MATERIALS CHARACTERIZATION SERIES

SERIES EDITORS: C. Richard Brundle and Charles A. Evans, Jr.

材料表征原版系列丛书

聚合物的表征

CHARACTERIZATION OF Polymers

Ned J. Chou
Stephen P. Kowalczyk
Ravi Saraf
Ho-Ming Tong

Mc Graw Hill Education

哈爾濱工業大學出版社
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Preface

Although a polymer specialist typically has the background needed to appreciate the subtleties of the polymer which are important for its application, he or she may not have the training to extract all the information available from the analysis of the polymeric material. Often, a polymer analyst has the opposite strengths and weaknesses. As a result, it is important for both the specialist and analyst to understand some aspects of the work of the other. But, whereas there are a number of books on surface and interfacial analysis written for the polymer analyst, there are few books written for the polymer specialist with a focus on surface and interfacial properties rather than the analysis. This series of books by Manning Publication Co., copublished with Butterworth-Heinemann, is intended to rectify this situation for polymers as well as ceramics, metals, semiconductors, and other materials.

The present volume, *Characterization of Polymers*, is intended for general polymer scientists and engineers without much experience in analysis but who have to deal with polymer surface and interface problems on a day-to-day basis. Because of the aforementioned focus on properties, and because many of the analytical techniques used for different types of materials are the same, this volume does not emphasize the characteristics of different techniques; this is accomplished in the lead volume of this Series, *Encyclopedia of Materials Characterization*. Instead, the present volume uses a case study approach to illustrate the importance of polymer problems and how they have been solved using surface and interfacial analyses. Each case study is carefully selected so that the whole range of important properties of polymers is adequately covered. The objective of this volume is not to make the reader an expert in analysis, but to get him or her started to become one. More importantly, the volume provides the reader with the knowledge to select appropriate characterization techniques which will help solve the problems at hand, and to plant questions and new ideas in the mind of the expert analyst with whom he or she is working. The techniques chosen are widely accepted techniques; novel techniques which have a high chance of acquiring wide acceptance in the near future are also mentioned.

Scope and Organization

The first two chapters give an overview of polymer chain structure and synthesis and fabrication techniques encountered commercially. The next five chapters discuss surface properties and modification techniques in the order of chemical composition, microstructures and related properties, structures and morphology of interfaces and thin films, thermodynamics, and surface modification. These are followed by four chapters dealing with interfacial properties involving at least one polymer.

Topics covered are adhesion, polymer–metal, polymer–ceramic, and polymer–polymer interfaces, as well as friction and wear pertaining to polymer damages caused by two contacting materials in relative motion. Chapter 7, on surface modification, bridges these two parts of the book because such techniques affect both surface and interfacial properties. Finally, in Chapter 12, references (e.g., books and handbooks) are given to aid in future studies. A brief description of all chapters is provided below to assist the reader in planning his or her studies:

Chapter 1, on chain structures and polymer synthesis, describes the chain structures in natural and synthetic polymers and the various routes of polymer synthesis. Also included is a brief description of polymer surface structure. Emphasis is placed on commodity structural polymers, engineering thermoplastics, high-temperature polymers, typical copolymers, and polymer blends.

Chapter 2 gives an overview on commercial polymers, their applications, and commonly used fabrication techniques for their processing. Polymer fabrication techniques discussed include foam processing, film forming/casting, composite processing, extrusion, and molding. Examples on the application of various fabrication techniques are described in some detail. When applicable, analytical methods are mentioned as they pertain to property studies or tailoring. The effects of processing on surface properties and others (e.g., mechanical and physical properties) are also discussed.

Chapter 3, on chemical composition, discusses the techniques and methodologies used to characterize the chemical composition of polymers. The main techniques used to determine chemical composition are summarized, and the types of information obtained from each are described. Chemical composition aspects that are addressed include degree of stoichiometry, functionality determination, completeness of reactions, reactive moieties, contaminations, dopants, surface segregation, and multilayer integrity.

A critical review of various microscopy techniques to measure the morphology of polymer surface and thin films is given in Chapter 4. This chapter describes contrast mechanisms and optics for various microscopy techniques, with specific examples from mesomorphic polymer systems to give an appreciation of the techniques. Apart from visualization, the chapter explains microscopy as a tool to obtain quantitative structural information when complemented with other methods. Recent scanning probe techniques such as atomic force microscopy and scanning tunneling microscopy, and modern developments in scanning and high-resolution electron microscopy, are also covered.

Surface morphology study using scattering methods is described in Chapter 5. The chapter outlines the theoretical and experimental aspects of the methods to provide an appreciation of their limitations and advantages. Less common methods such as surface wave probes and surface second-harmonic-generation methods that are established techniques but are not commonly used on polymer interfaces are also covered to highlight recent developments. Moreover, other surface methods such as grazing incidence X-ray scattering, reflectivity, and optical wave guiding covering length scale form 10^3 μm to 1 nm are covered.

Chapter 6, on surface thermodynamics, discusses the physical chemistry of polymer surface in terms of specific and dispersive interactions. This chapter outlines the theory of wetting and (work of) adhesion in terms of acid–base and London attraction. It provides the details on contact angle measurement techniques, adsorption isotherm methods and calorimetry, which are important in obtaining quantitative information on surface energy of interfaces with polymers. The chapter also touches upon ellipsometry serum replacement, inverse gas chromatography and infrared spectroscopy for the characterization of polymer surfaces.

Surface modification of polymers is covered in Chapter 7. Surface modification is an indispensable processing tool for the fabrication of a wide variety of polymer and plastic products. This chapter covers surface modification by mechanical means, by wet chemical treatments, and by dry processing techniques. This chapter also describes how surface modifications are monitored, as well as some of the tools that are employed in dry processing.

The successful application of polymers is quite often dependent on their adhesion to other materials. Chapter 8, on adhesion, reviews the basic concepts of adhesion. Some of the techniques to measure adhesion are described, along with their pitfalls. This chapter also discusses the issues of locus of failure, surface modification, and environmental stability.

Chapter 9, on primarily polymer–metal and polymer–ceramic interfaces, deals with the chemistry involved at these interfaces. Besides addressing the reactivity of these interfaces, the chapter deals with thermal stresses and interfacial fracture. These properties are particularly important for multilevel structures such as would be found in multichip modules important in microelectronics.

Chapter 10 details various techniques to characterize polymer–polymer interfaces. This chapter discusses the relevance of concentration profile of the polymers across the interface—a crucial property for adhesion and other interfacial properties. It also describes techniques such as forward recoil spectroscopy, neutron reflectivity, and dynamic SIMS nuclear reaction for quantitatively measuring interfaces of compatible and incompatible polymer systems.

In the preceding three chapters, ensuring strong adhesive bonding between materials is the aim. Chapter 11, on friction and wear, addresses how to minimize polymer damages caused by two contacting materials in relative motion. This chapter discusses the mechanisms and measurement of tribological properties and correlations between these properties with chemical, physical, and mechanical properties.

Chapter 12 provides readers with references for their future studies in the various subject areas covered by this book. Also given are references dealing with the investigation of polymers in general, polymer characterization and test methods, the advances in the use of computers for polymer research, and environmental effects on polymers. These references are included to help the reader formulate a well-rounded approach even though they may not be specifically related to polymer surfaces and interfaces.

We take this opportunity to thank the authors of the present volume, as well as Dr. Marjan Bace, Ms. Lee Fitzpatrick, and the editorial staff at both Manning Publications Co. and Butterworth-Heinemann for making this volume a reality. Thanks are also due to Dr. Richard Brundle, one of the two series editors, for many stimulating and informative discussions.

Ho-Ming Tong, Steven P. Kowalczyk,
Ravi Saraf, and *Ned J. Chou*

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1

Polymer Structures and Synthesis Methods

CHARLES E. ROGERS and ROBERT SIMHA

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1.1 Introduction
1.2 Chain Structures in Natural and Synthetic Polymers
1.3 Polymer Synthesis
1.4 Summary

1.1 Introduction

The purpose of this chapter is twofold. First, to introduce briefly certain basic notions and ideas in polymer science and the characterization of molecular structure, important for physical properties. Second, to sketch the various modes of preparation of synthetic polymers. Several of the topics mentioned here are given more detailed consideration and application in subsequent chapters.

1.2 Chain Structures in Natural and Synthetic Polymers

The Nature of Polymeric Materials

The essential difference between high polymers and most organic compounds resides in the word "high." Polymeric materials are characterized by high molecular weights and by a distribution of molecular weights in any given sample. Chemically, they are identical with their low-molecular-weight analogues. It is the very high molecular weights of polymeric materials that give them their properties, especially their mechanical properties, and, conversely, lead to difficulties in their characterization.

Most polymers are composed of long sequences of identical repeat units, the few exceptions being some naturally occurring and structurally complex polymers such as proteins and nucleic acids. The overall chemical composition of a polymer and

its distribution of molecular weights are major factors affecting its structure and properties.

The chain configuration—that is, the arrangement of the atomic groups along the chain, which cannot be changed except by breaking and reforming chemical bonds—is established by the synthesis process. It, and the environment of the polymer chain, determine the arrangement of the atomic chain in space, the chain conformation. That arrangement can be changed by rotations about single bonds. Intrachain and interchain interactions between groups on polymer chains significantly affect chain conformational structures.

Highly regular chain configurations allow solid polymers to form crystalline regions. The size and complexity of polymer chains usually limits the attainment of completely crystalline solids, in contrast to low-molecular-weight materials of the same general composition. Crystalline regions of polymers also contain many more defects. The topic of morphology considers the semicrystalline texture of polymeric materials.

A characteristic feature is the greater or lesser degree of chain flexibility, depending on structure. The chain conformations of polymers are almost always different in solution from what they are in the dry solid state. The changes in chain conformations induced by the presence of a solvent in various concentrations not only change its properties but also provide a valuable degree of freedom in characterization of the polymer. General and specific interactions in solution affect chain conformations in predictable and measureable ways.

The effects of temperature and added solvents on polymer conformational rearrangements, as related to the segmental mobilities of various groups and chain sequences of different size in the polymer, are important both for understanding structure-property relationships and for characterization. Transitions (melting, glass transition, secondary transitions) can be well-defined experimentally as functions of temperature, frequency, and solvent type and content.

Depending on their chemical compositions and consequent physical structures, polymers are familiar to us as elastomers, plastics, fibers, composites, coatings, adhesives, etc. Many polymeric materials are combinations of several different materials such as ceramics, metals, and other polymers. Low-molecular-weight additives serve as plasticizers, lubricants, antioxidants, flame retarders, etc. All of these components modify the polymeric material to some extent and must be accounted for in characterization of structure and properties.

A major categorization is into the classes of thermoplastic and thermosetting polymers. Thermoplastic polymers can melt or soften so that they flow and can be formed from one shape into another. In concept, this procedure could be repeated indefinitely. However, in practice, the polymer is subject to degradation at high temperatures, limiting the number of times it can be processed and still retain useful properties. Thermoplastics also can be dissolved, if a suitable solvent can be found. In both cases, after melting and cooling and after dissolution and precipitation, the thermoplastic material is nominally unchanged in its chemical composition.

Thermosets are polymers cross-linked into one giant molecule. After cross-linking into a three-dimensional network structure, they cannot be melted or dissolved, but only swollen by suitable solvents to form gels. They can be destroyed, either thermally, chemically, or mechanically, into compounds of composition and structure different from the starting material. Thermoplastics may be converted into thermosets, but we cannot go in the reverse direction. A vulcanized rubber tire is a good example: it can be burned or ground up, but it cannot be returned to a mobile melt state capable of flow to fill a mold.

The Composition of Polymeric Materials

The chemical composition of polymers is the single most important factor determining their structure and properties. Our ability to control the composition is the major factor which has led to the use of synthetic polymers in ever-expanding areas of application.

Polymeric materials may be based on the polymerization of a single starting material, a monomer, or on the simultaneous polymerization of two or more monomers in the same polymerization reaction. In the first case, the resultant polymer is termed a "homopolymer." The polymerization of polyethylene is an example:

$$n\mathrm{CH_2{=}CH_2} \rightarrow -(-\mathrm{CH_2}-\mathrm{CH_2}-)_n-$$

Repeat structures for typical homopolymers are illustrated in Tables 1.1–1.3. Table 1.1 lists the most widely used thermoplastic materials, characterized by moderate price and moderate to good properties. The first five polymers listed (to include a wide range of polymers based on polystyrene) comprise about 85% of the total amount of all polymers used for applications. Table 1.2 lists so-called engineering polymers, which generally are more expensive but have good to excellent properties. Polymers with good to excellent properties at high temperatures over a useful time span are given in Table 1.3.

When more than one monomer is used, the resulting polymer is a "copolymer," which has a composition reflecting the proportion of the component comonomers in the mixture and the relative reactivities of the different components. This dependency leads to sequential chain distributions (i.e., the sequence of occurrence of the different components along the main chain) of the polymerized components, which have a great effect upon the properties of the copolymer material.

The four general types of copolymer that can be made are classified as follows:

random: ~ABBAABAAABBABBBA~

alternating: ~ABABABABABABAB~

block: ~AAAAAAAABBBBBBBB~

graft: ~AAAAAAAAAAAAA~
└ BBBBBBBBBBBBB~

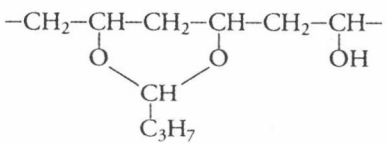
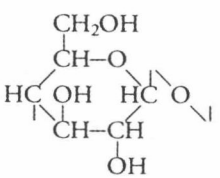
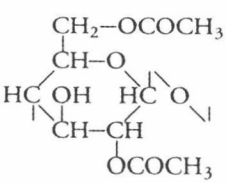
Polymer	Chain Repeat Unit	T_g/T_m, °C
Polyethylene, linear density = 0.96 g/ml	$-CH_2-CH_2-$	−80±10/138
Polyethylene, branched density = 0.92 g/ml	$-CH_2-CH_2-$	−80±10/105
Polypropylene, isotactic	$-CH_2-CH(CH_3)-$	−10/165
Poly(vinyl chloride)	$-CH_2-CH(Cl)-$	82/
Polystyrene, atactic	$-CH_2-CH(\varnothing)-$	100/
Polymethylacrylate	$-CH_2-CH(COOCH_3)-$	6/
Polymethylmethacrylate	$-CH_2-C(CH_3)(COOCH_3)-$	105/
Polyacrylonitrile	$-CH_2-CH(CN)-$	~100/~319d
Poly(vinyl acetate)	$-CH_2-CH(OCOCH_3)-$	28/
Poly(vinyl alcohol)	$-CH_2-CH(OH)-$	85/
Poly(vinyl butyral) (13.5 mole % of residual −OH)		49/
Cellulose		
Cellulose acetate		

Table 1.1 Commodity structural polymers.

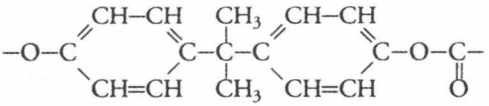
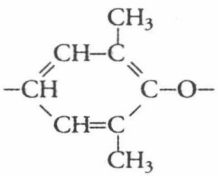
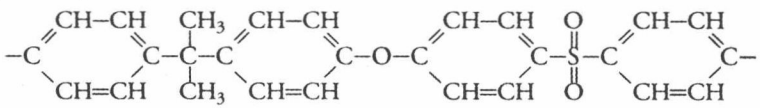
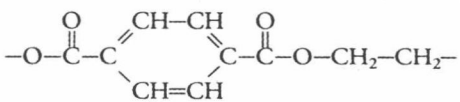
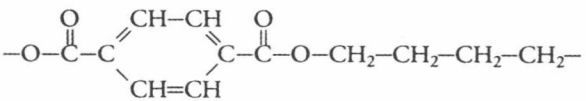
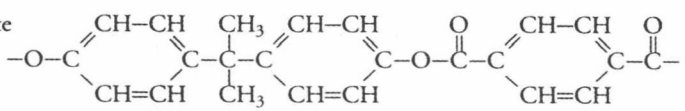
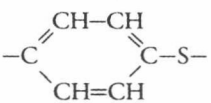
Polymer	Chain Repeat Unit	T_g/T_m, °C
Poly(hexamethylene adipamide) (Nylon 66)	$-NH-(CH_2)_6-NH-CO-(CH_2)_4-CO-$	~57/267
Poly(ε-caprolactam) (Nylon 6)	$-NH-(CH_2)_5-CO-$	55/221
Polycarbonate		149/
Poly(2,6-dimethyl phenylene oxide) (PPO)		135/261
Poly(ether sulphone)		190/
Polyoxymethylene	$-CH_2-O-$	−85/180
Polytetrafluoroethylene	$-CF_2-CF_2-$	−150/327
Poly(ethylene terephthalate)		70/265
Poly(butylene terephthalate)		17/240
Polyarylate		190/
Poly(phenylene sulfide)		185/285

Table 1.2 **Engineering thermoplastics.**

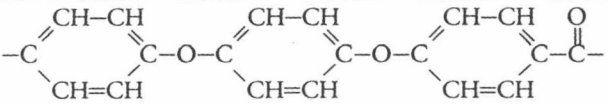
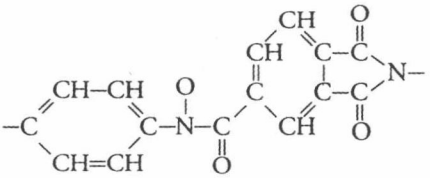
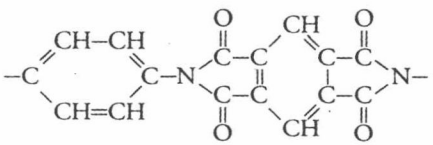
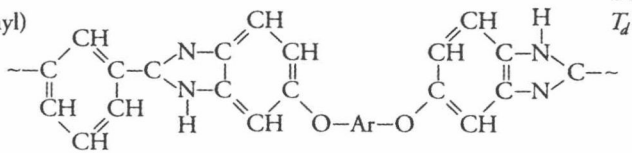
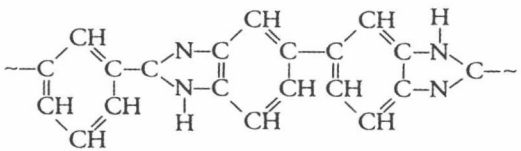
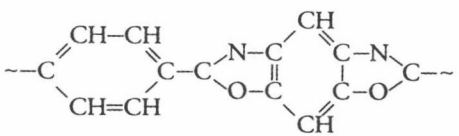
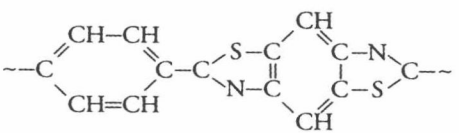
Polymer	Chain Repeat Unit	T_g/T_m, °C
Poly(ether ether ketone) (PEEK)		144/335
Poly(amide imide)		>290/
Polyimide		$T_d \approx 400$
Polyetherimide (Ar = 4,4′-biphenyl)		247/ $T_d \approx 460$
Poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (PBI)		~430 (500)/ $T_d \approx 420$ (480)
Poly(*p*-phenylene benzobisoxazole) (PBO)		$T_d > 400$
Poly(*p*-phenylene benzobisthiazole) (PBT)		$T_d > 400$

Table 1.3 **Polymers for high-temperature applications. T_d is the temperature (in °C) of onset of thermal decomposition (~1% weight loss per day).**