Block Copolymers

OVERVIEW AND CRITICAL SURVEY
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To our wives, Florence and Marlene, and to our children. We are indebted to them for their patience and support, and for their endurance of the inconveniences associated with our absence from home on many an evening.
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Preface

An enormous amount of interest has been generated in block copolymers in recent years. Our search of the literature, based primarily on "Chemical Abstracts" from 1960 through mid-1976, uncovered over two thousand references on block copolymers and related systems. Such a prolific outpouring can lead to considerable confusion, especially for those new to the area. This situation has generated a need for clarification of both the potentials and limitations of block copolymers. We felt that this need could best be fulfilled by writing a critical review of block copolymer technology—embracing all structural types and all facets of the field—that enunciates general principles and at the same time describes the individual systems in detail.

A bilevel strategy has been employed to achieve these dual goals and to serve two types of audiences. The book is comprised of two parts: (1) a concise, critical overview of block copolymer technology and (2) a comprehensive critical survey on the synthesis, characterization, properties, and applications of the specific block copolymer structures reported in the literature. The overview (Part One) presents a summarized and unified picture of the block copolymer field as a whole. It also attempts to place this field in perspective within the general framework of polymer science and to indicate some fruitful areas for future effort. Accordingly, this portion of the book should be useful both to those readers who want to become generally conversant with the technology and also, as a starting point, for those who need to delve more deeply into the subject. The latter audience is served by the critical survey portion of the book (Part Two), which discusses in greater detail the individual block copolymer structures. The copolymers are organized according to both segmental architecture and chemical composition. The organizational format of the book is described further in Chapter 1.

We felt that a book addressing the above-described goals should be written by a minimum number of authors in the interest of cohesiveness, and should be devoted exclusively to block copolymers, aside from discussion necessary to establish perspective. Although other books have appeared with the words "block copolymer" in their titles, they have been directed to different objectives, since they are compila-
tions of symposium papers or collections of individually authored chapters, or they deal with nonblock as well as block copolymers.

We hope that our active involvement in a variety of block copolymer synthesis and property investigations over the past decade has helped us to properly digest and evaluate the literature data. However, the reader should recognize that this experience may also have resulted in the appearance of a few opinionated statements.

We would like to acknowledge the encouragement for writing this book given by the Union Carbide management, particularly Drs. L. Shechter, T. T. Szabo, N. L. Zutty, E. F. Cox, and L. M. Baker. We would also like to thank several of our staff associates at Union Carbide, especially Drs. M. Matzner and L. M. Robeson, for many useful discussions. In addition, a number of colleagues, including Drs. G. L. Wilkes, L. J. Fetters, and P. C. Juliano, provided helpful comments and suggestions on portions of the manuscript.

Our sincere thanks are also extended to the many secretaries who transformed our often illegible penmanship into neat type: Mary Gallo, Barbara Cochilla, Ruth Horvath, Peggy Cox, Pat Kralovich, Joan Stryker, Rosemary DeSiato, Louise DeCastro, Kathy DeFeo, Kathy Moschak, and Pam Featherson.

We are grateful to the staff of Academic Press who helped bring this book to fruition.

Allen Noshay
James E. McGrath
Introduction and Format

Simply stated, the central theme of this book is that block copolymers, as one form of macromolecular architecture, have both potential and limitations. In some respects they offer unique possibilities not attainable with other polymeric materials; in others they offer no advantages. It is hoped that some degree of success will be achieved in elucidating this theme by providing a perspective picture of block copolymers.

This book has an organizational format that differs significantly from those employed in previously published volumes relating to block copolymers (1–10). It is divided into two parts. The first part, comprised of Chapters 2, 3, and 4, is an overview of block copolymer technology. Chapters 5, 6, and 7 constitute the second part, which is a critical survey and encyclopedic compilation of the many block copolymer systems reported in the literature.

Part One is intended to provide a qualitative understanding of what block copolymers are, how they are made, and what they can and cannot be expected to do. In addition, it serves as a guide to the second part of the book. In Chapter 2, block copolymers are defined and compared with other types of polymer “hybrids,” i.e., polymer blends, random copolymers, and graft copolymers. Chapter 3 describes the various segmental architectures that are possible with block copoly-
1. INTRODUCTION AND FORMAT

mers. Chapter 4 summarizes and compares (a) the various synthesis techniques applicable to block copolymers, (b) the characterization methods capable of elucidating block copolymer structures, and (c) the physical properties displayed by these systems. In addition, some of the applications of commercially available block copolymers are discussed in this chapter. Finally, Chapter 4 also identifies some future challenges for block copolymer technology in an attempt to stimulate further thinking along these lines and to focus attention on some of the important problems that still need to be solved.

Part Two discusses in considerable detail the synthesis, characterization, and properties of the various block copolymers described in the literature. The three chapters of Part Two are arranged according to block copolymer architecture, i.e., Chapters 5, 6, and 7 are devoted to A-B, A-B-A, and \((A-B)_n\) structures, respectively. Within each of the chapters, the copolymers are further subdivided according to chemical composition.

Specific block copolymers can be located by consulting the Table of Contents under the appropriate structural heading. The following, somewhat arbitrary, "structural hierarchy" was employed in organizing those chapter sections that deal with heteroatom-containing segments: polysiloxane > polycarbonate > polyurethane > polyanide > polyester > polyether > polyvinyl. A block copolymer in question will most often be found in that section pertaining to the segment most highly placed in the "hierarchy"; e.g., polysiloxane–polycarbonate systems are described in the polysiloxane section rather than the polycarbonate section. Since it was not always possible to adhere strictly to this general rule, the surest approach would be to consult the sections pertaining to both segments.

The literature references cited in this work include both publications and patents. Emphasis was placed on the publications, the more fundamental papers often being singled out for extensive discussion in order to illustrate important points. Most of the references are cited in the Part Two chapters (5, 6, and 7). For points of reference in Part One (Chapters 2, 3, and 4), the reader is usually directed to the appropriate sections of Part Two. In addition to the citation of references within the text, summary reference tables are provided in many of the sections of Chapters 5, 6, and 7. The letter prefix of reference citations reflects the chapter section, e.g., reference C15 is the fifteenth reference cited in Section C of a given chapter. Combined sectional reference lists are presented at the end of each chapter. In addition Supplemental References are provided at the end of Part Two. Subject and Author Indexes are located at the end of the book.
In Part Two an attempt has been made to provide (a) a complete compilation of all of the specific block copolymer structures reported, (b) a discussion of the major conclusions drawn by the workers (in many cases accompanied by critical comments), and (c) a convenient collection of the references pertaining to the various structures to permit “digging deeper.” However, detailed comparisons of characterization and property data (e.g., molecular weight, intrinsic viscosity, melting point) are not made unless required to illustrate a point. This was made necessary by the wide diversity that exists in the breadth and depth of the reported data. Characterization and property data are, in many cases, not available or cannot be compared from one reference to another in a meaningful way, since they had been determined by different techniques. Furthermore, in many instances, properties are attributed to an assumed but not adequately proved structure. Therefore, routine recitation of detailed data would be cumbersome and of questionable value. The original literature references provide a source of such detailed information for those seeking it.

IUPAC has not yet established a uniform system of nomenclature for block copolymers. Lacking this, it was decided to use an informal system of nomenclature in the interest of easier and more comprehensible reading. In many cases, the prefix “poly-” is omitted, resulting, for example, in the identification of a polystyrene–polybutadiene block copolymer as “styrene–butadiene” or simply “SB.” Liberties such as these are only taken, however, when it is obvious from context what the abbreviated forms mean.

Another decision made in the interest of conciseness was to minimize discussion of the polymerization chemistry and polymer characterization techniques that are generally applicable to all macromolecular systems. Thus, it has been assumed that the reader has a general knowledge of polymer science. This has, we hope, allowed us to focus more intently on those aspects that are unique to block copolymers: (a) the chemistry especially suitable for the synthesis of block structures, (b) the analytical tools that are particularly useful for characterizing them, and (c) the special physical properties that can be achieved.

REFERENCES

1. INTRODUCTION AND FORMAT


PART ONE

OVERVIEW
A. INTRODUCTION

The variety of macromolecules commercialized over the past four to five decades is truly phenomenal. The large number of products available to materials scientists for a given end use application is bewildering. Even design engineering experts have a difficult time in selecting the best material based on cost and performance. By far, the polymers most commonly used commercially are homopolymers. However, to a continually increasing degree, sophisticated applications are being developed that demand combinations of properties not attainable with simple homopolymers. As a result of this need, several techniques for producing polymer "hybrids" have arisen.

There are essentially two general approaches for forming polymer hybrids. The first and simplest approach is that of physically blending two polymers. The second general approach is "chemical" blending, i.e., the formation of copolymers. The latter can be further subdivided into random/alternating copolymers, graft copolymers, and block copolymers. Another, though less general, hybrid type is the interpenetrating network (A1), which contains one or more thermosetting resins. Many of these polymer hybrids, in addition to combining the
properties of their components, display unique, previously unanticipated behavior.

One purpose of this chapter is to briefly discuss properties that can be achieved with physical blends, random/alternating copolymers, and graft copolymers, giving illustrative examples of each. A second purpose is to compare these polymer hybrids with block copolymers as a general class of materials. The overall intent is to thereby place block copolymers in meaningful perspective vis-à-vis the other polymer hybrids. This will serve as an introduction to the remaining chapters of the book, where the various types of block copolymers are discussed.

B. PHYSICAL BLENDS

From a preparative point of view, the most direct and versatile method for producing polymer hybrids is the physical blending of two or more polymers. In most cases, this is also the most economical approach. Many commercially available products are blends of either two rigid polymers, two elastomeric polymers, or combinations of the two types. Since blends of crystalline polymers are considerably more complex and less well understood than amorphous blends, they are beyond the scope of this brief section. Accordingly, the discussion will be limited to amorphous blends.

The properties and, therefore, the utility of physical blends are strongly dependent upon the degree of compatibility of the components. The great majority of amorphous physical blends are highly incompatible (B1–B10). A very small number of amorphous polymer–polymer pairs are thermodynamically compatible, i.e., truly soluble in each other. Blends that display an intermediate degree of compatibility also exist. These are usually based on random copolymer rather than homopolymer components in order to achieve more closely matched compositions. These systems have been termed “mechanically” compatible (B11, B12). The salient features of each of these blend categories are described below.

1. Incompatible Blends

As already mentioned, high molecular weight polymer blends are nearly always grossly incompatible. Polystyrene–polybutadiene, polybutadiene–styrene/butadiene rubber (SBR), and polysulfone–poly(dimethylsiloxane) systems exemplify this type of blend. Incom-
compatibility is observed in dilute solution as well as in the solid state and in the melt. This is a direct consequence of the well-known relationship for free energy ($\Delta G$) given by the equation (B13):

$$\Delta G = \Delta H - T \Delta S$$

Polymers have very small entropies of mixing ($\Delta S$) due to their high molecular weight. Therefore, even a slightly positive enthalpy ($\Delta H$) due to endothermic mixing is sufficient to produce a positive free energy, thus resulting in incompatibility (i.e., polymer–polymer insolubility).

The incompatibility of the blend components provides a driving force for each to aggregate in separate phases. These two-phase morphological systems are coarse dispersions in which the particles are usually (a) large, (b) inhomogeneous, and (c) characterized by poor interphase adhesion. This behavior has important ramifications for the optical and other physical properties of the blends (B11). Since the phases are usually larger than the wavelength of light, excessive light scattering occurs at the phase boundaries, resulting in opacity. An exception to this behavior occurs if the refractive indices of the blend components are tailored to be nearly identical, in which case the two-phase blends can be transparent (B14). The poor interphase adhesion characteristic of highly incompatible blends usually results in very poor mechanical properties, e.g., tensile strength, elongation, and impact strength. This behavior is presumably related to a high degree of stress concentration in the vicinity of the interface. The thermal properties of these blends reflect the transitional characteristics of both components (B11).

2. Compatible Blends

It is very rare to find a pair of polymers that are truly compatible, i.e., completely soluble in each other. However, a few systems of this type do exist. The most familiar example is that of polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (B15, B16). Other examples include blends of amorphous polycapro lactone and poly(vinyl chloride) (B17) and blends of butadiene–acrylonitrile copolymers with poly(vinyl chloride) (B18). The reason for the compatibility of polystyrene with PPO has not been completely elucidated. However, it is believed (B5, B16) that the two materials have essentially identical solubility parameters. There may also be some weak intermolecular interactions that contribute to compatibility. The two poly(vinyl chloride) blend examples referred to above clearly owe
their compatibility to relatively strong specific interactions and/or “acid–base” interactions between the polar substituents (B19). These interactions produce exothermic heats of mixing and, hence, negative free energies, thereby resulting in compatible systems.

These compatible blends are characterized by single-phase morphology. As a result, they are transparent and exhibit physical properties intermediate to those of the components. The glass transition temperature (B20), rheology (B21), permeability (B22, B23), and mechanical properties displayed by these blends are predictable by the same techniques that are well known for random copolymers (B5).

3. Mechanically Compatible Blends

The incompatible and compatible blends described above represent the two extreme cases. However, some blends, which are most often based on random copolymer components, display intermediate behavior that can only be explained on the basis of partial miscibility or compatibility. A well-documented example of this type of mechanically compatible (B24) system is the blend of butadiene–acrylonitrile copolymer and styrene–acrylonitrile copolymer. This alloy constitutes one form of acrylonitrile-butadiene-styrene (ABS) resin (B10). Another example is the blend of polystyrene with SBR, which was one of the early but inefficient forms of impact-modified polystyrene. The borderline compatibility displayed by blends of this type is believed to be due to the similar but not identical solubility parameters of the components and also to possible weak specific interactions.

These mechanically compatible blends are essentially identical to the incompatible blends in their thermal behavior; i.e., they display two major glass transitions. However, their morphology is finer and they are more translucent. In addition, they display a higher degree of interphase adhesion, which is reflected in improved mechanical properties (B12).

C. RANDOM/ALTERNATING COPOLYMERS

The most common types of chemical hybrids are random copolymers and alternating copolymers. Random copolymers are characterized by a statistical placement of the comonomer repeat units along the backbone of the chain (see Fig. 2-1). They are the most versatile, economical, and easily synthesized type of copolymer. A wide variety of free radical and ionic addition and ring-opening polymerization