Liquid Crystalline Order in Polymers

edited by

Alexandre Blumstein

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Contributors

Donald G. Baird
J. J. Beres
Alexandre Blumstein
Y. Bouligand
C. R. Desper
Bernard Gallot
Edward C. Hsu
J. Preston
E. I. Rjumtsev
Edward T. Samulski
N. S. Schneider
I. N. Shtennikova
V. N. Tsvetkov
J. H. Wendorff

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Alexandre Blumstein

Department of Chemistry
Polymer Program
University of Lowell
Lowell, Massachusetts

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List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

*Donald G. Baird** (237), Monsanto Textiles Company, Pensacola, Florida
J. J. Beres (299), Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts
Alexandre Blumstein (105), Department of Chemistry, Polymer Program, University of Lowell, Lowell, Massachusetts
Y. Bouligand (261), E.P.H.E., Histophysique et Cytophysique, C.N.R.S., Centre de Cytologie Expérimentale, Ivry-sur-Seine, France
C. R. Desper (299), Polymer and Chemistry Division, Army Materials and Mechanics Research Center, Watertown, Massachusetts
Bernard Gallot (191), Center for Molecular Biophysics, Orléans, France
Edward C. Hsu (105), Department of Chemistry, Polymer Program, University of Lowell, Lowell, Massachusetts
J. Preston (141), Monsanto Textiles Company, Monsanto Triangle Park Development Center, Inc., Research Triangle Park, North Carolina
E. I. Rjumtsev (43), Institute of Macromolecular Compounds, Academy of Sciences of USSR, Leningrad, USSR
Edward T. Samulski (167), Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Connecticut
N. S. Schneider (299), Polymer and Chemistry Division, Army Materials and Mechanics Research Center, Watertown, Massachusetts
I. N. Shtennikova (43), Institute of Macromolecular Compounds, Academy of Sciences of USSR, Leningrad, USSR
V. N. Tsvetkov (43), Institute of Macromolecular Compounds, Academy of Sciences of USSR, Leningrad, USSR
J. H. Wendorff (1), Deutsches Kunststoff Institut, Darmstadt, West Germany

* Present address: Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 24061.

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Foreword

For many years we have known that certain solutions of rigid chain polymers could show nematic (or cholesteric) ordering, and the field appeared to many of us as devoid of mysteries. But suddenly, inventions of physical chemists (both in the U.S. and the U.S.S.R.) have brought the subject to the forefront: "magic fibers" can be obtained from certain nematic phases containing rodlike macromolecules as explained by J. Preston in Chapter 4. The impact of these findings reminds me of the days when the group at RCA discovered the "dynamic scattering" of nematics in electric fields and immediately produced a great increase in research on liquid crystals all over the world. Data on polymeric mesophases have been accumulating very quickly; this book gives us the first detailed survey of what is known in the field. In particular, it has become increasingly clear that many *flexible* polymers also show remarkable organization:

(1) Chains with mesogenic side groups display nematic and smectic ordering which is described by Blumstein and Hsu in Chapter 3. In the nematic phases the backbone often has a disturbing effect on the order; but fortunately, nematic alignment can still be found in a number of cases in both homopolymers and copolymers.

(2) A very interesting field for future research is that of chains in which the *backbone* is made up of mesogenic moieties connected by suitable flexible links. Chapter 1 by J. H. Wendorff contains some examples of such structures, and I hope to hear more about them in the future! Here we would expect weaker disturbances of the nematic order. On the other hand, in reticulated structures, we should find a remarkable coupling between nematic and mechanical properties—e.g., an isotropic–nematic phase transition induced by stress, with resulting nonlinear mechanical responses.

(3) It may well be that certain of the "magic fibers" are not completely rigid when in dilute solution, but become simultaneously rigid and nematic at higher concentrations. This effect, which I associate with the heroic motto "United we stand, divided we fall," is currently under theoretical study. On the experimental side, the careful measurements on dilute solutions performed by the Strasbourg and Soviet schools and described here by V. Tsvetkov (Chapter 2) are fundamental. Of course, they should be supplemented later by studies on chain elasticity in the concentrated nematic phase.

At this point we meet one aspect of a general problem: how to connect the local (single chain) viewpoint with the global mesomorphic properties. One

attractive example is discussed here by E. Samulski (Chapter 5): the helical pitch in cholesteric PBLG solutions can to some extent be predicted from a simple discussion based on single chain polarizabilities. Another question of similar nature is related to the Frank constants of the nematic phase. In a rigid rod system both splay and bend are "hard." In a system of flexible coils that become nematic through local interactions, I expect the bend to become "soft," the splay remaining "hard": this may provide a simple distinction. There should be many other observations of this kind.

Certain *geometric concepts* will be essential in the analysis of polymeric liquid crystals; some of these are very clearly illustrated in the discussion by B. Gallot on block copolymers (Chapter 6). One crucial parameter is A, the "area per polar head" of lipid–water systems or its long chain counterpart which I characterize by a chain current $\mathbf{J}$ ($J = 1/A$). In block copolymers AB we often expect that there will be no chain ends inside one region (A or B). Then $\mathbf{J}$ is a conserved current and this implies many important properties for layers, rods, etc. Inside a layer we can also measure the quadrupolar alignment $\mathbf{Q}$ discussed here by Tsvetkov (Chapter 2). What is the relation between $\mathbf{J}$ and $\mathbf{Q}$ in dense polymeric systems?

Another geometrical problem is the classification of the phases observed: for instance, the remarkable phase shown by some phosphazenes (Chapter 9) and muscle structures (Chapter 8) are probably "canonical" phases (with strict periodicity in a plane normal to the optical axis) rather than nematic. This distinction is clearly stated by the authors, and is not purely academic. (A nematic can be twisted by cniral solutes and it also has a strong intrinsic turbidity, but these two features are not expected in a canonical phase.)

A third kind of geometrical problem is related to the *entanglements* of long chains when they are at least partly flexible. Entanglements are not readily detected through structural studies but they play an essential part in the dynamics of chains. The rheological properties of these polymeric phases are thus expected to be very complex but they will carry important information; on the other hand they dominate the field of fiber applications. They are reviewed here in clear terms by D. G. Baird (Chapter 7).

This volume gives us a broad coverage of the properties of these new materials. It presents a balanced combination of innovative chemistry and theoretical approach: Professor Blumstein, who is one of the pioneers of the field, has now, as an editor, made this information accessible to a large scientific community, and should be heartily congratulated.

P. G. de Gennes

Preface

The field of liquid crystalline order in polymers has come in recent years to the forefront of activity. The impetus was provided by the development of ultrahigh strength/high modulus fibers spun from nematic solutions of macromolecules with rigid backbones.

The topic of liquid crystalline order in systems containing rigid synthetic macromolecular chains, as interesting and as important as it may be, is but a limited area of a much vaster field that includes various aspects of liquid crystalline order in natural and synthetic macromolecules. In spite of the interest, most of the literature concerning liquid crystalline order in polymers is scattered throughout a great number of scientific journals and symposia and the patent literature. Thus we felt that the time had come to review the field and to concentrate the information available in a book entirely devoted to this subject. The book should also provide a balance of topics which seem to have been strongly shifted in favor of topics of immediate industrial concern.

Each chapter of the book provides a self-contained and up-to-date "state of the art" review of one important area of the field. Chapter 1 (Wendorff), although devoted to scattering in polymer systems with liquid crystalline order, provides the reader with an introduction to the field of liquid crystals and a general overview of the topics to be treated in some of the following chapters. Chapter 2 (Tsvetkov, Rjumtsev, and Shtennikova) treats the origin of liquid crystalline order in macromolecules by describing the in-depth study of conformation of such macromolecules in their unassociated state. Such studies not only are at the root of understanding the intramolecular order of macromolecules with mesogenic segments, but are also important in the understanding of their intermolecular ordering in bulk or in concentrated solution. The chapters which follow describe successively the liquid crystalline order in polymers with mesogenic side groups (Blumstein and Hsu) and rigid backbones (Preston), in polypeptides (Samulski), and in block copolymers (Gallot). The rheology of such systems is described in Chapter 7 (Baird).

The diversity of the field of liquid crystalline order in macromolecules is well illustrated in the three chapters that encompass the formation of lyotropic liquid crystallinity in block copolymers (a topic of considerable technical importance), liquid crystalline order in biological materials

(Bouligand), and mesomorphic order in the realm of polymers with inorganic backbones (Schneider, Desper, and Beres). Professor Bouligand's chapter vividly shows the extraordinary variety of liquid crystalline organizations, be they at the molecular level of biomembranes, at the supermolecular level of cell organelles, or at the macroscopic level of various tissues. It demonstrates that liquid crystalline order in biological systems plays an important part in the functions and properties of living matter.

It is my hope that this book will provide the polymer scientist, the materials scientist, and the biologist with a valuable source of information. I also hope that the graduate student will be stimulated by this book to study a new and fascinating interdisciplinary field which, judging from the great diversity of natural and synthetic materials displaying liquid crystalline order, holds high hope for the future.

I would like to take this opportunity to express my thanks to the authors for their efforts and to the publisher and the staff for efficient cooperation.

1

Scattering in Liquid Crystalline Polymer Systems

J. H. Wendorff

Deutsches Kunststoff Institut
Darmstadt, West Germany

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I. Introduction

Polymers that display structures that are intermediate between the three-dimensionally ordered crystalline state and the disordered isotropic

fluid state have been given considerable interest in the last few years for the following reasons:

(i) These polymers can be considered as model systems for isotropic amorphous polymers, where semiordered regions have been proposed to exist, and for drawn amorphous polymers, where by the drawing process a high degree of orientational order can be introduced.

(ii) Polymers that form partially ordered melts or partially ordered solutions can be processed in such a way that fibers with a very high degree of orientational order and chain extension are obtained. This specific structure leads to superior mechanical properties of the material.

(iii) Polymers with ordered melts are of technological importance for the same reasons that low molecular weight systems with anisotropic melts are used widely today in technical products such as electrooptical displays. Additional advantages are expected for polymeric systems, since parameters such as side group structure formations or copolymer formations will lead to a large variety of properties of semiordered melts.

(iv) Finally, if the polymerization is carried out in semiordered liquid phases of the monomer or in semiordered solutions, it is possible to study the polymerization process in ordered systems. This will allow a deeper insight into the reaction mechanism. Also, by this procedure, macroscopically ordered polymers may be obtained if the monomer phase is macroscopically ordered, for instance, due to an external field or due to forces exhibited by specific surfaces. In this case interesting optical properties are expected for the polymeric system.

For these reasons a variety of different studies has been made of polymers with potentially ordered melts or solutions in the last few years. The polymers studied were polymers in which the ordered structure was displayed by the side groups. In this case the structure of the main chain is only of secondary importance. It is intended to give in this chapter a survey of structures that are encountered in low molecular weight liquid crystalline systems, of methods that can be used to analyze these structures, and of studies of structural analysis of polymers with semiordered melts. A considerable part of the chapter will be devoted to a description of the molecular structure displayed by these phases and of specific structural studies of these phases. The author felt that because of recent advances in the structural analysis of polymeric systems and liquid crystalline systems (such as neutron small angle scattering on partially deuterated samples), and in view of the small number of detailed structural studies of polymers with semiordered melts, a general survey of the problem would be useful.

II. Characteristic Properties of Liquid Crystalline Phases

A. Physical Properties

Liquid crystalline phases have been known to exist in low molecular weight systems since the end of the nineteenth century. Reinitzer (1888) observed a peculiar melting behavior for a number of esters of cholesterol. He found that the crystals of the substances melted sharply to form not an isotropic melt but an opaque melt. The conclusion drawn from this observation was that some type of order still existed in the molten state. Reinitzer furthermore observed that the opacity vanished at a higher temperature called the clearing temperature. Two years later, Lehmann (1890) reported that ammonium oleate and *p*-azoxyphenetole exhibited turbid states between the truly crystalline and the truly isotropic fluid state. Subsequent studies by these authors indicated that these opaque systems were thermodynamically stable states (Gray, 1962). They also concluded that the structure of these phases had to be intermediate between the crystalline and the fluid state.

To describe this strange behavior of the fluid state, Lehmann introduced the term "Flüssige Kristalle" (liquid crystals). Later Friedel (1922) proposed that it would be more reasonable to refer to these phases as mesophases or mesomorphic phases. It was soon recognized that mesophases may arise as a result of temperature variations, thus the term thermotropic mesophases is used. Mesophases may, however, also result from changes of the concentrations of solutions. With increasing concentration, a transition from a nonordered isotropic solution to an ordered anisotropic solution can take place. For such systems the term "lyotropic liquid crystals" is used. Lyotropic systems show also thermotropic behavior: on heating they become isotropic. A mesomorphic phase characterized by a reversible phase transition is referred to as "enantiotropic." "Monotropic" liquid crystalline phases are stable only in the supercooled state. Monotropic phases are therefore characterized by a transition temperature that is lower than the transition temperature of the neighboring phase.

Since the early work on liquid crystalline phases, a large amount of work has been performed in order to elucidate the peculiar structure and the specific properties of the mesophases. The studies were primarily concerned with the detection of new mesomorphic substances and with measurements of their optical properties. The supermolecular structure was in general studied by means of the polarizing microscope (Gray, 1962). Conclusions with respect to the molecular structure of these phases were drawn from the supermolecular structure and from the miscibility behavior of different