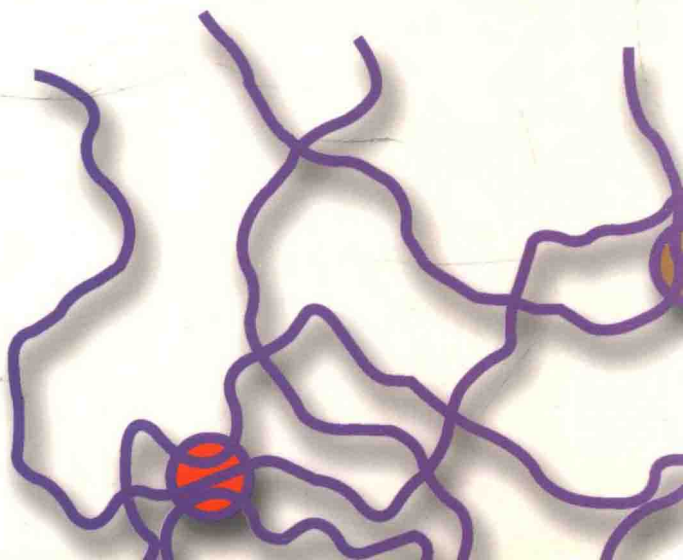
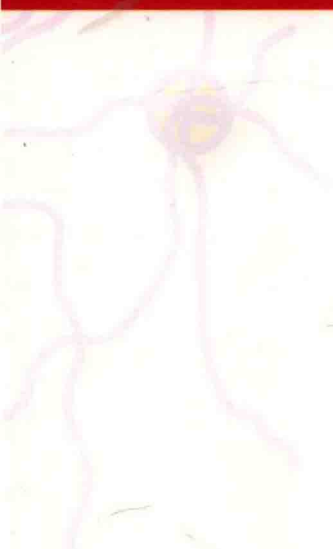
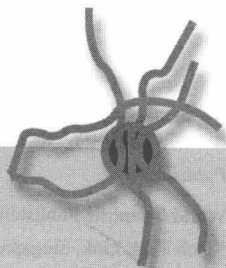


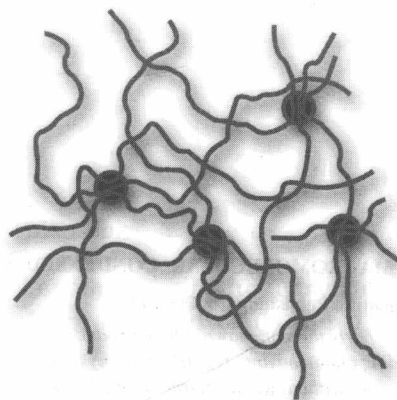
Perspectives on the Macromolecular Condensed State

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Perspectives on the Macromolecular Condensed State

Preface

For quite some time I had been reluctant to consider writing a book about polymer physical chemistry or polymer physics. Science and technology had been advancing so fast in the latter part of the past century that a publication on science would be out of date in a few years. Three years ago I gave a series of lectures at the Institute of Chemistry, Chinese Academy of Sciences, on "Aspects of the Macromolecular Condensed State," summarizing the research results of a project on "Study of Some Basic Physical Problems in the Macromolecular Condensed State." These lectures were well received by my colleagues and students. Then Prof. Rongben Zhang of the Institute urged me to write up the lectures, as so many new ideas, physical concepts and research directions had emerged during those studies. Now this book is completed after almost three years of work. I am greatly indebted to Prof. Zhang for his encouragement and generous offer of help in various ways, without which the writing of this book would never have been started.

Having worked through the subject matter of this book, I strongly feel that the present status of our understanding of the molecular behavior of polymers in the condensed state is very unsatisfactory — in some areas not even on a sound basis. I do hope that the presentation of the many new physical concepts in this book is clear enough to stimulate further deliberation and developments. The physical concepts of single chain and interpenetrated multichain condensed states, Gauss chains and looped chains are to be scrutinized. The role played by intersegment cohesion in the formation of the macromolecular condensed state, and the understanding of the polymer crystallization process and the molecular behavior of interpenetrated Gauss chains in their relaxation process

and mechanical deformation processes, are to be further explored. I shall be happy to see if the physical concepts presented in this book are proved or disproved, or modified and improved by the younger generation. Polymers are a class of important materials. We are quite bewildered by the fact that so many new polymer materials appear in the literature from time to time, which may have potentially important applications and be suitable for large scale production. There is no question that these frontier subjects of wide, deep interest should be the focus of major research efforts, in order for us to achieve fast economic development. In the meantime, it is wise to have some people engaged in unveiling the true physical nature of a phenomenon or process, which leads to the advancement of science.

Last but not the least, I would like to thank all my former students, co-workers and collaborators who have contributed to the development of the ideas and concepts discussed in this book throughout the last two decades. I am also grateful to the Chinese Academy of Sciences, the National Natural Science Foundation of China and the Ministry of Science and Technology for their continuing support of the research done on the macromolecular condensed state for the past fifteen years. Thanks are also due to Prof. Yong Huang of the Institute of Chemistry, Chinese Academy of Sciences, for the unpublished electron micrographs of disclinations of cholesteric liquid crystalline polymers, to Ms Jiazhi Zheng for her painstaking preparation of the figures, and to the publisher, World Scientific, for their kind and efficient cooperation. Finally, I would like to express my gratitude to my wife, Dr. Yansheng Yu, for her good help, fine care and forbearance on occasions of solitude and inconvenience during the two years when I was absorbed in writing this book.

Renyuan Qian

Beijing; September 18, 2001

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Introduction

0.1 In Retrospect

The development of polymer science started from the establishment — by H. Staudinger in the 1920s¹ — of the concept of macromolecules as long chain molecules with repeating chemical structural units and a molar mass exceeding 10^4 , instead of an aggregate of small molecules as colloid particles. It took almost ten years to gain universal recognition of this illuminating concept among the scientific community. The experimental determination of molar masses of these macromolecules played an important role in establishing a firm basis for the concept of macromolecules. This led to the evolution of a new branch of science and a wide field of scientific investigations on the structure and properties of synthetic and naturally existing polymer molecules.

In the evolution of polymer chemistry, the important events may be outlined as follows. The polymerization reaction was soon understood as either stepwise polycondensation or addition polymerization of chain type reaction of vinyl compounds and dienes by free radical, cationic and anionic initiators. Studies on the mechanisms of polymerization reactions, molar mass and molar mass distribution of polymers resulted; chain branching and crosslinking, copolymerization, and molecular chain structure and sequence structures followed. Then came the development of polymerization catalysts and polymerization technology for industrial mass production of commodity polymers. This made polymers a material of huge production capacity — already comparable to that of metals — and of so diverse applications in daily life and in advanced technology as to represent a synthetic polymer age in human

civilization. More refined progress has been made in the direction of polymerization reactions to yield polymers of defined molar mass and molar mass distribution, intended chain microstructure and tacticity, designed chain architecture and function, so that there will eventually be a new era of molecular engineering of polymers.

In the evolution of polymer physics, the understanding of rubber elasticity² played a central role, as this is the unique physical property of flexible long chain molecules. Internal rotation of the back bone chain bonds and chain conformation are the basis for our understanding of the physical structure, flexibility and intrachain thermal motion of molecular chains. A random walk chain known as a Gauss chain morphology was introduced as a model for the long chain molecule. It was recognized quite early that intermolecular interactions between chain segments, and between chain segment and solvent molecules in a polymer solution, have a very distinctive effect on the morphology of single chains in dilute solution. This led Flory to introduce the concept of the θ temperature³ or θ state for polymer solutions and for chain morphology, where the long range intersegmental interactions vanish (long range in the sense of "along the chain") and the chain morphology is truly a Gauss chain. Flory's conjecture⁴ is that in the amorphous molecular condensed state of polymers the chain morphology of each chain in this multichain system is the same as that in a θ solution. This was confirmed by small angle neutron scattering experiments twenty years later. An immediate deduction from this is that in the amorphous state of polymers, either in fluid, rubbery or glassy states, the macromolecular chains are interpenetrated with each other to a high degree. This is a first step in our understanding of the amorphous macromolecular condensed state. Application of the scaling concept to polymer physics⁵ produced a new impetus to the study of concentrated polymer solutions, which is on the doorstep of understanding the macromolecular condensed state. The concept of chain entanglement has been widely referred to for the behavior of concentrated solutions and bulk amorphous polymers,⁶ especially in the flow of polymeric fluids. However, its precise nature is still not clear up to the present. Investigations of the viscoelasticity of polymers played a very important role in our understanding of the dynamic properties of polymers.⁷ A wide distribution of relaxation times and time-temperature equivalence and superposition are characteristic properties of polymers. Glass transition and the phenomenon of so-called physical aging,⁸ i.e. the effects of annealing at sub-glass-transition temperatures, are important for our understanding of the glassy state, but they are still very bewildering. The discovery of single crystals of polymers from

dilute solution⁹⁻¹¹ changed our view of the chain morphology in semicrystalline polymers from fringed micelles to regular folded chains. Although a large number of studies have been done on the crystallization process of polymers, the present status of our understanding of the crystallization process is still greatly controversial. The polymeric liquid crystalline state opened a new chapter on liquid crystals.¹² Owing to the long relaxation time of polymer chains, many transitory and unstable defect states, like disclinations of director orientations, could be easily observed in liquid crystalline polymers.¹³ The appearance of band texture in liquid crystalline polymers after being subjected to either shearing¹⁴ or solidification¹⁵ is far from being properly understood. Recent observations of single chain single crystals have provided insights into the crystallization process from dilute solutions, and, more important, have led to a new field of the single chain macromolecular condensed state.¹⁶

0.2 Key Issues

The footprints of development in our understanding of the behavior of long chain molecules outlined above have made polymer physics a science of some degree of maturity. However, many issues of basic importance remain to be understood, particularly on the molecular level. In the first place the term “condensed state” is not in common usage for polymers. There is no clear idea what kind of molecular condensation is meant for polymers, and the process of molecular condensation between polymer chains has not been well studied. Of course, molecular condensation is a manifestation of intermolecular van der Waals interactions, in which the intermolecular attractive interaction plays an important role, deprived of which the formation of a condensed state would just be impossible. For polymers this attractive intermolecular interaction, hereafter referred to as cohesive interaction, should mean the intrachain and interchain interactions between structural units of the chains. Although this cohesive interaction energy between two structural units of a chain is very weak, there are a large number — say, 10^3 – 10^6 — of structural units per chain, and consequently the sum total cohesion energy per chain would be a very large number, as compared to the cohesion energy between two small molecules. In the amorphous state of a bulk polymer the macromolecular chains are interpenetrated to a high degree, as mentioned in the previous section; the interchain cohesion energy would involve the sum total of cohesion energy of the whole structural units of the chains. That is why a polymer chain would be

thermally decomposed before being vaporized. Consequently the process of macromolecular condensation could only be studied by going from a very dilute solution, where polymer chains are isolated, to a concentrated solution, and eventually to a solid, where the chains are interpenetrated. This technologically important process of film formation from polymer solutions has not been well studied from the viewpoint of molecular condensation, because of the complexities of the process. The conformation of an isolated chain in a dilute solution is well known to be sensitive to the intersegmental interactions and segment — solvent interactions, as displayed by the effects of temperature and the nature of the solvent on intrinsic viscosity, which is a measure of the hydrodynamic volume of the chain. Here and throughout this book a chain segment will mean a chain structural unit or a few neighboring units. The so-called coil expansion — or, more correctly, coil swelling — in a good solvent is a manifestation of intersegmental decohesion by solvent molecules, which acts as if there appeared an intersegmental repulsive interaction, and hence is usually called volume effect. The important effect of intersegmental cohesion for an isolated coil was first brought to attention by Stockmayer,¹⁷ who introduced the term “coil collapse” for significant shrinkage of the coil dimension when cooling a dilute polymer solution below its θ -temperature. In other cases, even in the condensed state of polymers, the cohesive interaction is always considered so small as to be unimportant. The repulsive interaction between closed electron shells of all atoms is very short-ranged, with an interaction potential $U_{\text{rep}}(r) \propto r^{-12}$ (r is the interatomic distance), while the cohesive interaction is longer-ranged, with an interaction potential $U_{\text{coh}}(r) \propto r^{-6}$, after Lennard-Jones.¹⁸ The equilibrium configuration of molecular packing in the condensed state of molecular solids is mainly determined by the repulsive interactions between molecules, and is true for long chain polymers as well. But it should be emphasized here again that in the process of formation of a condensed phase the cohesive interaction plays an important role and should be of prime consideration.

A condensed state of polymers is of course a multichain system except for the case of the single chain condensed state of polymers, which has become an emerging field of study only recently. In general we have not dealt properly with the behavior of interpenetrated coils as compared to that of a single coil. In the past, one always considered the behavior of a single coil to be the model, or at least a first step toward understanding the behavior of a real multichain system. We have been successful, in fact, in demonstrating the important properties of flexible chain polymers like rubbery deformation very early (Kuhn¹⁹), and

viscoelastic behavior involving a spectrum of relaxation frequencies (Rouse²⁰) with simple theories based on a single coil. On the other hand, the complexity of the system of interpenetrated coils renders the theoretical treatment very difficult to carry through. We are even not sure in what respect and to what extent the behavior of an interpenetrated multichain system is different from that of a single chain system. In dealing with the behavior of a macromolecular condensed state, one should always keep in mind whether an interpenetrated multichain system or a single chain system is involved.

0.3 The Scope of This Book

This book will start from the process of formation of a macromolecular condensed state, i.e. the transition from isolated single coils in a very dilute solution to a concentrated solution and then to a solid where the Gauss coils are interpenetrated. It is followed by a discussion on the behavior and salient properties of the amorphous state, the liquid crystalline state and the crystallization of polymers in succession with an increasing degree of molecular order of the condensed state. Finally, the single chain macromolecular condensed state, mainly single chain glass, single chain single crystal and a single chain in the rubbery state in a solution, will be described. The material of this book is based on the experimental findings obtained in recent years by many polymer scientists in China, who have been working on the National Key Projects for Fundamental Research — “Study of Some Basic Physical Problems in the Macromolecular Condensed State,” Ministry of Science and Technology, People’s Republic of China. A number of new concepts and sound physical pictures for the understanding of the macromolecular condensed state have emerged from these studies. Proper considerations for the cohesive interactions between chain segments in the formation of the macromolecular condensed state will be given and the difference in behavior of single chains and interpenetrated chains will be emphasized. Naturally, many questions will crop up throughout the book and remain unanswered; they may even be greater in number than the questions answered. Therefore the author hopes to see a fresh impetus to the study of many old problems which are basic to our understanding of the macromolecular condensed state. The discussion of the rubbery state of polymers will not be included in this book, as the author thinks that our understanding of the nature of the rubbery state is essentially correct, whereas, in other areas, like the amorphous state and the crystallization

process of polymers, despite the copious publications that have appeared in the literature, our understanding is in many respects still rather limited, especially on the molecular level. In some cases, even the basic physical picture is in a state of much controversy. The author believes that an illuminating physical picture which reveals the true physical nature of a process or phenomenon is the solid basis on which a good, refined theory of the process or phenomenon should be built. A good theory is to be judged from the correctness of its very starting assumptions and physical picture rather than merely from a quantitative agreement between the theory and the experimental results. Things are often complicated, especially for a complex system like a polymer. In view of the unavoidable simplifications and approximations (which sometimes may even be drastic) to be adopted for a mathematical formulation and a workable solution of the problem, one does not expect to have a precisely quantitative agreement in every detail between theory and experimental results for most cases. The real progress in scientific understanding of a process or phenomenon lies in the stepwise uncovering and comprehension of the true nature of the process or phenomenon in an asymptotic way by creative minds. Based on these sound physical ideas, quantitative theories are to be developed. Science will thus advance to a new level. In what follows in this book, out of the huge number of works in the literature, only those which are relevant to our discussion will be cited.

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Chapter 1

The Process of Formation of the Macromolecular Condensed State from Isolated Coils in a Dilute Solution

1.1 Concentration Regimes

For practical purposes, a polymer solution is usually classified as a dilute solution, a concentrated solution or a plasticized polymer, in order of increasing concentration of the polymer in the system. The boundaries between these concentration regimes are not precisely defined. In the development of scaling theory, de Gennes introduced the concept of semidilute solution¹ in the concentration region between a dilute and a more concentrated solution. The boundaries are defined as the overlap concentration c^* , where the polymer coils in solution begin to be in contact, and the concentration c^+ , where the segment density of the polymer chains in a concentrated solution reaches an almost uniform value everywhere in the solution. In a dilute solution, if it is dilute enough so that the polymer coils are isolated from each other, the space distribution of the segment density of the chains is necessarily nonuniform, being congested around the mass center of each coil and leaving the space between the coils entirely vacant. Qian² introduced the concept of dynamic contact concentration c_s ; above this concentration the coils in solution begin to “feel” the presence of neighboring coils in solution, and the coil dimension begins to shrink. The situation of the different concentration regimes can be visualized schematically, as shown in Fig. 1.1.

The physical concept of overlap concentration c^* is very simple and clear. It is easily calculated from the coil dimension in the solution at infinite dilution as obtained by light scattering of dilute solutions. However, the coil dimension in a solution of good solvent will shrink starting at c_s , not c^* , so that the value