

SUPRAMOLECULAR POLYMERS

EDITED BY
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Preface

Contributions from various noncovalent, supramolecular interactions are present in both low molecular weight and polymeric organic materials. Even conventional macromolecules, stabilized by mainchain covalent bonds as originally described by Staudinger, display a variety of supramolecular effects that control their intramolecular conformation and their intermolecular interactions. The selection of systems to be included in a book on supramolecular polymers was therefore a delicate task.

In the early stages of planning the book the tentative title *Supramolecular Polymerizations* was adopted. It was thus intended to restrict the content of the book to the new class of self-assembled polymers that undergo reversible growth by the formation of noncovalent bonds. This class (Part II) is wider than expected: not only mainchain assemblies of hydrogen-bonded repeating units, but also planar organization of S-layer proteins, micellar and related three-dimensional structures of block copolymers may be described as a result of supramolecular polymerization.

The title that was ultimately chosen allowed for the inclusion of polymers conforming to the preceding definition and also the new class of supramolecular polymers that may be stabilized by covalent bonds but nevertheless exhibit *novel* supramolecular features. The latter class (Part III) is exemplified by covalent chains based on 2-concatenane units, dendrimers, monolayers, and some engineered assemblies (Part IV).

Included in the book is a general introduction to supramolecular interactions and assembly processes (Part I) along with two theoretical chapters detailing liquid crystalline phases and micellar-like aggregation, two important driving forces in supramolecular polymerization. Expected developments in supramolec-

ular polymer chemistry leading to functional *materials* and *systems* are highlighted in Part V.

The book focuses on the assembly of synthetic polymers and only relatively simple biopolymers are included. Attempts to control the structure and the growth of supramolecular polymers have been largely empirical. It is hoped that the highlighting in this book of the polymers so far investigated—and of the relevant theoretical mechanisms—will guide the organic chemist in designing chemical units that can be assembled into tailored materials and eventually functional systems.

Several applications as functional materials are already considered in the individual chapters. Hierarchical assembling allows the scaling-up to dimensions exceeding the micrometer range in several instances. Supramolecular polymers include dynamic structures endowed with internal mobility and the potential for storing information. Yet, we are still struggling to learn how to couple these characteristics of supramolecular polymers with their possible functioning as micro-engines allowing, for instance, molecular computing or the motility of some biological systems. A typical case is the long known globular \leftrightarrow fibrous ($G\leftrightarrow F$) transformation of actin. A basic mechanism for the $G\rightarrow F$ polymerization has been theoretically described. However, the overall functioning of actin as a system involves a coupling of the association process to a chemical reaction and to additional proteins that control polymerization. Understanding and reproducing coupled mechanisms is a road to future development in supramolecular science and functional systems.

The book was not intended to be a collection of unrelated chapters and efforts were made to achieve at least a partly coordinated outlook. This was made possible by the commitment and patience of the authors. Several discussions followed the preliminary draft, and some of the authors participated in meetings to arrive at a consensus over controversial issues. We were saddened by the premature death of Professor Raymond Stadler shortly after he had confirmed his participation in the book. His symbolic presence and enthusiasm are assured by the contributions of two of his coworkers.

Special thanks are due to Ms. Anita Lekhwani, Acquisitions Editor at Marcel Dekker, Inc., who first saw the importance of the emerging field of supramolecular polymers and insisted that the book should be written. The use of facilities at the Chemistry Departments of both Duke University and the University of Genoa greatly helped the editorial task. The book could not have been written without the encouragement and active cooperation of my wife, Cinzia.

Alberto Ciferri

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1

Mechanism of Supramolecular Polymerizations

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I. THE WIDE MEANING OF SUPRAMOLECULAR POLYMERIZATION

A. Supramolecular vs. Molecular Polymerization

The concept of covalent polymerization of bifunctional monomeric units was pioneered by Staudinger [1] in the early 1920s. He introduced the term “macromolecule” and proposed structural formulas for natural rubber, polystyrene, and polyoxymethylene that are still valid today. The invariance of the colloidal properties of these compounds in different solvents was one of the proofs adduced to support the concept of a linear sequence of covalent bonds exhibiting a large degree of polymerization (DP). The alternative model of a colloid-type aggregate stabilized by weaker secondary interaction was dismissed. Polymer science was then born, growing—distinct from colloid science—to produce the outstanding developments that have affected our lives.

Given the emphasis on the methods of synthesis and on the desirable properties of molecular polymers which continues to the present day, it is all too natural that the concept of a polymer composed by a long sequence of repeating units linked by noncovalent bonds received only limited attention. Thus, in spite of the fact that very long linear assemblies of globular proteins [2] or micelles [3] have been known for quite some time, the recognition of the potential of noncovalently bonded polymers had to wait until the early 1990s when significant developments in *supramolecular chemistry* occurred [4].

According to accepted current definitions, supramolecular chemistry is the chemistry of the intermolecular bond distinct from molecular chemistry, which

is the chemistry of the covalent bond. Thus, it is now appropriate to regard a long sequence of units connected by secondary bonds as a supramolecular polymer [4], distinct from a molecular polymer when repeating units are linked by covalent bonds as originally shown by Staudinger.

Correspondingly, one can introduce the term *supramolecular polymerization* [5] to indicate the assembly processes of supramolecular polymers, distinct from the well-known molecular polymerization processes (e.g., condensation, radical, ring opening, . . .) leading to molecular polymers [6]. The scheme in Fig. 1A emphasizes the difference between the type of repeating units and the type of mainchain bonds in supramolecular and molecular polymers of large DP. In the latter case, a chemical reaction between functional groups performed on rather simple low molecular weight monomers leads to a stable linear chain. The extent of growth is controlled by the product of the probabilities of single additions [6]. In the latter case, a *molecular recognition* process [4] leads to a reversibly *self-assembled* chain based on either low or high molecular weight complex repeating units. This chapter is primarily concerned with the analysis of parameters that control supramolecular polymerization through the formation of *supramolecular mainchain bonds in linear self-assembled polymers growing to a large DP*.

It is essential to appreciate from the outset that the concept of supramolecular polymerization entails a much broader significance of the types of repeating units and of their spatial arrangement than is the case with molecular polymers. For instance, the H-bonded supramolecular polymers [7–11] in Fig. 2 (cf. also this volume, Chapter 4) bear similarity to molecular polymers in both the relative

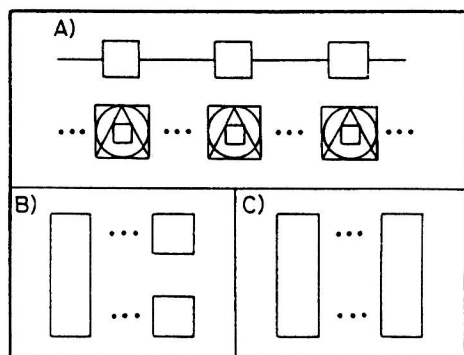


Figure 1 Schemes for: (A) linear molecular (small units, strong covalent bonds) and supramolecular (units of various size and shape, secondary bonds) polymerization; (B) supramolecular binding of small units to a molecular polymer; (C) supramolecular binding of two polymer chains.

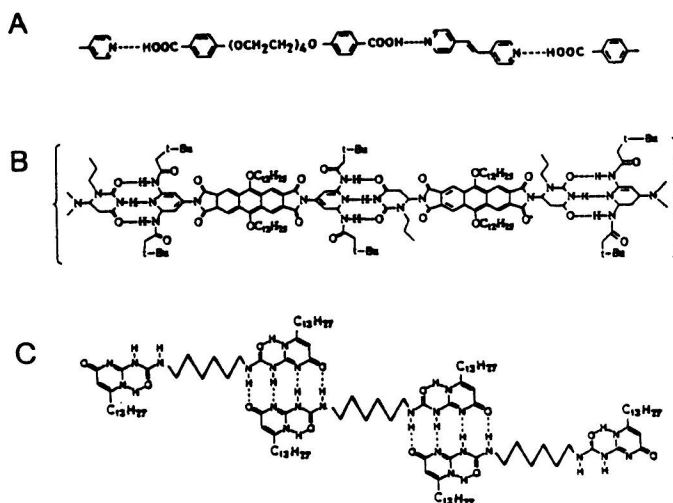


Figure 2 Supramolecular polymers stabilized by one (A, Ref. 7), three (B, Ref. 9), and four (C, Ref. 10) hydrogen bonds for repeating unit. Polymer A exhibits thermotropic liquid crystalline behavior ($T_{KN} = 168.5^{\circ}\text{C}$, $T_{NI} = 180^{\circ}\text{C}$). Polymer B forms a nematic lyotropic phase in 1,1,2,2-tetrachloroethane at RT. Polymer C is stable in isotropic solutions of chloroform.

small size of monomers and their chainlike assembly. Polymer A is stable in undiluted thermotropic mesophases. The rigid structure based on anthracene segments terminated by uracil or pyridine residues allows the stabilization of the supramolecular polymer B even in lyotropic mesophases in the presence of a solvent. Polymer C attains large DP even in isotropic solutions. The pseudopolyrotaxane assembly in Fig. 3 (cf. also this volume, Chapter 8) has H-bonded repeating units based on a dicarboxylic acid that contains a π -rich hydroquinone ring threaded through a π -poor tetracationic cyclophane cavity. Occurrence of linear pseudopolyrotaxane and their planar assemblies could be revealed by X-ray in the undiluted state [12].

The discotic 2,3,6,7,10,11-hexa-(1,4,7-trioxaocetyltriophenylene) amphiphilic molecule [13] in Fig. 4 (cf. also Section II.E and this volume, Chapter 2) can form single polymeric columnar assemblies stabilized by supramolecular bonds perpendicular to the monomeric surface in nematic solutions containing up to 50% solvent. The tapered 12-ABG-B15C5 compound [14] in Fig. 5, complexed with 0.4 M triflate salt per mole of the crown ether receptor B15C5, self-assembles into an hexagonal columnar (ϕ_h) mesophase revealed by X-ray and optical microscopy in the undiluted system. The column cross-section is based on disks

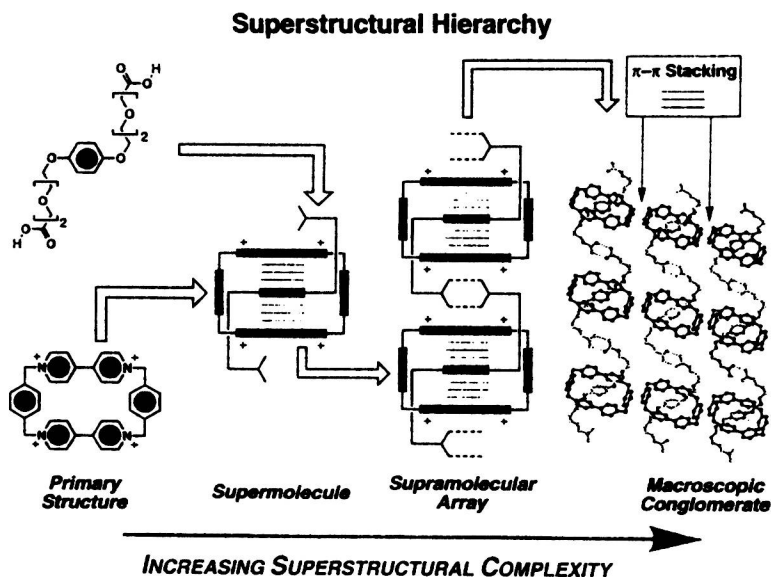


Figure 3 A dicarboxylic acid is threaded through a tetracationic cyclophane macrocycle to form a repeating unit which is connected to other units by a double H-bond. The evolution toward a pseudopolyrotaxane and a planar assembly stabilized by π - π stacking interaction is supported by X-ray data for the undiluted system. (From Ref. 12. Copyright 1997 Am. Chem. Soc.)

of five molecular units, the crown ether *endoreceptors* in the center being surrounded by the aromatic moieties, in turn surrounded by the melted alkyl tails of the *exoreceptor*. The latter may fold within each column, or interdigitate with adjacent columns. Electrostatic interactions between complexed and uncomplexed crown ether may assist the stacking of these units into channels parallel to the column axis. The disk can thus be regarded as the repeating unit of a tubular “polymeric” assembly.

Biological assemblies (Fig. 6A, B, C) such as fibrin [15,16], actin filaments [17], or microtubules [18] (cf. also Section III.C) are based on helical or tubular supramolecular polymers of globular proteins of high molecular weight, or of their oligomeric assemblies. These rigid assemblies attain lengths in the micrometer range. In the case of TMV, the tobacco mosaic virus (Fig. 6D), a molecular polymer (RNA) is hosted within the cavity of a supramolecular cylindrical assembly composed of 2,130 tapered proteins [19]. The above biological assemblies are stable in isotropic solutions even at rather low concentration. The linear assembly of cylindrical micelles [3,20] in the nematic phase (Fig. 7) should also

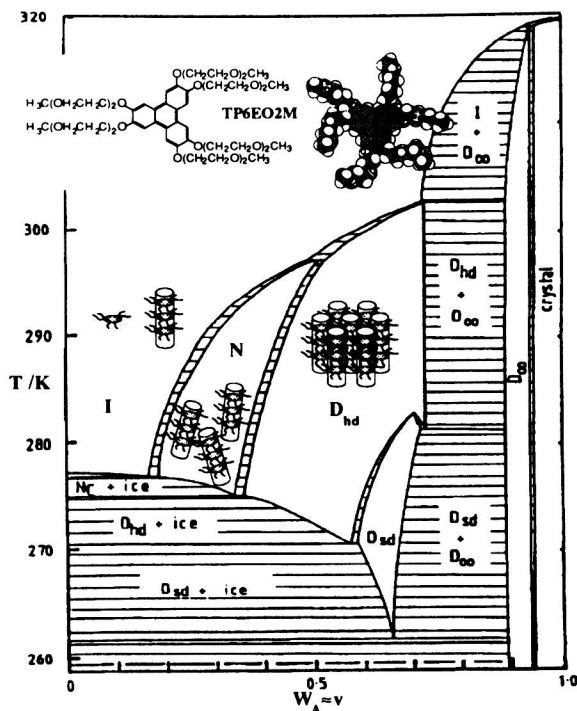


Figure 4 The discotic amphiphile 2,3,6,7,10,11-hexa-(1,4,7-trioxaocetyltriphenylene) is the repeating unit in a columnar stack stabilized by solvophobic interactions in D_2O . The temperature versus volume fraction phase diagram shows that single stacks occur in the nematic phase (N) at volume fraction as low as 0.2. Hexagonal columnar and eventually crystalline phases evolve upon increasing concentration. (From Ref. 13.)

be regarded as the result of a supramolecular polymerization driven by hydrophobic forces coupled with the orientational field of the mesophase.

The examples in the preceding figures show that only for some of the supramolecular polymers single assemblies of large DP are stable in diluted, isotropic solutions. In other cases (Fig. 4), single assemblies of large DP are stable only in relatively concentrated lyotropic solutions, when the orientational nematic field contributes to growth (cf. Sections II.E and III.B). In additional cases, the stabilization of single assemblies is restricted to undiluted thermotropic mesophases. These observations immediately suggest the occurrence of a variety of growth mechanisms that depend upon the strength and distribution of attractive interactions and the flexibility of the assembly.

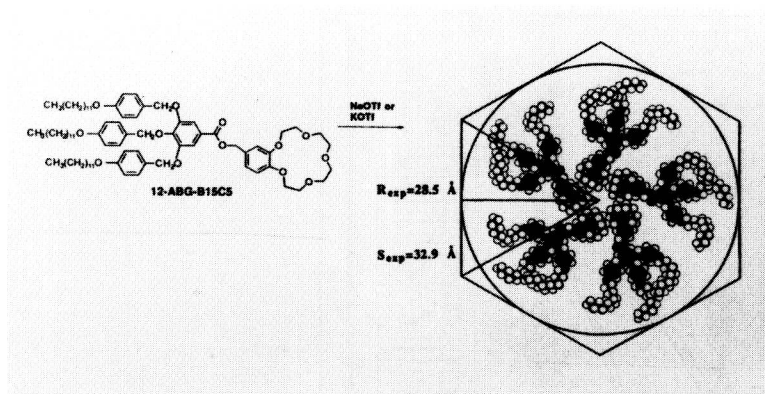


Figure 5 The assembly of the complex between 12-ABG-B15C5 and triflate salts produces undiluted hexagonal columnar mesophases based on stacks of disks each containing five molecular units (see also Fig. 8). (From Ref. 14.)

The concept of supramolecular polymerization need not be limited to linear or helical growth. Supramolecular interactions can develop into planar or three-dimensional structures capable of indefinite growth. In fact, organic crystals have been regarded as supramolecular entities [21]. A few examples of mesoscopic planar and three-dimensional supramolecular assembly are discussed in this chapter (Section III.D). More are to be found in other chapters. In particular, the solid state morphologies exhibited by block copolymers may also be conceived as a result of supramolecular polymerization with the axis representing the direction of molecular polymerization distinct from that representing the direction of supramolecular order. The concept of supramolecular polymerization can also be extended to organized aggregates such as closed micelles and open bilayers.

To further clarify the aims of this chapter, it should be pointed out that in addition to the mainchain interactions that control the growth of a supramolecular polymer, other types of supramolecular interactions do occur in both molecular and supramolecular polymers. Supramolecular effects in molecular polymers have been the focus of extensive study starting immediately after Staudinger's demonstration of the covalent nature of molecular chains. Conformation (or secondary structure) is controlled by supramolecular interactions among nonbonded atoms within a single molecular chain or supramolecular polymer. Sidechain binding, formation of multiple helices, liquid crystalline, and crystal morphologies are likewise controlled by supramolecular forces between chains or supramolecular assemblies. The current usage of the term supramolecular polymers also includes self-assembled systems in which the supramolecular interaction is not