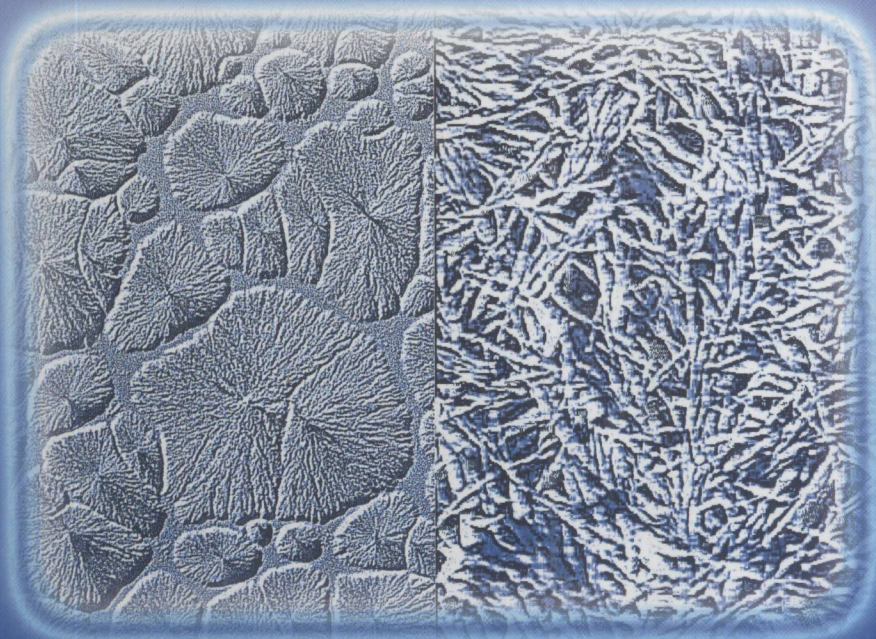




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Polymer-Solvent Molecular Compounds



Jean-Michel Guenet

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Polymer-Solvent Molecular Compounds

To my wife Chantal, and my daughters Delphine and Aurélie

To the memory of my parents

Cover pictures Left: spherulites from syndiotactic polystyrene/*trans*-decalin compound.
Right: fibrils from syndiotactic polystyrene/naphthalene compounds after naphthalene sublimation.

Foreword

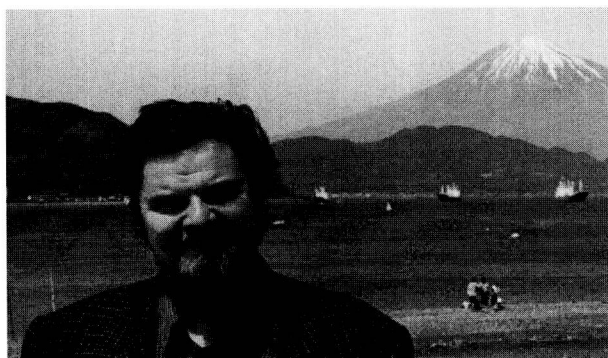
Crystallizable polymers represent a large proportion of the polymers used for manufacturing all types of products, and, as a result, have received the continued attention of scientists these past 60 years. The study of molecular compounds from crystallizable polymers, particularly from synthetic polymers, has been the growing subject of interest for the last 20 years or so. This is the case probably because many systems have been only recently discovered, as is the case of poly[oxyethylene] intercalates, or because the polymers have been newly synthesized, as is the case with syndiotactic polystyrene and syndiotactic poly[*para*-methyl styrene]. The present book is intended for bridging the gap and giving a description of the systems that have been extensively investigated. This book is divided into four parts. Part I is devoted to the presentation of important investigation techniques and some theoretical approaches. I have presented here what I felt was necessary for the understanding of this book. As will be discovered, temperature–phase diagrams are abundantly described, so a short section on how to map out and to decipher phase diagrams seemed to me necessary. Similarly, scattering and diffraction techniques are commonly used in the investigation of these systems and therefore a section on scattering and diffraction by rods, rod-like structures, and helices has been included, as the equations dealing with such systems seldom appear altogether in papers or books. A short section on a special aspect of NMR not frequently used but powerful for deciding whether compound formation takes place or not has also been written with the help of Professor J. Spěvák. Finally, a section is given on some theoretical approaches, which pertains essentially to the fibrillar gels. Parts II–IV describe the different polymers and biopolymers that are known to produce molecular compounds and that have been, and still are, extensively studied. Part II is therefore devoted to biopolymers, as these were certainly the first polymers known in relation to the production of molecular compounds, chiefly with water. These compounds very often already exist in the living systems from which the biopolymers have been extracted. In this case compound formation arises primarily from hydrogen bonding of the solvent molecules, in most cases water molecules, with the biopolymer. Part III deals with synthetic polymers where compound formation is either due to hydrogen bonding or to electrostatic interactions. Finally, Part IV describes intercalate and clathrate systems in which compound formation is mainly due to a molecular recognition process.

This book has been written over a period of several years, both in Strasbourg at Institut Charles Sadron, but also in my holiday house in Salviac in southern France during summer vacations. So, I have clearly to thank my wife Chantal and my two daughters, Aurélie and Delphine, for coping with a husband and father stuck to his computer for

hours, and being absent-minded for the rest of the time. My thanks also go to my colleagues who gave me valuable advice and/or read some chapters of this book to provide me with necessary criticisms and corrections. In particular, it is my pleasure to thank Dr Annette Thierry for reading the text on clathrates and intercalates, Dr Cyrille Rochas for perusing the section that deals with biopolymers, and Dr Alberto Saiani and Professor Yves Grohens for reading the section on PMMA gels. As aforementioned, Professor J. Spěvák helped me write the short section on NMR. I also benefited from discussions on poly[oxyethylene] intercalates with Professor Marcel Dosiere, who invited me as a guest-professor to Mons-Hainaut University, Belgium, on several periods. Discussions with Professor Hideyuki Itagaki on polystyrene systems during a stay as guest-professor in his laboratory at Shizuoka University, Japan, were more than helpful. I am also grateful to Professor Arun Kumar Nandi from IACS, Calcutta, who introduced me to the realm of poly[vinylidene fluoride]. Professor Larry Belfiore was also kind enough to read some of the chapters of this book and suggest appropriate corrections. I also wish to express my gratitude to my former PhD students and post-doctoral fellows Mohamed Ramzi, Christophe Daniel, Alberto Saiani, Sandrine Poux, Daniel Lopez, Biswajit Ray, Chinnuswamy Viswanathan, and, in particular, Sudip Malik, with whom we carried out investigations on syndiotactic polystyrene compounds, and who was of considerable help to me. Other colleagues were kind enough to provide me with the literature on different topics: Dr Henri Chanzy on cellulose and amylose, Dr Pascal Damman on poly[oxyethylene] intercalates, Professor Olli Ikkala on polyaniline, Professor Yashin Cohen on liquid-crystalline polymers, Professor Alain Domard on chitine, and Professor Vittoria Vittoria, Professor Gaetano Guerra, Professor Vittorio Petraccone, Dr Oreste Tarallo and Dr Christophe Daniel on syndiotactic polystyrene and syndiotactic poly[*para*-methyl styrene]. Note that, as far as it was feasible, figures appearing in this book have been redrawn from the original data for the sake of standardization. The references to the papers from which these data have been drawn are given when appropriate in the figure caption.

Finally, although I have tried to be as objective as possible, I would like to emphasize that this book is not just a review but a personal view on the domain.

About the Author



Professor Jean-Michel Guenet is Directeur de Recherche CNRS at Institut Charles Sadron, Strasbourg, France, a CNRS-owned laboratory associated with the Université Louis Pasteur. He was born in 1951 in Blanc-Mesnil, which is a suburb of Paris, France. He graduated in 1974 from Paris XIII University as a material science engineer and obtained a PhD degree in 1980 at Louis Pasteur University in Strasbourg. He was a post-doctoral fellow for one year at Bristol University, UK, with Professor A. Keller on a grant from the Royal Society. He was a visiting scientist at NIST with Professor G.B. McKenna, Gaithersburg, USA, in 1985, a visiting professor at Université de Mons-Hainaut, Belgium, with Professor M. Dosière from 1995 to 2004, and an invited professor at Shizuoka University, Japan, with Professor H. Itagaki in 2002. Apart from being the author of about 150 papers, he has also written a monograph on thermoreversible gels published by Academic Press in 1992 (*Thermoreversible Gelation of Polymers and Biopolymers*). In 1990, he was awarded the Dillon Medal of the American Physical Society for his work on polymer gels. He was the first non-American to receive this award. He is also the founder of a series of conferences entitled *Polymer-solvent Complexes and Intercalates*.

On ne doit pas exiger de cette classe d'hommes (les chercheurs) qu'ils professent et qu'ils enseignent, mais qu'ils inventent et qu'ils publient: car les découvertes sont rares; elles sont le fruit d'un long travail, de pénibles méditations; elles ne se commandent pas, et ne sont pas susceptibles d'être assujetties aux heures périodiques d'un cours public.

Antoine-Laurent de Lavoisier, *Réflexions sur l'instruction publique*

Introduction

The commonly accepted definition for a *compound* is a *chemical substance consisting of two or more elements chemically bonded with a well-defined ratio*. This ratio is termed the *stoichiometry* (from the Greek στοιχειον or *stoicheion*, which means 'element' and μετρειν or *metrein*, which means 'measure'). In many cases, the bonds are so strong (covalent bonds for instance) that the compounds exist in the three states, solid, liquid and gaseous (e.g. C_6H_6). The compounds of interest here are those that exist in the solid state but vanish in the liquid state, or even before melting through a *solid–solid transformation* process. This is so simply because the bonds between atoms or molecules are weaker and of the order of magnitude of kT . These systems are therefore not chemical compounds and are usually designated as *molecular compounds*. As will be discovered throughout this book, molecular compounds can also be designated as *crystallo-solvates*, *complexes*, *clathrates*, *intercalates*, or *inclusion compounds*, the use of which depends upon the system and/or the field of research.

Molecular compounds have been known for decades for atomic systems, such as some metallic alloys ($CuTi_2$, $AuSn$, $AuIn$, etc.), for minerals, such as salt hydrates ($NaCl \cdot 2H_2O$ etc.) and clays, and even for organic molecules such as urea inclusion compounds. There exist two categories of compound that display two different types of phase behaviour which are best described by the temperature–concentration (or composition) phase diagram (Figure 1): the *congruently melting* type, and the *incongruently melting* type.

Congruently melting compounds behave as a pure substance in that they have a well-defined melting temperature at the stoichiometric composition. For instance the alloy Cr_7C_3 melts spontaneously at $T = 1745^\circ C$ without prior solid transformation (Anderson 1987).

Incongruently melting compounds transform into another phase (solid phase or another compound of different stoichiometry) before the occurrence of the macroscopic melting

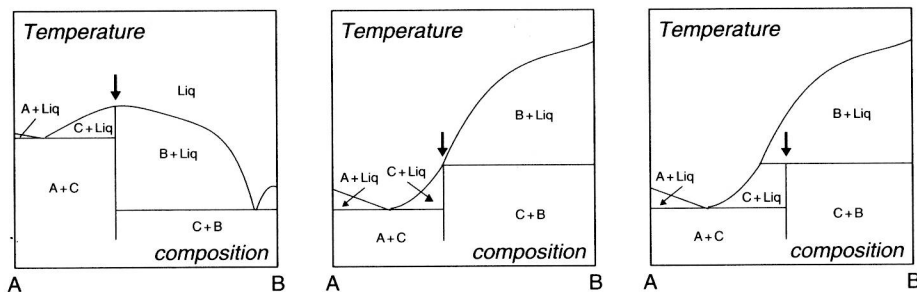


Fig. 1. Schematic temperature–composition phase diagrams for binary systems. **Left:** congruently melting compound; **right:** incongruently melting compound; **middle:** singular-melting compound. The phases in the different domains are labelled; C = compound, A and B = the two components of the binary system. The arrows indicate compound stoichiometry.

of the sample through a *solid–solid phase transition*. For instance $\text{NaCl} \cdot 2\text{H}_2\text{O}$ transforms into pure NaCl crystals by releasing water molecules at $T = 0^\circ\text{C}$. Similarly, the alloy Cr_3C_2 transforms into graphite and a liquid (Anderson 1987). Note that *peritectic transformation* is very often used for designating the incongruently melting process although it is not, strictly speaking, correct. As a rule, a peritectic system is closer to the case of a solid solution. Incongruently melting compounds are only a special case of peritectic.

The intermediate case between the congruently melting and the incongruently melting compound, designated as *singular-melting compound*, actually behaves like a congruently melting compound, in that no transformation of the type *compound* \rightarrow *solid phase* + *liquid* occurs, but direct melting. This is the case for alloys such as AuSb_2 (Chevalier 1989).

Molecular compounds possess a molecular arrangement in the solid state where each position of the crystalline lattice is occupied by a given atom or molecule (see Figure 2). The crystal unit cell of a molecular compound is not that of any of its constituent but one of its own. As a result, the diffraction pattern of a molecular compound differs from that of any of its components, and gives therefore an additional hint, together with the T–C

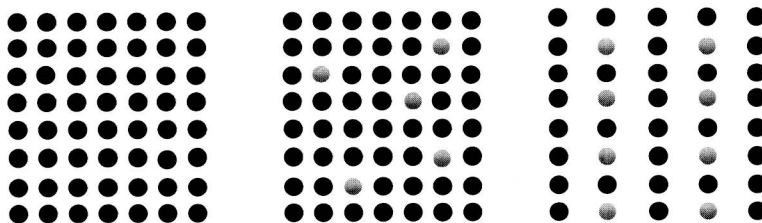


Fig. 2. Schematic representation by means of a 2D lattice of the molecular arrangement of a pure substance (**left**), of the solid solution of a binary mixture (**middle**) and of a binary molecular compound (**right**); here the stoichiometry is 1 grey molecule (atom)/4 black molecules (atoms).

phase diagram, of compound formation. This is clearly at variance with a *solid solution* where the atoms or molecules are dispersed randomly on positions of the crystalline lattice of the main component. In this case, increasing the minor component eventually leads to a phase separation. In the case of a molecular compound, gradual addition of the minor component increases the fraction of compound until the stoichiometric composition is reached. On reaching the liquid state through heating, all the components are randomly dispersed, and therefore what was previously a molecular compound with specific properties has simply become a homogeneous, liquid mixture.

In the case of macromolecules, aqueous molecular compounds were already known at the turn of the twentieth century for biopolymers such as cellulose and amylose. Some compounds of these polysaccharides with organic molecules, such as amines, were also studied. Since the synthesis of synthetic crystallizable polymers such as polyethylene, and, later, stereoregular polymers such as isotactic polypropylene, much attention has been paid to their crystallization behaviour, as well as to their molecular structure. In particular, the chain trajectory within the heterogeneous semi-crystalline environment was a matter of bitter debate between those scientists promoting regular chain-folding in the lamellar crystals, and those advocating random re-entry. The controversy was just fading away as growing evidence for regular folding were collected, when polymer-solvent intercalates were discovered for poly[oxyethylene] (PEO) (Point and Coutelier 1985; Point et al. 1986a; Point and Demaret 1987) and suggested for isotactic polystyrene (iPS) thermoreversible gels (Guenet 1986; Guenet and McKenna 1988). In the former case, this discovery was largely fortuitous. It turned out that the supposed growth of PEO single crystals in dilute solution of this polymer in a mixture of isomers actually produced PEO intercalates with one of the isomers of the solvent (see Intercalates in Chapter 14). The large difference in melting point between pure PEO crystals ($\sim 63^\circ\text{C}$) and PEO intercalates ($\sim 90^\circ\text{C}$) settled the issue, which might otherwise have gone unnoticed. Since then, other molecular compounds have been discovered with the newly synthesized syndiotactic polystyrene (Immirzi et al. 1988; Vittoria et al. 1988), but also with poly[vinylidene fluoride], poly[vinyl chloride], and many others that will be detailed in this book.

In the early days of polymer science, most known compounds were formed between biopolymers and water through hydrogen bonds. As a result, it was generally admitted that strong interactions, such as hydrogen bonds, were required. Yet, simple organic solvents could also do the trick thanks to a molecular recognition process between the microstructure created by the helical form of the polymer and the shape of the solvent (intercalates). Schematically speaking, one could therefore distinguish between two classes of compounds: *enthalpic* compounds formed through strong interactions, either hydrogen bonds or electrostatic interactions, and *entropic* compounds for which the driving force is molecular recognition and only involves weaker interactions of the van der Waals type. To be sure there exist hybrid systems where both mechanisms come into play. This is the case with some PEO intercalate compounds where hydrogen bonds are also involved.

The morphologies of these polymer-solvent molecular compounds can be of the *spherulitic* type or of the *fibrillar* type for the same polymer depending on the solvent used. The latter situation usually promotes the formation of thermoreversible gels. As

will be detailed in this book, the interaction at the molecular level between the polymer and the solvent molecules is mainly responsible for these morphologies by altering the chain persistence length.

Despite the wealth of investigations, there still exists a common, sometimes deeply rooted, prejudice in that crystallization and, in particular, thermoreversible gelation would be favoured in poor solvents on account of a phase separation process. This comes from a view inherited from Flory's theory on polymer solutions for which *liquid-liquid phase separation* occurs on cooling below the θ -temperature, namely on crossing the *binodal line* (Flory 1953). This line delimits a so-called miscibility gap, within which solutions of crystallizable polymers should supposedly be quenched to produce gelation. In early studies (Feke and Prins 1974), it was even considered that thermoreversible gelation resulted from *spinodal decomposition*, one of the two possible mechanisms of the liquid-liquid phase separation process (see Chapter 1). Yet, crystallization and gel formation are more likely to proceed through *liquid-solid phase separation* on cooling below the *liquidus* line, which does not imply that the solvent is necessarily poor. On the contrary, compounds can form in good solvents, 'good' in the sense of Flory's theory, namely well above the θ -temperature of the polymer-solvent couple. Indeed, a good solvent is capable of promoting aggregation of the type *polymer-solvent-polymer*, through molecular recognition for instance, particularly if the organized state (crystal in most cases) is more stable than the disordered state (the liquid). This is the case for many systems, as will be discovered throughout this book.

Before presenting polymer-solvent molecular compounds, the main investigation tools widely used for investigating and characterizing these systems are briefly described in the four chapters of part I.

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The butterflies spread their sails on the sea of light. Lilies and jasmines surge up on the crest of the waves of light, The light is shattered into gold on every clouds, and it scatters gems in profusion.

Rabindranath TAGORE in “Gitanjali” (1912)

PART I

Investigation tools

The easiest and most straightforward way of investigating molecular compounds is initially to map out the temperature–concentration phase diagram. This diagram provides invaluable information about compound formation, the different phases and domains, and, in many cases, the stoichiometry(ies). This should be the first step of any study. Once the various phases and domains have been identified, then and only then should further investigations be carried out. In particular, molecular structure and morphology can be investigated by use of scattering and diffraction techniques that will help establish the nature of the crystal unit cell and the type of helical structures involved. There will be a feedback which will help to confirm the outcomes from the phase diagram and resolve any ambiguities. The chapters in Part I are therefore dedicated to the presentation of the various techniques and theories – not necessarily detailed in standard textbooks – that may be useful for achieving these investigations.