCOPY). A vibration that gives a strong infrared signature may be weak in the Raman spectrum and vice versa. It is relatively easy to identify the occurrence of carbonyl, ethers, aromatic functions, hydroxyl groups, epoxy rings, carbon–halogen, and carbon–hydrogen bonds. The techniques are applicable to the study of solids (usually as very thin films), powders, and solutions. Raman spectroscopy is particularly useful when studying aqueous solutions, wet samples, or where differentiation between polymers with similar structures is necessary. Using laser sources, depolarization data associated with the Raman spectra can be obtained and conformational differences in molecular structure determined. At low frequencies, ca 100 cm^{-1}, the longitudinal acoustic mode (LAM) is observed in the Raman and is characteristic of the all trans structure of the polymer backbone and used to study the lamellar structure in crystalline polymers, such as polyethylene (29–32). Shifts in the Raman spectra have been used to indicate how local stresses are distributed within a sample (29,33).

Application of stress can induce changes in the infrared spectrum (34,35). Fourier transform infrared (FTIR) spectroscopy, in which rapid multiple scanning of the sample is possible (22,29), has allowed real-time observation of changes in the spectra. Studies have been reported of materials subjected to an applied external stress or used to follow the cure reaction of a thermoset. Computer libraries allow assignment of the spectra and identification of various functional groups within the polymer. Attenuated total reflection (ATR) attachments allow the surface of films to be explored (36). The ATR technique uses a glancing angle and total internal reflection of the infrared beam to collect information on the groups that lie close to the surface of the film (5–10 μm). Data manipulation techniques such as difference spectroscopy (spectral subtraction), factor analysis, spectral

deconvolution, and least squares fitting of calibration plots allow quantitative determination of the species present.

Nuclear Magnetic Resonance Analysis. Nuclear Magnetic Resonance (qv) (NMR) provides both qualitative and quantitative analysis with respect to monomer composition and the average configuration of the polymer chain (22,37, 38). Both solid-state and conventional NMR techniques provide information on molecular structure, dynamics of the chain, crystallinity, network formation, and chain entanglement (39–41). Many types of nuclei may be observed; but proton (^{1}H) and carbon-13 (^{13}C) are usually investigated. Other useful nuclei studied include silicon (^{29}Si), nitrogen (^{15}N), fluorine (^{19}F), and phosphorus (^{31}P). The use of FTNMR with superconducting magnets and wide bore magnets has allowed a wide range of materials to be studied.

Proton (^{1}H) NMR, initially, was used for structural characterization, and use of the Karplus equation has allowed conformational and configurational analysis to be carried out on a wide range of polymers in solution (42). The advent of various pulse sequences has enhanced the signal sensitivity and consequently the popularity of carbon-13 NMR spectroscopy. The natural abundance of ^{13}C is 1.1% and although there are problems of sensitivity, the spectra are simplified because carbon–carbon coupling is rarely observed in naturally-occurring materials. ^{1}H decoupling leads to spectra that consist of a series of single lines indicative of the types of chemical environment present. The inherent spectral separation of carbon chemical shifts is generally greater than for protons, ie, 0–220 ppm for ^{13}C compared with 0–10 ppm for ^{1}H, making assignment relatively easy. The ^{1}H decoupled line width is typically about 2–10 Hz for solution spectra. Grant and Paul (43) established that since the shifts are dependent on the s-orbital density, the observed shifts can be used to characterize the sequence structure of the polymer backbone. (22,44–50). Many molecular modeling packages contain software which will predict the ^{13}C spectrum. Subtle differences in both configuration and conformation of the polymer chain and changes in the dynamics of the chain backbone as a consequence of substitution can be observed (22,45).

Use of various pulse sequences has allowed solid-state NMR to be used to explore morphological features in solids. Studies of diblock copolymers of poly(styrene)–poly(methyl methacrylate) indicate domain sizes from 1 to 100 nm (51). Studies of the morphology and dynamics in poly(ethylene terephthalate) (52) and polyethylene (53) indicate the presence of a number of different phases. Motional heterogeneities within the phases of core shell particles composed of poly(n-butyl acrylate) (PBuA) and poly(methyl methacrylate) (PMMA) have also been demonstrated (54). The scope of the technique is continuing to develop and provide insight into the way in which chain–chain interactions influence the polymer morphology (55).

Detailed analysis of ^{1}H and ^{13}C NMR coupling constants obtained from solution spectra has allowed characterization of the chemical composition and conformation of racemic and meso dyads in glassy polystyrenes (56), and the stereoregularity in poly(methyl methacrylates) (57). With sufficient resolution, detection of tacticity at a pentad and higher level is possible, allowing validation of Bernouillian, Markov, or other statistical models for the description of polymerization processes and the tendency for block formation in copolymers. Geometric isomerism is readily detected in polybutadiene or polyisoprene, which form cis

and trans double bonds in the polymer backbone as well as undergoing 1,4 or 1,2 addition. Imaging has allowed the mapping of the diffusion of labeled species in solids (58,59).

Pyrolysis. Spectroscopic methods can provide an identification of the monomeric species present; however, pyrolytic degradation plays an important role in the final assignment of the structure. Pyrolysis-gas chromatography is used extensively for the analysis of synthetic (60–63) and natural polymers (64). Application of heat to a sample leads to Degradation (qv) and release of low molecular mass fragments. The composition and relative abundance of the pyrolysis products are characteristic of a given polymer. The technique is used in conjunction with other analytical methods, such as mass spectroscopy, infrared, and combinations such as pyrolysis-gas chromatography-mass spectroscopy. Pyrolysis can be carried out either in a continuous or a pulse mode; the latter has the advantage of minimizing the effects of secondary reactions on the fragmentation products. Small samples, in the microgram to milligram range, are rapidly heated either directly in the inlet of a gas chromatograph or separately in an attached unit. For pyrolysis-mass spectroscopy, the pyrolysis is carried out in vacuum in the mass spectrometer. In a pulse mode pyrolyzer, the sample is frequently heated by resistive heating of a filament or by radio frequency inductive heating of a ferromagnetic metal (Curie-point pyrolyzer). The sample may be deposited as a thin film obtained by drying a solution or a small sample placed on the filament.

Pyrolysis of poly(methyl methacrylate) at low temperature produces monomer, whereas other acrylics fragment with loss of side chains, scission of the chain backbone, elimination or rearrangement of the products. Knowledge of the degradation pathways for particular polymer sequences is required to interpret the fragmentation patterns obtained from pyrolysis (65–70).

UV Spectroscopy. UV spectroscopy is appropriate for characterization of aromatic or conjugated systems (22). The high sensitivity allows study of species at high dilution and is useful for intrinsically conducting polymers and light-emitting species (71,72). The absorption is characteristic of the $\pi-\pi^*$ transition; fluorescence and phosphorescence lifetimes are influenced by the state of aggregation and the matrix structure in which the absorbing species is localized. Many pigments and dyes have characteristic absorption and emission spectra. Luminescence techniques are valuable for the study of degradation and aging in polymers. Rotation and local motion of groups in dilute solution on the order of 10^{-10}–10^{-8} s in amorphous polymers and orientated films may be studied by fluorescence depolarization. Doped polymer films excited with polarized light will exhibit fluorescence depolarization, which is characteristic of the motion in the system.

Luminescence may be suppressed by the presence of antioxidants, light stabilizers, and pigments, which are able to transfer energy form the excited state to other nonfluorescing electronic states. Quenching of excited states also occurs when either oxygen or moisture is present.

Mass Spectrometry. Direct observation of polymers by means of Mass Spectrometry (qv) has traditionally been limited to molecules with molar mass of about 5000 or less. However, the advent of matrix-assisted laser desorption/ionization (MALDI) (73) has allowed accurate analysis of high molecular mass species to bed one (22). A high powered pulsed laser is used to transfer

into the vapor phase the polymeric species which has been dispersed in a low molar mass matrix. The matrix, present in large excess (molar ratio 1:2000), is chosen for its ability to absorb the laser energy and protect the analyte, transferring energy to it in a way that allows desorption and ionization of molecules without significant fragmentation. Surprisingly, this simple change in handling technique has allowed species of up to 10^6 to be studied. Delayed extraction techniques enhance resolution (74,75). Calibration is necessary to quantify the intensities, lighter molecules are preferentially desorbed and ionized with respect to those having higher mass, and correction to the data is necessary. The resolution achievable has been enhanced by the use of time-of-flight mass spectroscopy to give TOF-MALDI (76,77). TOF-MALDI has also been applied successfully to biopolymer systems with precise molecular weight determination being possible up to 400,000 Da (78).

Electrospray mass spectroscopy (ESMS) is used for the study of biological macromolar species (79,80). Spraying produces droplets of the polymer solution which are ionized in an applied electric field and the charged species measured using a mass spectrometer.

Molar Mass and Molar Mass Distribution Determination

The GPC/SEC approach can be used for the determination of the molar mass or the distribution of molar masses. Traditionally, refractive index detection has been used and allows concentration of polymer to be measured as a function of elution volume. Using this approach, and calibration with narrow molar mass distribution samples, it is possible to determine the *relative* molar mass. Use of more complex detector arrays allows internal calibration of the system to be achieved and *absolute* molar mass determination (22,81). The usual triple detector combination uses refractive index, capillary viscometry, and light scattering (82–88). The latter provides an *absolute* calibration of the instrument; the capillary viscometry data gives through the intrinsic viscosity and hydrodynamic volume, information on the polymer–solvent interactions. Using this approach, studies have been carried out on multibranched star-shaped polyethers having poly(ethylene oxide)s (PEO) arms (82) which illustrate how the method can provide information on the architecture as well as molar mass. Due attention must be given to validating the accuracy of the theory for the particular type of polymer being studied (82–88). The multidetector systems are able to provide information on the size of the polymer molecule in solution (89).

Average Molar Mass.   The molar mass of a polymer is usually described by an average molar mass. If the chains are counted by number it is the number-average molar mass $\overline{M}_n$, whereas if it is counted by weight it is the weight-average $\overline{M}_w$; higher averages, $\overline{M}_z$, etc, can also be calculated. The parameter M_w/M_n, known as the molar mass distribution, is characteristic of the method of synthesis. Ionic and coordination polymerization will have an M_w/M_n approaching 1.05, whereas a polymer produced using a radical initiated reaction has values between 1.5 and 4.5. Insertion polymerization, eg Ziegler–Natta olefin polymerization, yields values between 5 and 20. With condensation and ring opening step growth polymers, the value of M_w/M_n will be between 3 and 20. The