

POLYMERIC LIQUID. CRYSTALS

Edited by

ALEXANDRE BLUMSTEIN

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PLENUM PRESS • NEW YORK AND LONDON

Library of Congress Cataloging in Publication Data

Symposium on Polymeric Liquid Crystals (2nd: 1983: Washington, D.C.)
Polymeric liquid crystals.

(Polymer science and technology; v. 28)

Includes bibliographical references and index.

1. Liquid crystals—Congresses. 2. Polymers and polymerization—Congresses. I. Blumstein, Alexandre. II. American Chemical Society. Division of Polymer Chemistry. III. American Chemical Society. Meeting (1983: Washington, D.C.) IV. Title. V. Series.

QD923.S96 1983

548'.9

84-25478

ISBN 0-306-41814-2

Proceedings of the Second Symposium on Polymeric Liquid Crystals, Division of Polymer Chemistry, held as part of the American Chemical Society meeting, August 28–31, 1983, in Washington, D.C.

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A Division of Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

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Printed in the United States of America

PREFACE

This book originated in the Proceedings of the Second Symposium on Polymeric Liquid Crystals held by the Division of Polymer Chemistry in the framework of the 1983 Fall Meeting of the American Chemical Society.

At the First Symposium in 1977, the literature in this field could be encompassed in a single volume. Today, that is no longer possible. The field of Polymeric Liquid Crystals grew, and continues to grow, at a very rapid pace. At present, we know of every major mesophase in its polymeric form and of polymeric glasses, elastomers and fluids in their liquid crystalline form. Every year, new polymeric mesophases are being discovered.

The aim of this book is to go beyond a compilation of papers presented at the 1983 ACS Fall Meeting. It is conceived as a learning tool for the benefit of the scientist interested in Polymeric Liquid Crystals.

The book is divided into three sections. The first section contains articles discussing synthetic, physico-chemical, structural and rheological aspects of Polymeric Liquid Crystals in their generality. A chapter on methods currently used in this field is also included. There are also chapters on theoretical and classification aspects of PLCs. These self-contained tutorial chapters provide an introduction to this field as well as to the specific papers given in the book. They provide an exhaustive coverage of literature on the subject from its inception to the present.

The second and third sections deal with thermotropic and lyotropic LCP systems. Papers are grouped together by structure of the polymer chain rather than by the nature of properties investigated. The reader can thus compare research on similar polymers approached from different perspectives.

Rigid and semi-rigid main chain systems, historically the first synthetic PLCs studied, are treated with emphasis on structural, morphological, and mechanical properties. More recent flexible main chain systems are discussed, focusing mainly on structure-property relationships.

Various aspects of liquid crystallinity in flexible polymers with the mesogenic moiety in the side group are discussed in several articles. The focus here is on the liquid crystalline behavior in electric fields and possible applications of PLCs in electro-optical display and recording. The properties of a novel group of PLCs -- liquid crystalline elastomers -- obtained from mesogenic side group systems are also described.

In the last section of the book, lyotropic systems are treated. These concern derivatives of cellulose in various solvents as well as solutions of synthetic PLCs in low molecular mass liquid crystal solvents and polypeptide solutions in water. The last article illustrates the tremendous variety of polymeric bio-mesogens encountered in living matter.

Thus, this book provides an exhaustive cross-section of the field from the historical, tutorial and present day "state of the art" perspectives.

I would like to thank Mrs. Sarah Goldman for her invaluable help with the preparation of this book. I would also like to thank the authors for their efforts and Plenum Press for their efficient cooperation.

Alexandre Blumstein
Lowell, Massachusetts
May, 1984

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LIQUID CRYSTALLINE POLYMERS: PHENOMENOLOGICAL AND SYNTHETIC ASPECTS¹

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INTRODUCTION

Since the discovery of liquid crystallinity by Reinitzer³ in 1888 as he studied the melting behavior of cholesteryl benzoate, anisotropic structural ordering in fluid phases has been of considerable interest to chemists, physicists and other scientists. Polymers which exhibit liquid crystallinity either in solution (lyotropic) or in the neat state upon heating (thermotropic) have both theoretical and practical importance. Du Pont's Kevlar®, a high modulus polyamide fiber spun from a lyotropic solution, is a prime example of such an application. In order to profitably discuss the structure and properties of polymeric liquid crystals it is necessary to briefly describe and define several aspects of liquid crystallinity in small molecule (low molar mass) compounds.

Liquid crystallinity (mesomorphism) can be observed directly on heating from a solid phase (enantiotropic) or it can be seen only upon supercooling the isotropic liquid phase below the melting temperature (monotropic). In the former case the mesophase is thermodynamically stable and can be obtained on both heating and cooling cycles. In the latter case, the mesophase is metastable with respect to the solid and is seen in the cooling regime only. The liquid crystalline state is characterized by long range (as well as short range) orientationally ordered molecules. These molecules are usually rod- or lath- shaped and can exist in two major structural arrangements. These two types, the nematic and the smectic, are each characterized by parallelism of the major molecular axes and are shown in Figure 1. The nematic phase allows for translational mobility of constituent molecules; the smectic phase is composed of

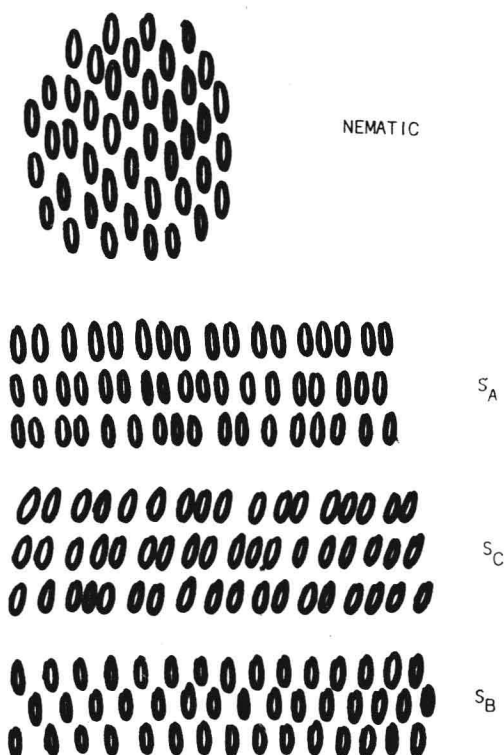


Figure 1. Schematic of Molecular Organization in Nematic and Smectic Phases.

molecular layers in which translational mobility is minimal. There are a variety of smectic phases classified as S_A , S_B , S_C , etc., differing in i) the ordering (or lack thereof) of molecules within the same layer, ii) the tilt (or lack thereof) of the "average" molecular axis with respect to the layer plane and iii) the positional correlation of molecules in different layers. The cholesteric phase is locally similar to the nematic phase. However the constituent molecules are chiral giving rise to an asymmetric helical packing of molecular "sheets" due to the spontaneous twist resulting from molecular chirality.

Compounds forming small molecule thermotropic liquid crystals usually have the following molecular structural features:

- high length: breadth (axial) ratio
- rigid units such as 1,4-phenylene, 1,4-bicyclooctyl,

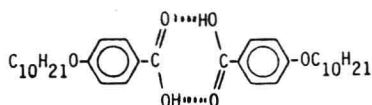
1,4-cyclohexyl, etc.

- rigid central linkages between rings such as -COO- , -CH=CH- , -N=NO- , -N=N- , etc.
- anisotropic molecular polarization.

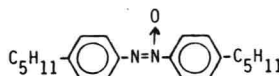
There are exceptions to each generalization above, but the list can serve as a rough guide to predicting liquid crystalline (mesomorphic) potential of a given compound. Examples of thermotropic compounds are shown in Figure 2. In general the nematic phase is predominant for compounds having short flexible tails and the smectic phase is dominant for compounds with long tails. Both phases are often seen when tail length is of intermediate length. Figure 3 shows this behavior in schematic form. Lyotropic liquid crystals result from very specific interactions between an amphiphilic solute and solvent(s). Typical low molar mass lyotropic combinations are sodium dodecyl sulfate/water/1-alkanol and phospholipid/water.

Characterization of Liquid Crystals

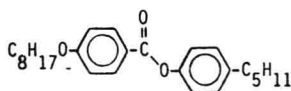
In this section liquid crystal characterization methods commonly employed by synthetic/organic chemists will be presented. This list



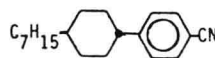
K97S_C122N142I



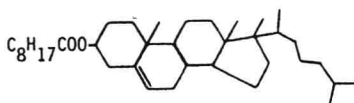
K22N65I



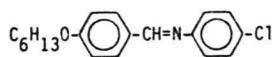
K80S_C100S_A165I



K30N55I



K80.5Ch92I



K59S_B91S_A98I

Temperatures between symbols represent transition temperatures between the two phases. Symbols are as follows:
K = crystal, N = nematic, Ch = cholesteric, I = isotropic liquid, S_A, smectic of type A, etc.

Figure 2. Representative Examples of Small Molecule Liquid Crystals.

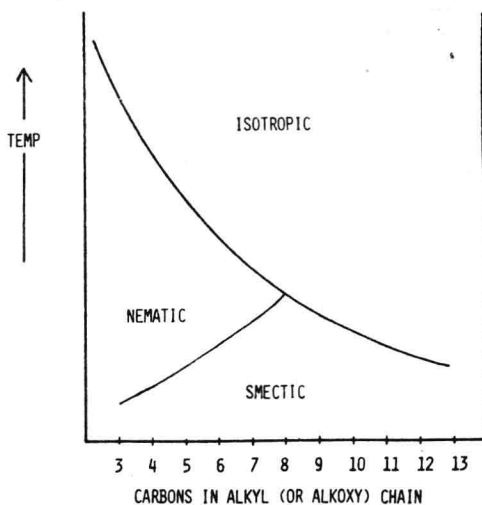


Figure 3. General Trend in Phase Type Versus Number of Carbons in Tail.

is not exhaustive, but merely represents the first tack at identifying fundamental mesophase behavior. In a capillary tube the mesophase often appears to the naked eye as a cloudy, turbid fluid. A liquid crystalline sample sandwiched between glass plates when viewed through a polarizing light microscope is often highly birefringent. The details of these (often beautiful) optical textures are highly dependent upon mesophase type, sample thickness, and surface treatment of the glass among other factors. There has been, however, a considerable effort to use optical textures to differentiate/identify phase type. In fact Sackmann⁴ and his school at Halle have produced a classification scheme for mesophases based on the criterion of complete miscibility of identical phases. Thus the mesophase of a new compound can be compared with known, standard mesophase types by miscibility using optical microscopy. There are available two excellent general references on phase identification by optical textures of liquid crystals^{5,6}.

Differential scanning calorimetry (DSC) is a valuable aid by which phase transition temperatures, transition heats, and transition entropies can be conveniently measured or calculated. This technique offers a direct and complimentary (to microscopy) evaluation of thermal behavior. Figure 4 shows the DSC curve for 4-octyloxybenzylidene-4'-chloroaniline⁷ in which can be seen K_1 - K_2 , K_2 - S_B , S_B - S_A , and S_A -I transitions. All transitions are enantiotropic and all are reversible. The most extensive supercooling occurs for the mesophase-solid transition, in this case the S_B - K_2 transition. Optical microscopy and/or x-ray diffraction is required to assign the specific mesophase type.

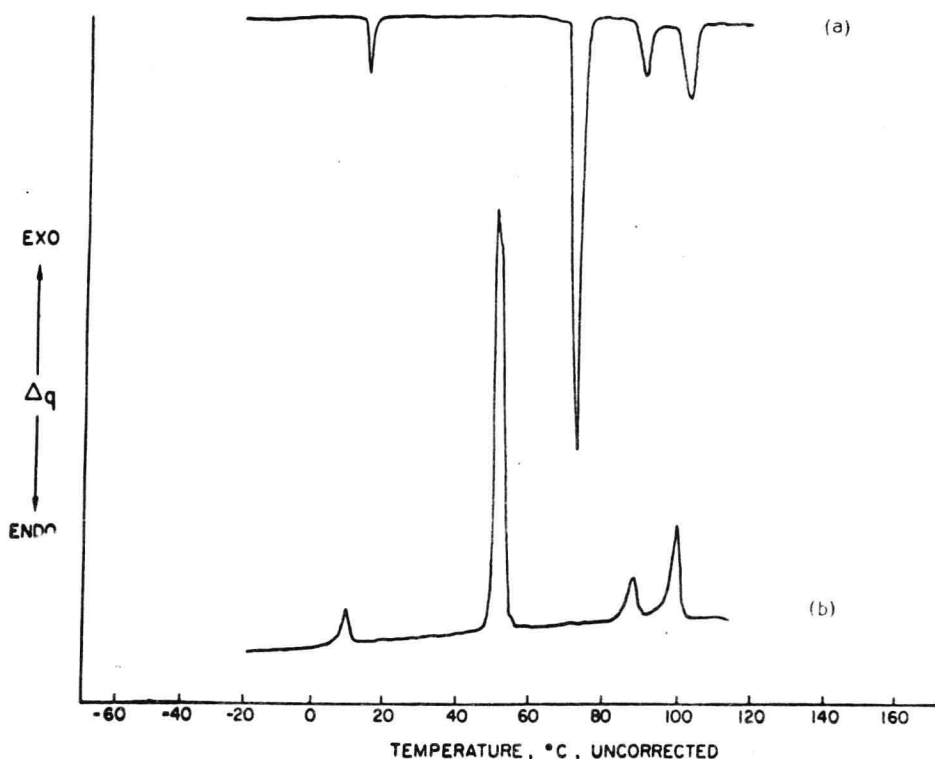


Figure 4. DSC Curves for 4-octyloxybenzylidene-4'-chloroaniline; (a) is the heating curve and (b) is the cooling curve.

Thermal optical analysis (TOA), sometimes known as depolarized light intensity (DLI), measures the intensity of light transmitted through a sample. This method uses circularly polarized light and the transmitted intensity can be directly related to sample crystallinity⁸. To date little use has been made of this technique in the study of liquid crystals for monitoring phase transitions and the intensity of birefringence, but the potential is great. This is particularly true for polymeric liquid crystals since the technique was originally developed to study polymers. Figure 5 shows a TOA curve for 4-octyloxybenzylidene-4'-trifluoromethylaniline⁷. The heating curve shows a sluggish solid-solid transition K_1 - K_2 , at low temperature, followed by relatively sharp K_2 - S_B and S_B -I transitions. Upon cooling the I- S_B transition is seen (with slight supercooling) followed at much lower temperature by a S_B - K_1 transition after extensive supercooling of the S_B phase.

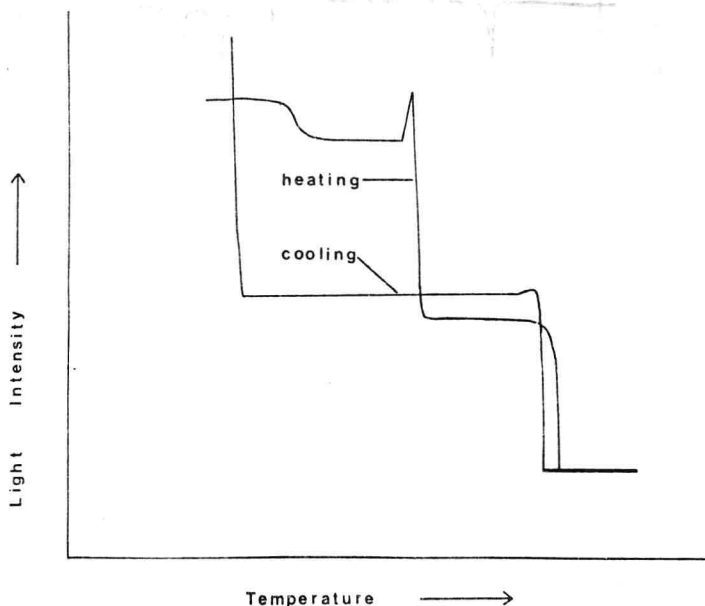


Figure 5. TOA curves for 4-octyloxybenzylidene-4'-trifluoromethyl-aniline.

X-ray diffraction is becoming increasingly more important in the initial characterization of liquid crystals. Although single-crystal determined atom maps and the analysis of diffraction by oriented mesophases are still in the hands of experts in the field of x-ray diffraction, the use of x-ray data from powder samples (often unoriented) is becoming ubiquitous. Nematic and smectic samples yield comparatively simple diffraction patterns when powder samples are run in the mesophase with no applied external orienting field. The nematic phase exhibits a weak diffraction maximum around 4.5\AA related to the average distance separating these parallel rod-like molecules. In the smectic phase an additional maximum appears at lower angles (inner ring) which is related to the smectic layer thickness. From this value the conformation and pairing of molecules in the smectic phase can be inferred. A schematic diagram of an x-ray diffraction photograph of an unoriented smectic phase is presented in Figure 6.

LYOTROPIC POLYMER SYSTEMS

The most extensively studied lyotropic polymer is poly- γ -benzyl-L-glutamate (PBLG)⁹. This polymer exists in solution as a rigid rod-like α -helix. A variety of solvents including dimethylformamide,

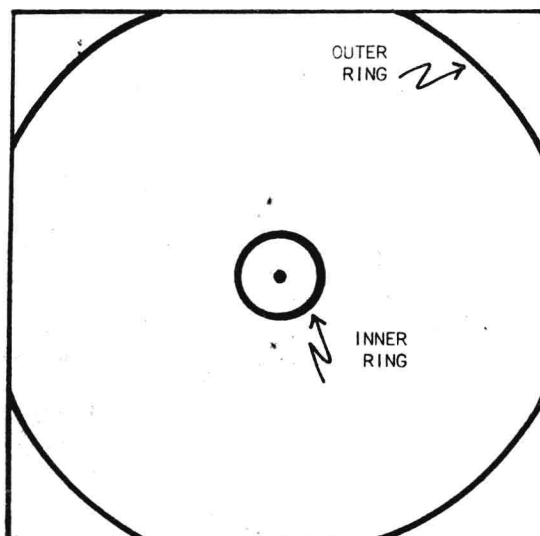
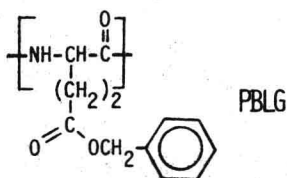


Figure 6. Generalized X-ray Powder Diffraction Photograph for a Smectic Sample.

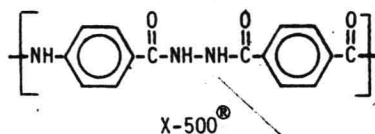
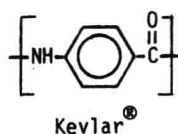
chloroform, meta-cresol, 1,4-dioxane and methylene chloride at



certain concentration and temperature ranges can selectively weaken specific PBLG crystalline lattice sites resulting in lyotropic mesomorphism—a fluid yet still structurally ordered state. An intriguing type of liquid crystallinity arises from the interaction of certain block copolymers with solvents which have different affinities for the different block types. The resulting lamellar structures are quite closely related to smectic organization¹⁰. Other examples of lyotropic polymers (many involving water as the solvent) are nucleic acids (DNA, RNA), collagen fibrils, glycoproteins, cellulose derivatives and certain viruses, such as Tobacco Mosaic Virus, which have a cylindrical supramacromolecular structure.

Synthetic polyamides such as du Pont's Kevlar[®] and Monsanto's

X-500® are examples of commercialized high-modulus, high-strength



fibers spun from liquid crystalline solution. The characteristic dramatic change in viscosity upon increasing concentration of the rod-like solute is shown in Figure 7 in which the viscosity increases rapidly until a critical concentration is reached and a sharp decrease in viscosity then accompanies the formation of the lyotropic mesophase. Other examples of such polymers have been recently collected and described¹¹. They include aromatic, aliphatic, heterocyclic, ring-substituted and hydrogen bonded materials.

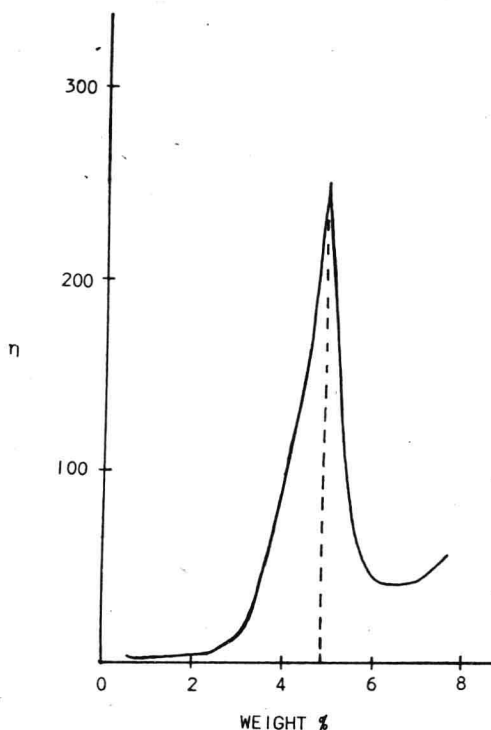


Figure 7. Schematic Diagram of Viscosity versus Concentration Profile for a Lyotropic System Exhibiting the Characteristic Viscosity Decrease upon Formation of the Mesophase.