Chiroptical Properties of Lyotropic (Acetyl)(Ethyl)cellulose Liquid Crystals

By

Jian Xin Guo

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

Department of Chemistry
McGill University
Montreal, Québec, Canada

November, 1992

ISBN 0-315-87608-5

Canada

Name: JIAN XIN GUO
Student number: 8803385
Department: Chemistry

A shorten version of the Ph. D. thesis title: (66 characters)

Chiroptical properties of (acetyl)(ethyl)cellulose liquid crystals

To my wife and parents

Abstract

(Acetyl)(ethyl)cellulose (AEC) polymers with an ethyl degree of substitution (DS) of 2.5 and acetyl DS ranging from 0 to 0.5 form chiral nematic liquid crystals in many organic solvents. The chiroptical properties of these lyotropic AEC mesophases are extremely sensitive to the acetyl DS of AEC and the nature of the solvents although the acetyl group and solvents are achiral and all the polymers share the same chiral cellulose backbone. As the acetyl DS increases from 0 to 0.5, the pitch of AEC mesophases in a given solvent varies from a few nanometer to infinity and a reversal of handedness occurs at a compensated degree of acetylation (DA*), where the corresponding mesophase is characterized by an infinite pitch and the absence of macroscopic chirality. The value of DA* and the sign of the temperature dependence of pitch depend on the solvent. Achiral dyes dissolved in these AEC mesophases display liquid crystal induced circular dichroism (LCICD), which results from the helicoidal orientation of the dyes by their chiral matrices. The sign and magnitude of the LCICD are correlated with the handedness and pitch of the AEC mesophases. The mechanism for the handedness inversion for lyotropic AEC mesophases with variation in acetyl DS is discussed.

Résumé

Des (acétyl)(éthyl)celluloses (AEC) ayant un degré de substitution (DS) en éthyle de 2,5 et en acétyle de 0 à 0,5 forment des cristaux liquides nématiques chiraux dans différents solvants organiques. Bien que seule la chaîne cellulosique soit chirale alors que le groupe acétyle et les solvants ne le sont pas, les propriétés optiques chirales des ces mésophases lyotropiques dependent du DS en acétyle et du solvant. Dans un solvant donné, lorsque le DS en acétyle augmente de 0 à 0,5, le pas des mésophases augmente de quelques nanomètres jusqu'à l'infini, pour ensuite rediminuer avec un sens d'hélicité inversé. Le DS correspondant au pas infini est appelé degré d'acétylation compensé (DA*). La valeur du DA* ainsi que la variation du pas avec la température dépendent du solvant. Lorsque des colorants non chiraux sont dissous dans les mésophases d'AEC, un dichroïsme circulaire induit par le crystal liquide (DCICL) apparait, résultat de l'orientation hélicoïdale des colorants par la matrice chirale. Le signe et l'intensité du (DCICL) sont comparés avec l'hélicité et le pas des mésophases. Le mécanisme d'inversion du sens de l'hélicité de ces mésophases en fonction du DS en acétyle est discuté.

Foreword

This thesis is structured according to the option provided by section B(#2) of the Guideline Concerning Thesis Preparation.

> *The candidates have the option, subject to the approval of the department, of including, as part of their thesis, copies of the text of a paper(s) submitted for publication, or the clearly-duplicated text of a published paper(s), provided that these copies are bound as an integral part of the thesis.*
> *— If this option is chosen, connecting texts, providing logical bridges between the different papers, are mandatory.*
> *— The thesis must still conform to all other requirements of the "Guidelines Concerning Thesis Preparation" and should be in a literary form that is more than a mere collection of manuscripts published or to be published. The thesis must include, as separate chapters or sections: (1) a Table of Contents, (2) a general abstract in English and French, (3) an introduction which clearly states the rationale and objectives of the study, (4) a comprehensive general review of the background literature to the subject of the thesis, when this review is appropriate, and a final overall conclusion and/or summary.*
> *— Additional material (procedural and design data as well as descriptions of equipment used) must be provided where appropriate and in sufficient detail (e.g. in appendices) to allow a clear and precise judgment to be made of the importance and originality of the research reported in the thesis.*
> *— In case of manuscripts co-authored by the candidate and others the candidate is required to make an explicit statement in the thesis of who contributed to such work and to what extent; supervisors must attest to the accuracy of such claims at the Ph.D. Oral Defense. Since the task of the examiners is made more difficult in these cases, it is in the candidates interest to make perfectly clear the responsibilities of the different authors of co-authored papers.*

This thesis is presented in six chapters. Chapter 2, 3, 4 and 5 each describe a unique aspect of the thesis and have been written in a paper format to be submitted to scientific journal. Each of these chapters contains introduction, results and discussion, conclusion and reference section. Chapter 1 and 6 present a general introduction and overall conclusion to the thesis. The only co-author on all publications will be the thesis director, Dr. D.G. Gray.

Acknowledgments

I would like to express my sincere gratitude to Dr. D.G. Gray for his kind advice, his full support, his great patience and his enthusiasm throughout the course of this research project and the preparation of the thesis.

I would also like to thank the following people who provided assistance during this project:

Dr. R.S. Werbowyj for her kind advice, valuable discussion, and for her assistance in operating IR spectrometer and computer.

Dr. J.-F. Revol for his advice and for translating the thesis abstract.

Professor M.A. Osipov, Moscow State University, for sending us a copy of his review prior to publication.

Drs. Kondo, Harkness, Budgell, Kimura and Ritcey for their valuable discussion.

Dr. Brown for allowing use of the optical microscope in his laboratory and Ms. J.M. Marentette for her assistance in using the microscope and video analysis software.

Mr. Y.L.Yu for his assistance in performing ^{13}C NMR measurements.

Mr. R. Rossi for his assistance in solving problems of CD spectropolarimeter.

My wife for her great support and patience.

The Pulp and Paper Research Institute of Canada and McGill for library services.

A special thank to the Third Floor Tea Club in the Pulp and Paper building for creating an enjoyable and a nice English-learning environment.

The Pulp and Paper Research Institute of Canada for Carl Winkler Memorial Fellowship and Studentship Award. The Department of Chemistry, McGill University, for a Department Research Scholarship.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

CD	circular dichroism
DA*	compensated degree of acetylation
DP	degree of polymerization
DS	degree of substitution
FTIR	fourier transform infrared
ICD	induced circular dichroism
LB	linear birefringence
LCICD	liquid crystal induced dichroism
LD	linear dichroism
NMR	nuclear magnetic resonance
ORD	optical rotatory dispersion
AAPC	(acetoacetoxypropyl)cellulose
AEC	(acetyl)(ethyl)cellulose
AMC	(acetyl)(methyl)cellulose
APC	(acetoxypropyl)cellulose
CA	cellulose acetate
CBEC	(carbamoylethyl)cellulose
CC	cellulose cinnamate
ClPC	3-chlorophenylurethane cellulose
CMC	carboxymethylcellulose
CTA	cellulose triacetate
CTC	cellulose tricarbanilate
EC	ethylcellulose
HBC	(hydroxybutyl)cellulose
HEC	(hydroxyethyl)cellulose
HPC	(hydroxypropyl)cellulose
MC	methylcellulose
NC	nitrocellulose
PBLG	polybenzyl-L-glutamate
PBDG	polybenzyl-D-glutamate
PEC	(propionyl)(ethyl)cellulose
TBC	tri(butoxyethyl)cellulose
TEC	triethylcellulose

THC	triheptylcellulose
TMEC	tri-O-(2-(2-methoxyethoxy)ethyl)cellulose
TrHC	6-O-trityl-2,3-O-hexylcellulose

AA	acetic acid
AO	acridine orange
AP	aqueous phenol
DBM	dibromomethane
DCA	dichloroacetic acid
DCE	dichloroethane
DCM	dichloromethane
DEME	diethylene glycol monomethyl ether
DMAC	dimethylacetamide
EMK	ethyl methyl ketone
MMNO	N-methyl-morpholine-N-oxide
MPK	methyl propyl ketone
TCE	tetrachloroethane
TCP	tetrachloropropane
TFA	trifluoroacetic acid
THF	tetrahydrofuran

Chapter 1

Introduction

1.1. Introduction

The term *chiroptical activity* implies a combination of physical concepts; *chirality* and *optical activity*. The former is a geometric property of molecules or objects and is defined as the lack of reflection symmetry. The latter is an electro-magnetic property of a substance and refers to phenomena resulting from the different interaction of left and right circularly polarized light with chiral molecules or aggregates of molecules. The corresponding chiral molecules or aggregates of molecules are termed optically active. A carbon tetrahedrally bound to four different atoms or groups possesses chirality and therefore its molecules can exhibit optical activity with circularly polarized light.

In nature, most objects are not identical with their mirror images and therefore are said to possess chirality. The chirality manifests itself in the distinction between left and right and is thus referred to as handedness. A preference for left or right is displayed by nature on many levels ranging from atomic to cosmological[1]. At intermediate scales, most helical seashells and winding plants are right-handed (as are humans). Proteins and DNA wind predominantly in right-handed helixes, however, their main constituents, amino acids and sugars in nucleotides, are almost always left- and right-handed, respectively, in natural organisms[1,2]. The origin of chiral asymmetry in nature has been of great interest to biologists, physicist and chemists, but remains unknown so far. However, the macroscopic displays of chirality must fundamentally be related to dissymmetry on a molecular level.

Biopolymers are a major component of living objects. Three major classes of the biopolymers are proteins, nucleic acids and polysaccharides, whose constituent monomers are all optically active. The common feature among the proteins, nucleic acids and some polysaccharides, such as schizophyllan, is their helix conformation[3,4], e.g. single, double or triple helical, as a result of hydrogen bonding and steric effects. *In vitro*, these chiral biopolymers have been shown to form spontaneously helicoidally ordered liquid phases (liquid crystals)[3,5]. The similarity of the molecular organization in these phases to the ordered structures *in vivo* observed for living objects such as insect cuticle, wood cell walls, etc. has led to a suggestion that the existence of the ordered liquid in nature provides a mechanism for the biogenesis of chiral fibrous networks[6]. In other words, the liquid crystalline phase may be one of the important states, because of its fluidity and self-ordering nature, involved in the bioprocessing of chiral molecules into naturally occurring biostructures which exhibit macroscopic chirality. Although establishing this direct linkage is still beyond our knowledge at present, understanding

which factors govern chiroptical behaviour of liquid crystals may be a necessary and important step in confirming this linkage.

Cellulose is one of the main classes of naturally occurring polysaccharides. It often exists in nature as microfibrils embedded in matrices such as in plant cell walls. A predominance of right-handed helical twisting of the microfibrils in the middle layer of the secondary cell wall has been found for over 250 species of woody plants[7]. The capability of self-ordering in solution by cellulose derivatives was first discovered fifteen years ago[8]. Since then it has been found that this self-ordering feature is also exhibited by cellulose itself in solution[9-12] and even by cellulose microfibrils, an aggregated form of cellulose found in nature, in aqueous suspensions as recently reported by Revol et al[13]. A common helicoidal arrangement of cellulose was observed in all these ordered phases and is well preserved in solid films or crosslinked gels when these are fabricated from the ordered phases[13,14-16]. The analogy in the helical arrangement of cellulose *in vivo* and *in vitro* implies that lyotropic cellulosic liquid crystals may be the precursor of naturally occurring helical cellulose microfibrils. In other words, the chirality displayed by cellulosics at different levels may have a fundamental connection, e.g. chiral carbons→ chiral glucose monomers→chiral cellulose molecular chains→chiral aggregates of cellulose in liquid crystalline phases→chiral cellulose microfibrils existing in nature. A hypothesis for these interrelations is represented schematically in Figure 1.1. The main concerns of this research in this thesis are going to focus only on the chiroptical properties of cellulose derivatives in the liquid crystalline state, rather than in the non-ordered liquid or ordered solid states, in the hope of correlating some molecular structure to the macroscopic chirality displayed by the liquid crystalline phase.

The term *liquid crystal* refers to partially ordered fluid phases that are intermediate behaviour between the three-dimension ordered crystalline state and the disordered or isotropic fluid state. The liquid crystalline structure on a molecular scale is characterized by the existence of a positional and /or orientational order. Consequently, a liquid crystal can flow like a liquid, but in its other properties such as birefringence, it is reminiscent of the crystalline phase. Another common name describing this phase is *mesophase*. The mesophase usually displays anisotropic properties and is thus referred to as an *anisotropic* phase as well.

The first report of the existence of a liquid crystalline phase dates back to 1888 by Reinizer[17]. He found that cholesteryl benzonate exhibited two apparent melting points between which the compound was cloudy but a fully liquid melt. At intermediate temperature striking colours were observed. Such new states of matter were later observed in the cholesterol derivatives and other organic compounds[18].

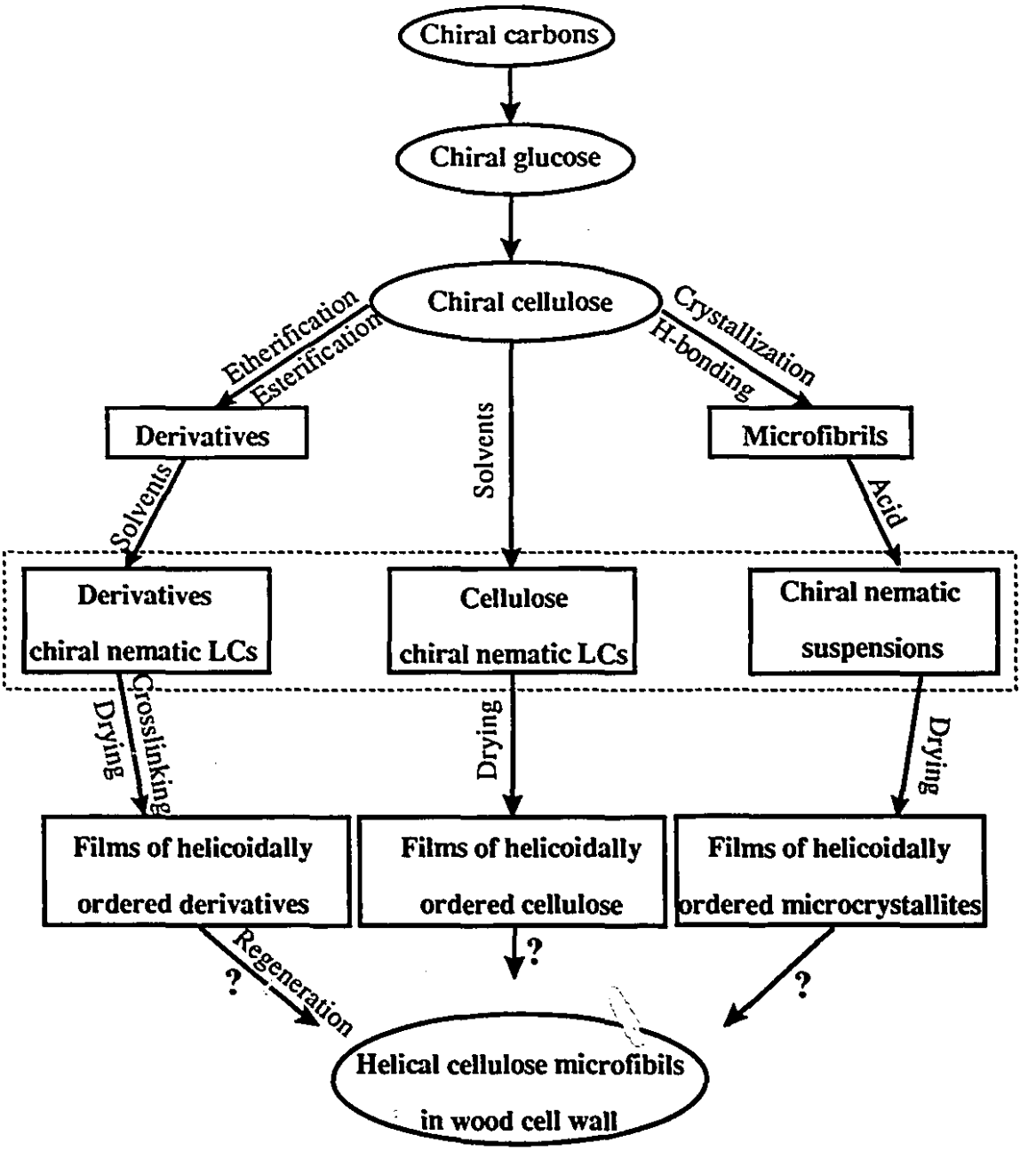


Figure 1.1. Schematic representation of a hypothesis for the interrelations among chiral structures displayed by cellulosics at different levels.

Compounds capable of forming liquid crystalline phases are commonly referred to mesogens. The liquid crystalline phase can be classified into two types: thermotropic and lyotropic[19]. The *thermotropic* phase is the state that exhibits mesomorphic behaviors for pure mesogenic molecules in a definite temperature range and the *lyotropic phase* is the state that exhibits mesomorphic behaviour for mesogenic molecules in solution. The temperature range in which lyotropic phases exist is mainly determined by the nature of the solvent and concentration. The lyotropic mesophase is important in life processes.

According to the specific nature of the molecular order, liquid crystals are further classified as nematic, smectic or chiral nematic. The molecular arrangement in nematic mesophase is schematically illustrated in Figure 1.2 (a). The nematic liquid crystals are characterized by long-range orientational order and random distribution of the centres of mass of the molecules resulting from three transitional degrees of freedom. Thus the average alignment of the molecules with their long axes parallel to each other leads to a macroscopically preferred direction in space. Heating a nematic mesophase results in a phase transition to an isotropic liquid at a temperature called the *clearing point.*

The smectic mesophases are characterized by both orientational and positional order in at least one direction. The centres of the molecules are, on average, arranged in equidistant planes. There exist many types of smectic phases, indicated as S_A, S_B, S_C, ... S_I, which reflect the symmetry properties of the mesophases[20]. They differ in (i) the orientation of the preferred direction of the molecules with respect to the layer normal (orthogonal and tilted); (ii) the organization of the centres of the molecules within the layers. The molecular arrangement in three common types of the smectic phases S_A, S_B and S_C, are illustrated in Figure 1.2 (b), (c) and (d).

Chiral nematic liquid crystals are formed only when optically active molecules (mesogenic or non-mesogenic) are incorporated into the nematic phase or when optically active mesogens exhibit mesomorphic behavior either in bulk or in solution. The mesophases are characterized by the fact that in addition to the long-range orientational order in each molecular layer, there exists a screw axis perpendicular to the directors of the molecules, leading to a helicoidal structure. This molecular arrangement are schematically illustrated in Figure 1.3. The important structural features in this model is its helicoidal pitch and handedness. The pitch, P, is defined as the distance between two the layers in which the molecular directors are approximately the same as a result of a full 360° rotation along the helicoidal axis. The handedness of the chiral nematic structure can be either left or right. The molecular director for a left-handed structure undergoes a counterclockwise rotation along helicoidal axis whereas for right-handed structure the molecular director undergoes a clockwise rotation along the helicoidal axis. Both

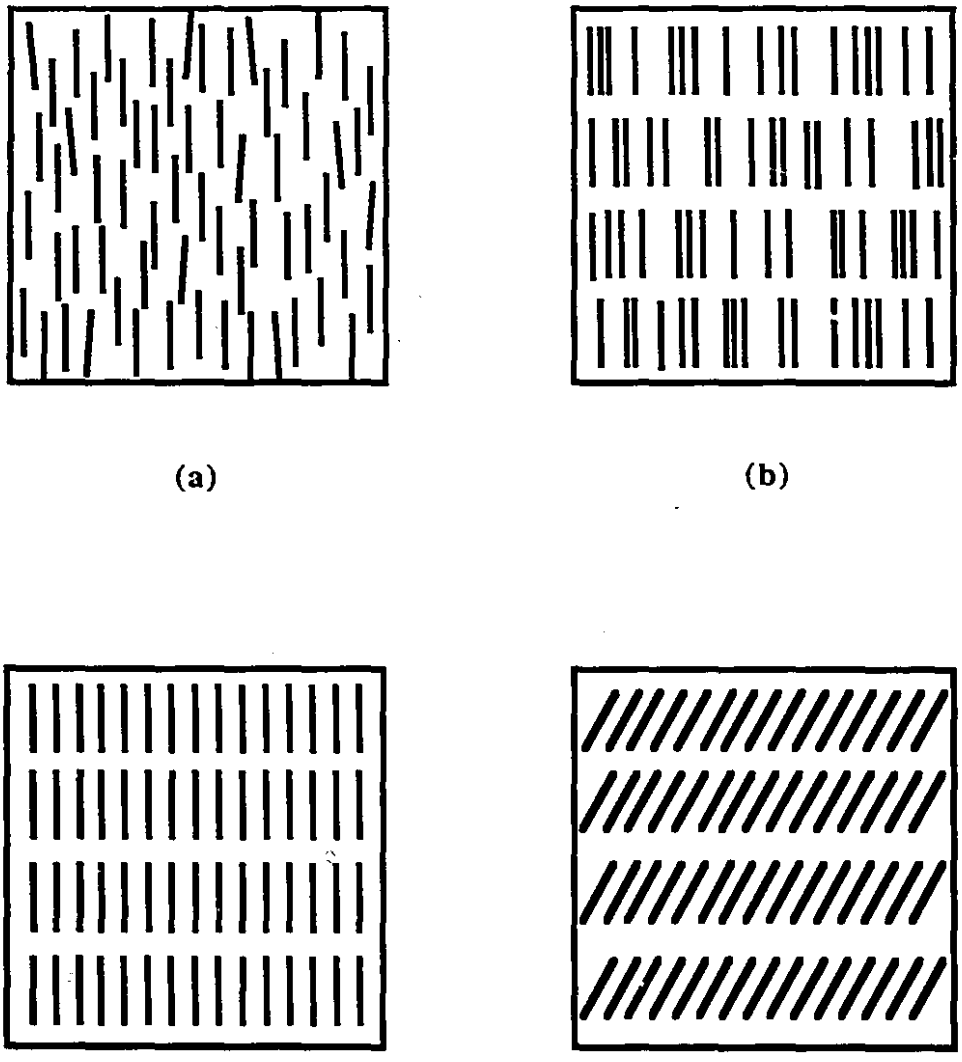


Figure 1.2. Schematic representation of molecular orientation in nematic (a), smectic A (b), smectic B (c) and smectic C (d) liquid crystals

structural models are shown in Figure 1.3.

Although the nematic and chiral nematic liquid crystals are very similar in terms of positional order and unique optical axes (behaves optically like a uniaxial crystal), the former is optically positive whereas the latter is optically negative. On the other hand, the chiral nematic phase is also very similar to smectic phase in that the mesogenic molecules form a "layered structure". However, the molecules within the layer of the former phase have only one-dimension order, while the molecules in the latter case have two-dimension order except for S_A. Actually the layers in the chiral nematic phase are not physically defined. In this respect, the chiral nematic should be regarded as an independent phase rather than in the family of nematic phases as it appears in some literature. Chiral nematics used to be called *cholesterics* because this type of liquid crystal was first found in cholesterol derivatives, but this type of mesophase is by no means restricted to members of the cholesterol family now. Another reason for the use of the name chiral nematic rather than cholesteric in this thesis is that cholesteryl esters display other distinct "blue phases" just below their clearing temperature[21].

In general, the anisotropic geometrical shape and stiffness of molecules are fundamental requirements for forming liquid crystalline phase. For small molecules, the majority of mesogens have rod-like and disc-like shapes. For polymers, similar mesogens are required to be present on the main-chains linked by flexible spacer or as side-chains attached to flexible main-chains. The former are called *main-chain* and the latter *side-chain* liquid crystalline polymers. In the case of those polymers without mesogenic groups on the main- or side-chains, the rigidity of the polymer chains becomes relatively important since anisotropic geometrical forms exist inherently to some extent in most polymers. The rigidity of the polymer chains is a result of hindrance to internal rotation of the atoms about each bond and is also affected by intrachain hydrogen bonding. Most polypeptides belong to the class of rigid polymers and thus display a rod-like shape due to adoption of a α-helix conformation via hydrogen bonding between the amide group of one residue and the carbonyl group of neighboring residues. Another class of rigid polymers is found in those polymers which contain cyclic groups in the main-chain, e.g. para-substituted aromatic polyamides or polyesters, and β-linked glucopyranosic cellulose and its derivatives. These polymers are considered to be semirigid because of the steric effects from the cyclic groups and some intrahydrogen bonding in the backbone (e.g. cellulose chain). A common feature of these two classes of polymers is their capability of forming liquid crystalline phases either in the melt or in solution.

Several theories have been proposed to evaluate the rigidity of polymers and to what extent the polymers are able to form self-ordering mesophases[22-24]. Among them,

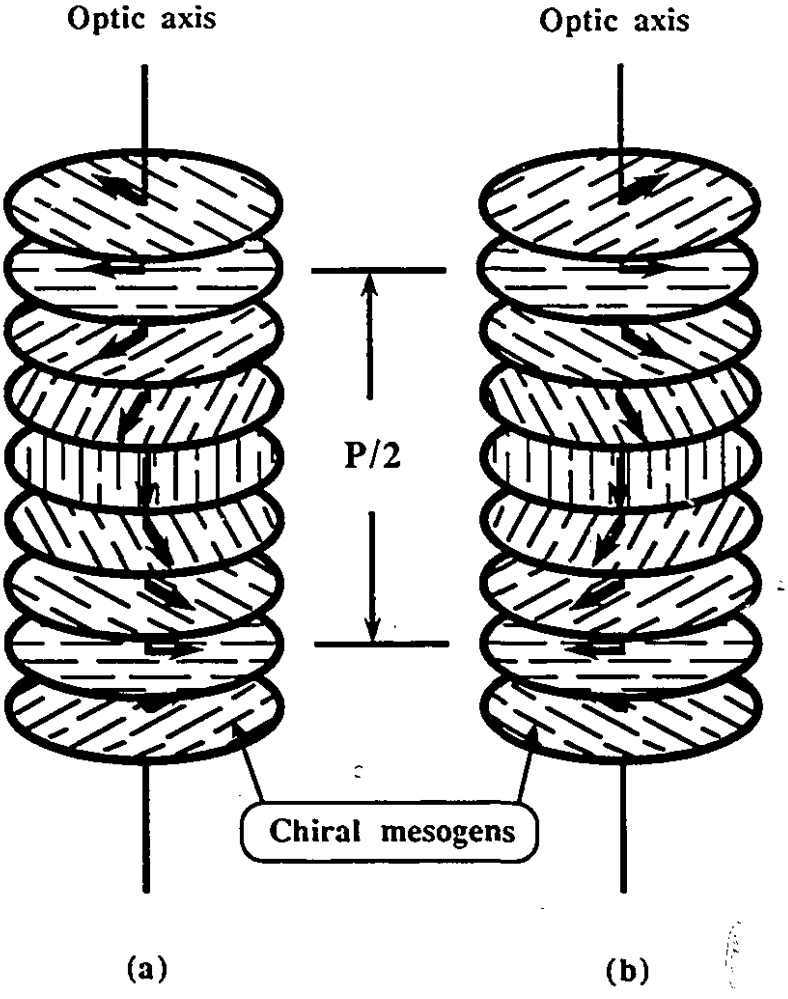


Figure 1.3. Schematic representation of the helicoidal structures in a left-handed (a) and a right-handed (b) chiral nematic liquid crystals.

Flory's theory[22] is a more classical and comprehensive representation. Flory applied a lattice model to describe the phase separation or self-ordering for rigid polymers in solution. After the free energy of mixing was minimized, it was found that the solution is separated into two phases (ordered and non-ordered) at a concentration that depends on the axial ratio of the rigid polymers. The formation of ordered phase is thus entropically favored. The critical concentration is expressed as

$$V_C^* = \frac{8}{x}\left(1 - \frac{2}{x}\right) \qquad [1]$$

where V_C^* is the critical volume fraction and x is the polymer axial ratio. The theoretical prediction is very close to the experimental data for rigid polymers such as poly(*p*-benzamide)[25] and poly (γ-benzyl-glutamate)[26]. Based on his theory, he also predicted that cellulose-based polymers might be able to form liquid crystals in some suitable solvents[22]. This was experimentally confirmed twenty years later[8].

Later modification of his original theory by taking into account polydispersity, chain flexibility, diluent effects, etc. has led to an increase in the applicability of the resulting theories[27,28], e.g. the revised theory works for less rigid polymers.

Liquid crystalline polymers are currently receiving considerable attention because of their academic and industrial interest. Firstly, the complexity of polymer liquid crystals in terms of orientational and positional order is a theoretical and experimental challenge. Secondly, as mentioned above, many biopolymers exist in nature with ordered structures similar to liquid crystals. The knowledge of mesomorphic behavior of polymeric liquid crystal is important in order to understand the life process from the view of biologists. Thirdly, the product of the liquid crystalline polymers possess a high modulus and tenacity, high heat resistance, good chemical stability and light weight. These important properties are required for engineering materials. It has been predicted that liquid crystalline polymers might replace metals, especially those used in automobile, electronics and electrical parts, and, because of the above characteristics, become dominant polymeric materials for the next generation[29].

1.2. Chiral nematic liquid crystals

1.2.1. Textures

The term *texture* refers to the appearance of a thin layer of liquid crystal observed under a polarizing microscope. It reflects the orientation (on the scale of microns) of the anisotropic fluid. Chiral nematic phases between two flat substrates can exhibit several different textures as a result of the difference in degree and direction of chiral nematic ordering relative to an observer.

1.2.1.1. Planar texture.

This texture is observed when the helicoidal axis of the sample is normal to the substrate surfaces (Figure 1.4 (a)). If the sample thickness, d, is much greater than the chiral nematic pitch ($50\mu m > d \gg P$), the planar texture is readily obtained by a gentle tangential movement of the untreated cover substrates. The planar mesophase has a minimum of birefringence and exhibits extraordinary optical properties which will be discussed later. Textures with oily streaks is often observed for a polydomain planar chiral nematic sample[30].

1.2.1.2. Homeotropic texture.

This texture is formed when the helicoidal axis of a sample is parallel to the substrate surfaces. The resulting picture resembles a fingerprint consisting of equidistant and alternating dark and light lines (Figure 1.4 (b)). The periodicity results from a change in molecular alignment along the helicoidal axis, leading to a periodic change in refractive index. The distance between the neighboring lines is equal to half of the pitch.

1.2.1.3. Focal conic texture.

This texture is also called non-uniform planar and is formed when the directions of the helicoidal axis in various chiral nematic domains are along the azimuth and are not parallel to the substrate surfaces (Figure 1.4 (c)). The focal conic texture scatters light strongly, mainly at the boundaries between the chiral nematic domains where a change in the refractive index occurs. The application of shear can convert the focal conic texture into a planar texture.

1.2.2. Optical characteristics

1.2.2.1. Optical activity.

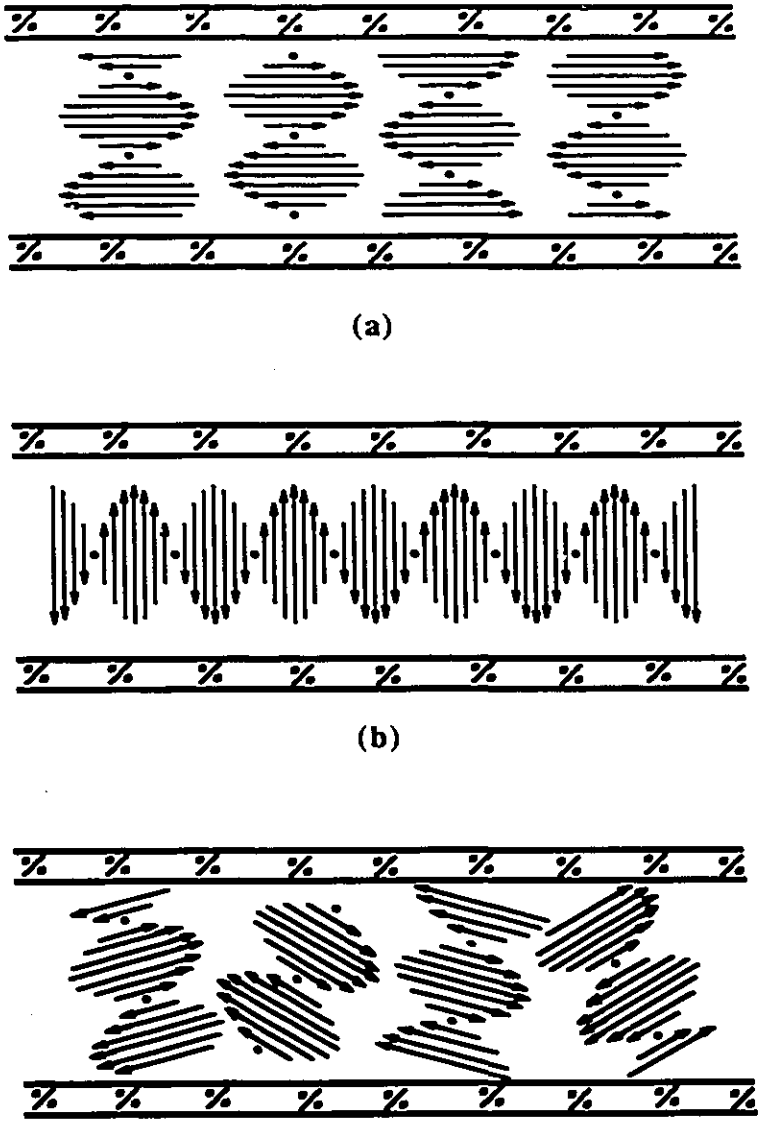


Figure 1.4. Schematic representation of textures of a chiral nematic liquid crystal between two substrates, (a) 'planar' (b) homeotropic (c) 'focal conic'. The arrows in the textures represent the molecular directors of the nematic-like layers in the helicoid, projecting on the plane parallel to the helicoidal axis and the sheet.

Chiral nematic phases exhibit unique optical properties because of their helicoidal supermolecular structure and thus differ significantly from those of other types of mesophases[31]. When white light passes through a chiral nematic phase, a selective reflection occurs over a small region of spectrum. If the incident light is parallel to the helicoidal axis of a monodomain planar texture, the reflected and transmitted components are circularly polarized. When the electric vector of the right or left circularly polarized component of the incident beam matches the pitch and the handedness of the helicoidal structure, then the matched components of the incident beam are selectively reflected and the other components transmitted by the mesophase. The reflection of one circularly polarized component is unique because its handedness of rotation is unchanged. For example, if an incident left-handed circularly polarized component is reflected by a chiral nematic phase, the resultant reflected light will also be left-handed circularly polarized (Figure 1.5). This is in contrast to normal reflection (e.g. from metal mirrors) where the handedness of circularly polarized light is reversed. By definition, if the incident right-handed circularly polarized light is selectively reflected and the left-handed circularly polarized light transmitted by a helicoidal structure, the corresponding mesophase is right-handed. The reverse is a left-handed mesophase. Therefore, the reflection of light by a chiral nematic phase is selective with respect to not only wavelength but also handedness.

Another important optical property exhibited by a chiral nematic structure is very high optical rotatory power when the incident plane polarized light is parallel to the helicoidal axis[31]. The magnitude of the optical rotation is up to 10^3-10^5 degree per millimeter for visible light, much greater than the intrinsic optical activity arising from the mesogens. Furthermore, an anomalous optical behavior is exhibited at the reflection band, the optical rotatory power exhibiting opposite signs for wavelengths below and above the reflection wavelength. This phenomenon is similar to that observed for chiral chromophores in their absorption region and is thus called a pseudo Cotton effect.

De Vries[32] has formulated a theory to explain the above optical properties, where the chiral nematic structure is modeled as of a pile of thin birefringent layers normal to the optic axis (equivalent to the helicoidal axis). The expression for the wavelength dependence of the optical rotation, α, for a chiral nematic liquid crystal is given by

$$\alpha = \frac{\pi \Delta n^2 P}{4\lambda^2[1-(\lambda/\lambda_0)]} \qquad [2]$$

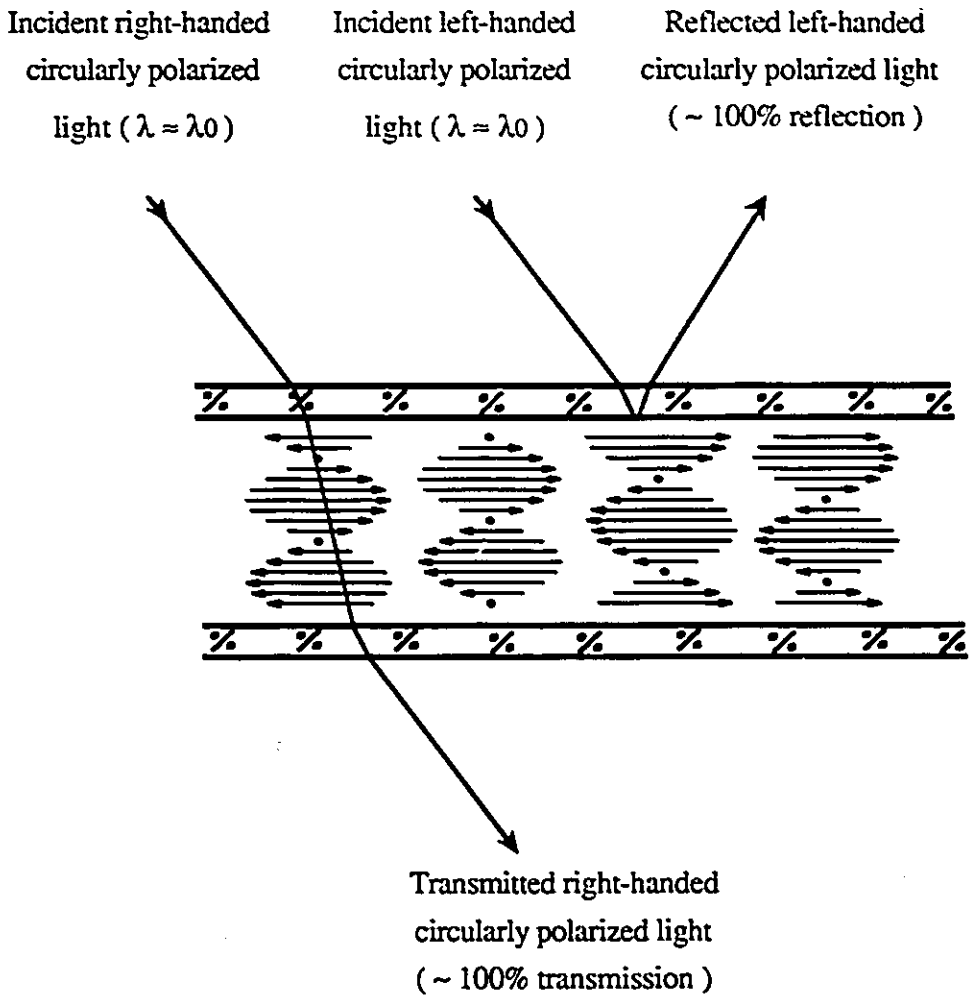


Figure 1.5. Schematic representation of the selective reflection of a left-handed circularly polarized light by a planar left-handed chiral nematic liquid crystal with a pitch equal to $\lambda_0/\bar{n}$. The arrows in the texture are defined in Figure 1.4.

where Δn is the layer birefringence, P the pitch (taken to be a pseudoscalar that is positive for a right-handed helicoid and negative for a left-handed helicoid) and λ_0 the wavelength of reflected light. λ_0 is equal to $\bar{n}|P|$, where $\bar{n}$ is the mean refractive index of the mesophase. The equation predicts a change in sign for the rotation as λ approaches and passes λ_0, This is in good agreement with above-described optical behaviour. For the case of $\lambda_0 \gg \lambda$, the above equation reduces to

$$\alpha = \frac{\pi \Delta n^2 P}{4\lambda^2} \qquad [3]$$

This means that a plot of α versus $1/\lambda^2$ will give a straight line. This prediction was later confirmed by Robinson for polypeptides liquid crystalline systems[33].

1.2.2.2. Birefringence.

Like other types of liquid crystals, chiral nematic phases also exhibit birefringence characteristic of crystals and liquid crystals. The chiral nematic phase behaves like a uniaxial crystal with respect to optical properties because of the helicoidal arrangement of molecules. Consequently, the chiral nematic phase exhibits a negative birefringence[34], that is, the refractive index of the extraordinary light (along the optic axis) is smaller than that of the ordinary light (along molecular layers). In contrast, nematic and most smectic liquid crystals exhibit positive birefringence.

1.2.2.3. Compensation

The term *compensation*, when applied to chiroptical activity, originally referred to the situation where two optical enantiomers were mixed on equal proportions, giving a racemic mixture and exhibiting optical inactivity. For chiral nematic liquid crystals, the optical activity is mainly determined by their helicoidal structures characterized by the pitch and handedness. When the pitch of a chiral nematic phase is very large, enough approaching infinity, the mesophase looks structurally like a single nematic layer and the macroscopic chirality does not exist any more. As a result, the mesophase behaves optically like a nematic phase, optically inactive. It appears that the compensation phenomena in chiral nematic phases is by no means restricted only to racemic mixtures since their pitch and handedness depend not only on the chirality of the chiral mesogens but also on temperature and the nature of other constituent mesogenic or non-mesogenic molecules. Moreover the compensated mesophase may still exhibit intrinsic optical

activity (defined in next section) but this is negligible relative to the chiral nematic optical activity. In addition the compensated mesophase may also exhibit other optical properties similar to nematics. For example, the sign for the birefringence may become positive and a schlieren or thread-like texture may be observed under a polarizing microscope because of nematic orientational characteristics[34].

In thermotropic liquid crystals, the handedness is normally determined by the chirality of the constituent chiral molecules, the handedness for a chiral nematic phase of an optical isomer is normally opposite to that of its mirror image isomer. When equal moles of both isomers are mixed, a compensation occurs. An unequal mixture of the isomers may form either a right- or left-handed chiral nematic phase. Binary mixtures of cholesterol derivatives[35,36] may also form a compensated mesophase at a critical temperature, termed the *compensated temperature*. Recently, single component chiral molecules such as polypeptide copolymers[37] and cellulose derivatives[38] have been found to form thermotropic compensated mesophase at compensated temperatures.

In lyotropic liquid crystals, the handedness depends not only on the chirality of constituent chiral molecules but also on the nature of the solvent surrounding the chiral molecules. As a result, the compensation takes place not only in a racemic mixture or at compensated temperatures but also in certain solvent mixtures in which the handedness of the individual lyotropic phase is opposite. These phenomena have been widely observed in lyotropic polypeptide liquid crystals[26].

1.2.2.4. Extrinsic optical activity

Optical activity exhibited by inherently dissymmetric molecules or aggregates of molecules is normally called *intrinsic optical activity*. The optical activity may also be displayed by optically inactive or *achiral* molecules present in an asymmetric environment. This type of optical behaviour is referred to as *induced optical activity* or *extrinsic optical activity*.[39] As a result of asymmetric features, chiral nematic liquid crystals may behave like chirally perturbed moieties when achiral molecules are incorporated within the mesophases[40]. Consequently, the achiral molecules intrinsically bound to the chiral mesogens or physically intercalated into the chiral nematic phases exhibit an extrinsic optical activity. Since the optical activity is induced by the liquid crystal, it is also called liquid crystal induced optical activity. The extrinsic optical behaviour has been observed for achiral chromophore molecules dissolved in thermotropic as well as lyotropic chiral nematic phases by means of CD spectroscopy[39].

A critical review of liquid crystal induced optical activity and the extrinsic phenomena observed for cellulosic liquid crystals in this study will appear in Chapter 4 of this thesis.

1.2.3. Molecular theories of chiral nematic liquid crystals

As previously described, the chiral nematic structure can be considered as consisting of a series of nematic-like molecular layers, each of which is twisted relative to its neighbours. Consequently, most theories for chiral nematic ordering of chiral molecules are extensions of nematic theories with consideration being given to the asymmetric contributions from the constituent chiral molecules. Basically the chiral molecules are treated as rod-like in the model in most theories and the intermolecular interactions between the rod-like chiral molecules are assumed to be in a minimum free energy state. A simple model for the interaction between the chiral rods is schematically represented in Figure 1.6.

Keating[41] was the first to attempt to formulate a theory for the chiral nematic ordering of chiral molecules. He proposed that the asymmetry in the shape of the molecules leads to hindered rotation and this causes anharmonicity in the forces coming from the nearest neighbours, which resist twisting to give a non-zero average. An expression for the chiral nematic pitch was obtained as follows

$$1/P = Ak\mathrm{T}/4\pi\mathrm{I}\omega_0^4 \qquad [4]$$

where A is a constant characterizing the anharmonicity, k is Boltzman's constant, T is temperature, I is the moment of inertia and ω_0 the angular frequency of the rod-like molecules about their long axes. The negative temperature dependence of pitch predicted in this equation is in agreement with experimental observations on most small molecule systems such as cholesterol derivatives. However both negative and positive temperature dependence of pitch are often observed for polymeric chiral nematic liquid crystals.

Another approach proposed by Goossens[42] extended the mean field theory of Maier and Saupe for nematic ordering to include dipole-quadruple as well as dipole-dipole interactions between rod-like molecules. The resulting intermolecular potential is related to the angle, θ_{12}, between the direction of the long axis alignment in planes 1 and 2 separated by a distance r_{12} (Figure 1.6). The expression for the potential $V_{1,2}$ is given by

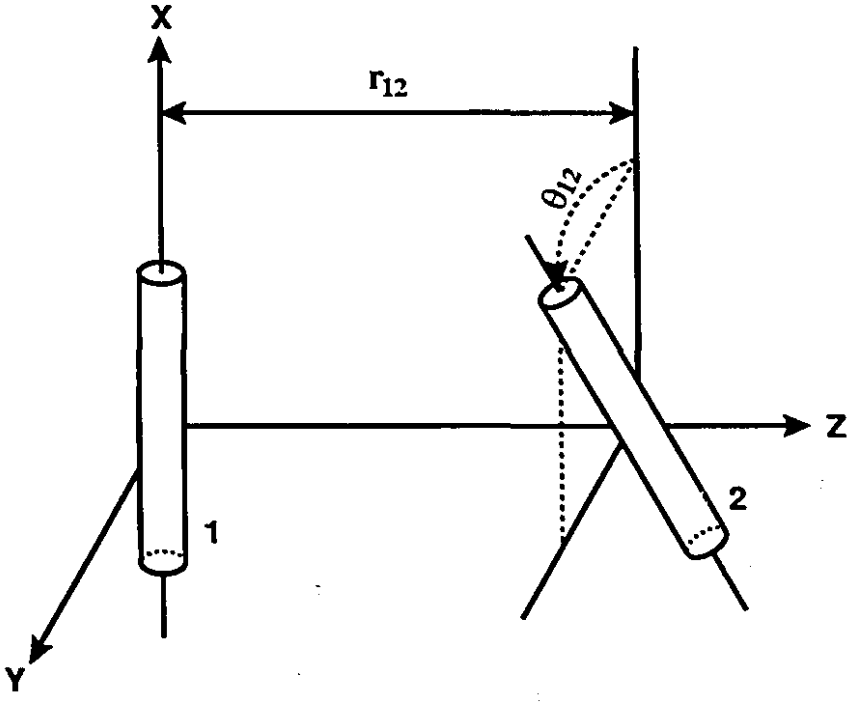


Figure 1.6. A simple model of the twist interaction between two rod-like chiral molecules

$$V_{1,2} = -(3/16r_{12}^4)\,[\alpha \cos 2\theta_{12} + (2\beta/r_{12}) \sin 2\theta_{12}] = -(3/16r_{12}^4) \cos 2(\theta_{12} - \theta_0) \qquad [5]$$

where θ_0 is the twisting angle when the potential is a minimum or $\theta_0 = 1/2 \tan^{-1}(2\beta/\alpha r_{12})$, where α is the coefficient of the symmetric part of the potential, which is related to the anisotropy of the molecular polarizability and β is the coefficient of the asymmetric part related to the dispersion energy determined by dipole-quadruple interaction. The β term vanishes for molecules which contain a mirror plane of symmetry or which are allowed to rotate freely about their major axes. This feature explains well the formation of an induced chiral nematic phase in a mixture of nematic solvent and an optically active solute and the formation of a compensated achiral nematic phase in a racemic mixture of chiral molecules. However the symmetric form of the potential $V_{1,2}$ in equation 5 also leads to another conclusion that the pitch (or twisting power) is almost independent of temperature. Obviously, this contradicts the strong temperature dependence of pitch observed for chiral nematics.

Finkelmann and Stegemeyer[43] extended Goossens' model and took into account the effect of rotation of rod-like chiral molecules about their long axes. In their theory, one of the two mutually perpendicular directions for the short molecular axis is thought to be energetically more favorable, resulting in a certain amount of rotational order. At increasing temperature the rotation becomes less restricted and the resulting twist angle decreases. The predicted temperature dependence of the pitch is consistent with experimental data for a variety of induced chiral nematic systems.

Combining the theories of Keating and Goossens, Lin-Liu et al.[44] developed a model in which the intermolecular potential is required to contain a chiral contribution as a result of symmetric considerations. The resulting theory, based on a mean field analysis, is able to account for the origin of the helicoidal ordering of chiral nematic phases and the temperature dependence of pitch. According to the theory, the temperature dependence of the pitch is determined by the shape and position of the intermolecular potential $V_{1,2}$ as a function of the intermolecular twist angle, θ_{12}. Thus a positive and negative temperature dependence of the pitch is well illustrated by their proposed forms of potentials. Another consequence of their prediction is that an increase or decrease in temperature would result in an increase in the pitch to infinity at $\theta_{12} = 0$, and then a decrease in the pitch, accompanying a change in handedness. This is the so-called thermally-induced compensation. This phenomenon is observed in polypeptide and cellulosic liquid crystals[37,38].

In addition to the above theories Böttcher[45], Wulf[46] and Van de Meer[47] also proposed similar models to those of Keating, Goossens and Lin-liu. Chilaya and Lisetski[48] recently developed a more realistic model by combining the above models to allow a semiquatitative comparison with experimental data. It should be noted that the above-described models were originally proposed for thermotropic rather than lyotropic liquid crystals since the effect of non-mesogens such as solvent on chiral interactions was not considered. Lyotropic polypeptide liquid crystals exhibit many interesting chiroptical properties, e.g. a solvent dependence of handedness and pitch and/or solvent-induced compensation even though the polypeptides preserve their α-helix conformation and the solvents are achiral[26], which has led to considerable interest by theorists. As a result, several expanded theories have arisen from those mentioned above for thermotropic mesophases and have been developed specifically for lyotropic system.

Samulski and Samulski[49] made the first efforts to relate the nature of the solvent and chirality of the constituent chiral molecules to the helicoidal ordering in their theory. Their energy calculation of the van der Waals-Lifshitz forces between two rod-like chiral molecules embedded in an isotropic dielectric medium is based on the McLachlan susceptibility theory[50]. The resulting asymmetric term in the pair potentials leads to a non-zero dihedral angle between the major axes of the chiral rods. However, they predicted that the asymmetric term will vanish if the dielectric constant of the solvent medium meets a critical condition, as given below

$$\varepsilon^* = \pm \sqrt{\varepsilon_1 \varepsilon_2} \qquad [6]$$

where ε_1 and ε_2 are the principal values for the dielectric constant perpendicular to the long axis of the chiral rods. In other words, a compensated nematic should be formed. When the dielectric constant of the solvent is larger or smaller than ε^*, the corresponding chiral nematic phase should exhibit opposite handedness. Lyotropic polypeptides in non-interactive solvents appear to behave in agreement with the predictions of the theory[26]. However, the temperature-induced compensation observed for lyotropic mesophases can not be explained by this theory.

Assuming that α-helix polypeptide molecules have a helically grooved rod like shape (Figure 1.7 (a)), Kimura et al.[51] developed a statistical theory where the effect of attractive dispersion forces and geometric repulsions between the coiled rods are both taken into consideration. Summing these two intermolecular forces, they obtained an expression for the twisting power:

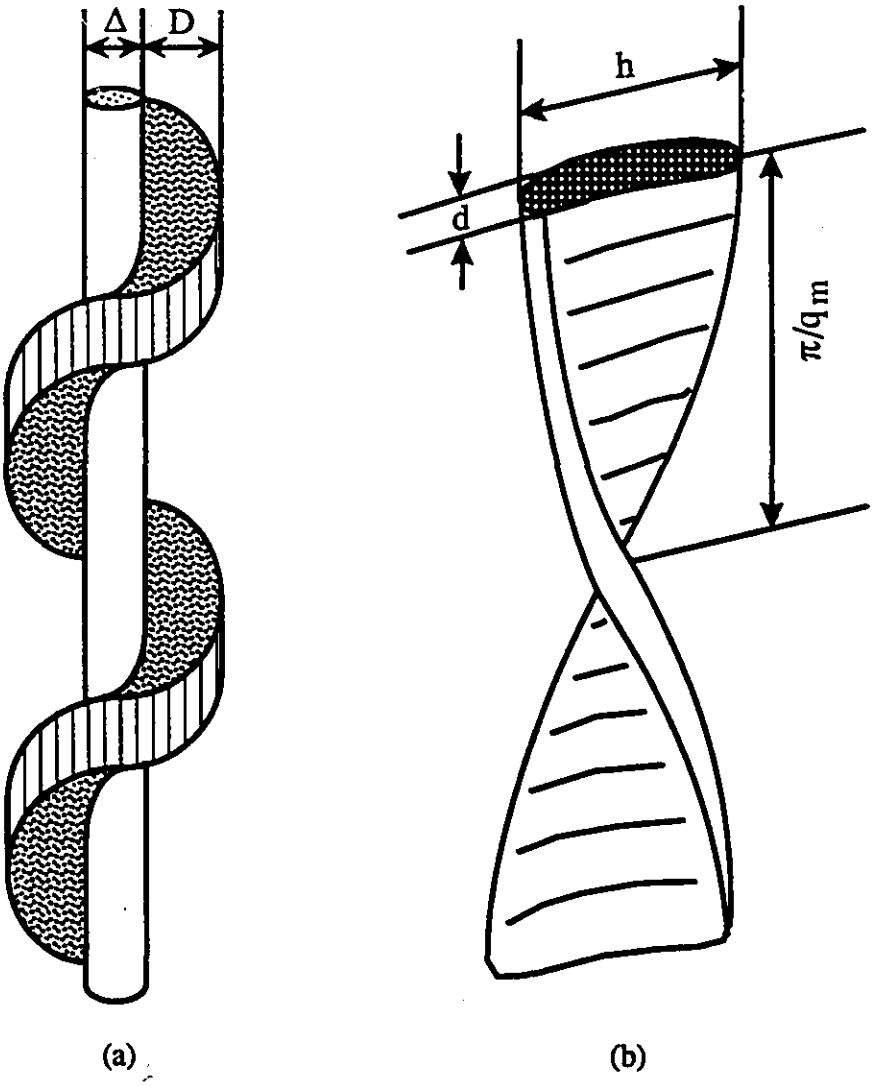


Figure 1.7. Schematic representation of models for chiral macromolecules, (a) helical rod (b) twisted belt.

$$\frac{2\pi}{P} = \frac{24\lambda\Delta}{\pi LD} cf(c) \left(\frac{T_N}{T} - 1 \right) \qquad [7]$$

where L and D is the length and diameter, respectively, of the rod, λ is a numerical factor, Δ is the height of the ridge of the coil (corresponding to the length of the side-group measured from the core of the polypeptide rod), and T_N is the temperature at which the pitch is infinite. The concentration function f(c) is defined as

$$f(c) = (1 - c/3) / (1 - c)^2 \qquad [8]$$

The importance of this theory is the introduction of molecular exclusion into an energy calculation and a correlation of the molecular structural parameter and the amount of solvent (concentration) to twisting power. The theory explains well the thermally-induced compensation and concentration dependence of pitch observed for lyotropic polypeptide mesophases. Unfortunately, the theory fails to explain the solvent-induced handedness inversion for the same lyotropic mesophases, presumably because the nature of the solvent is not included in the attractive force contribution.

In the most complete theory to date, Osipov[52] also took into account both steric and attractive interactions in his calculation of intermolecular potential. In addition, the effects of the dielectric nature of the solvent surrounding the chiral rods (polypeptides) on chiral interactions is also considered, as in Samulski's model. The resulting chiral interaction potential is a function of the anisotropic permittivity and optical activity of the chiral molecules and dielectric constant of the solvent. This relation is expressed in equation 9

$$2\pi / P = - \rho^2 [J_0 (\varepsilon_m) - \lambda k_B T] S (S + 2) / 6 K_{22} \qquad [9]$$

where ρ is the number density of chiral molecules, k_B is a constant, K_{22} is the elastic twist constant of the mesophase, S is the orientational order parameter, $J_0 (\varepsilon_m)$ is a coupling constant related to molecular polarizability and optical activity and solvent dielectric constant, and λ is a pseudo scalar parameter, determined by the steric repulsion between chains. In the case of polypeptides, $\lambda \approx L^2 \Delta D/2$. According to the above expression, the handedness (defined by the sign of the pitch) is altered by the variation of ε_m and T. Compensation occurs when $T^* = J_0 (\varepsilon_m) / \lambda \kappa T$, where the compensated temperature T* is dependent on the dielectric constant of the solvent, ε_m. Therefore the solvent dependence of the sign and magnitude of the pitch, and solvent- and temperature-

induced compensation observed for lyotropic polypeptide mesophases are qualitatively explained by this theory.

Recently, Osipov[53,54] noticed that the class of semirigid chiral molecules such as cellulosics are not appropriately represented by a rod-like model. By assuming that the cellulose chain adopts a "twisted belt" conformation (Figure 1.7 (b)) rather than a helix (Figure 1.7 (a)) he further extended his original theory to lyotropic cellulosic liquid crystals by considering molecular flexibility, and he arrived at the following expression for twisting power, which is similar in form to equation 9

$$2\pi / P = - \rho^2 (\chi - \lambda k_B T) / 2 K_{22} \qquad [10]$$

where χ is related to the attraction interaction, ρ is the number density of rigid segments, $\rho = cL/l_o$, where c is the number density of the macromolecule chains and l_o is the length of the segments. In the case of perfect orientational order of the molecules ($S \rightarrow 1$), the pseudoscalar parameter λ in the "twisted belt" model can be expressed as equation 11

$$\lambda = -(kT/2) \rho^2 q_m h^2 (d + 5h/3\pi) l_o^2 \qquad [11]$$

where d and h are thickness and breadth of the belt, respectively, and q_m is equal to $2\pi/P_m$, where P_m is the period of the twist. The equation 11 is valid when $q_m/(d+h) \gg 1$. The term, $(\chi - \lambda k_B T)$, determines the handedness of cellulosic liquid crystalline solution. Therefore the handedness depends not only on the temperature and steric repulsion of the chains for cellulose derivatives, λ, which is related to the nature and position of the substituents on the cellulose main-chains, but also on the attraction interaction between cellulosic chains, χ, which involves a contribution from the nature of the solvent surrounding the cellulosic chains. In other words the solvent-cellulosic interactions are taken into account. Again the Osipov's theory can only provide a qualitative explanation for the chiroptical properties of semirigid cellulosic mesophases.

More recently, Varichon et al.[55,56] extended Lin-Liu's molecular statistical theory[44] by explicitly considering orientational entropy terms. After minimizing the total free energy for a chiral nematic liquid crystal with respect to the orientational distribution, they obtained an expression for chiral nematic pitch

$$\frac{2\pi d}{P} = \frac{n_0 + \frac{\hat{x} m_1 + \hat{x}^2 n_2}{n}}{\frac{\lambda_2}{\gamma_2} + \frac{\hat{x} d_1 + \hat{x}^2 d_2}{n}} \qquad [9]$$

where the parameters in the equation are defined in detail in reference 55 and are related to the ratio of the second and fourth order parameters S(T), the chiral interaction parameter μ_m, and the nematic interaction parameter γ_2. The magnitude and sign of the pitch are correlated to temperature, concentration, and degree of polymerization (DP) by these parameters. The resulting theory is in qualitative and semiquatitative agreement with some experimental results in which the pitch and handedness of cellulosic liquid crystals depend on temperature and concentration, and molecular weight and substituents. The solvent in this theory was considered to act only as a diluent for the anisotropic solution. Consequently, the theory at present does not explain the solvent dependence of handedness.

In summary, the intermolecular interaction potentials responsible for the helicoidal ordering of chiral molecules in all these theories can be classified as (i) chiral dispersion interaction, (ii) molecular repulsion, or (iii) hindrance of rotation about the major molecular axes. As Chilaya and Lisetski[48] pointed out "chiral nematics appear to be the most complicated systems in the field of liquid crystals"; thus real intermolecular interactions among chiral molecules can not simply be described by the above models. As a result, none of the above theories is applicable to all chiroptical behaviour exhibited by chiral nematic phases. A comprehensive theory for chiral nematic liquid crystals needs to be further developed.

1.2.4. Helicoidal structural characterization

The most important structural parameters in the model for the chiral nematic structure depicted in Figure 1.3 are the pitch and handedness. In different chiral nematic systems, the pitch values may vary from a few nanometers up to hundreds of micrometers. It is impossible to measure the pitch through this range using the same techniques. Similarly, the techniques for the assignment of the handedness are also restricted by the range of the pitch of the sample. In addition, the texture exhibited by the sample is also an important factor in selecting the best technique to characterize the pitch and handedness.

1.2.4.1. Measurement of the pitch.

i. Selective reflection from the planar texture. As discussed earlier, the selective reflection of light is one of this texture's main optical characteristics and the wavelength of maximum reflection, λ_0, is related to the pitch by the following formula[57]

$$\lambda_0 = \frac{\bar{n}|P|}{m} \cos\frac{1}{2}\left[\sin^{-1}\left(\sin\frac{\varphi_i}{\bar{n}}\right) + \sin^{-1}\left(\sin\frac{\varphi_r}{\bar{n}}\right)\right] \qquad [13]$$

where m is an integer, $\bar{n}$ is the mean refractive index for the mesophase and φ_i and φ_r are the angles of incidence and reflection, respectively. Both angles are measured with respect to an axis perpendicular to the substrate plane. The selective reflection technique is considered quite reliable relative to other techniques, especially in the visible region of λ_0 (0.2 μm <|P|< 0.6 μm)[48]. In practice, the technique is applicable to the samples with polydomain planar textures.

ii. Selective transmission from the planar texture. The selective reflection from the helicoidal structure causes an apparent absorption of transmitted light. Provided that a chiral nematic phase contains no chromophore either inherent to the mesogens or within the mesophase as a guest, or if any, absorption bands from the chromophores must appear at wavelengths away from λ_0, the same relationship between the |P| and λ_0 in equation 13 can be generally applied. The pitch for samples with reflection band below 800 nm can readily be obtained from commercial spectrophotometer. For some special spectrophotometers, the pitch range can be measured up to 2 μm. If measurements are made using a CD or ORD spectrometer, the handedness of the sample can be obtained at the same time.

The calculation of the pitch from the above selective reflection and transmission measurements assumes that the sample refractive index $\bar{n}$ is available and can be measured using a refractometer or in some other manner.

iii. Bragg diffraction from the fingerprint texture. When a fingerprint textured sample is irradiated with an incident light, a diffraction will take place. The diffraction condition may be described by the following equation in which the incident light beam λ_0 is related to the angles of incidence and reflection φ_i and φ_r [58].

$$\lambda_0 = \frac{|P|}{2m}\left(\sin\varphi_i + \sin\varphi_r\right) \qquad [14]$$

For normal incidence where $\varphi_i = 0$, the above equation reduces to $\lambda_0 = (1/2)\,|P|\sin\varphi_r$, where m is an integer. In this case, the fingerprint sample behaves like an optical grating with a spacing equal to half of the pitch. When monochromatic light is incident on a polydomain fingerprint texture, a diffraction ring will be observed on a screen placed behind the sample and perpendicular to the beam. The pitch is thus related to the radius of the diffraction ring and the sample-image distance by $\tan\varphi_r$ and can be calculated without knowing the refractive index of the mesophase. If a He-Ne laser beam is used as light source, reliable data can be obtained for samples with pitch ranging from 0.8 to 10 μm[48].

iv. Microscopic measurements from the fingerprint texture. The simplest method is to measure the distance between adjacent dark or light lines in the fingerprint texture directly by using a polarizing microscope. The measured distance corresponds to the half of the pitch. The best results are obtained for samples with pitches larger than 1.5 μm.

v. Cano-wedge technique. This method involves introducing a chiral nematic sample into a wedge-shaped cell and measuring the distance *l* between disclination lines observed under a polarizing microscope[59]. The pitch is then calculated according to equation, $|P| = 2\alpha l$, where α is the angle of the wedge. Pitches up to 200-300 μm may be estimated by this method.

In general, the above-mentioned methods give a relative error of around 10% in the determination of the pitch[60]. If a wide range of pitches for a sample are to be measured, the various methods described above may be combined so that a more accurate result can be obtained.

1.2.4.2. Determination of handedness

i. Circular dichroism (CD) spectroscopy. The CD spectrometer is designed to produce circularly polarized light and measure the difference between transmitted left- and right-handed circularly polarized light as a function of wavelength. When the circularly polarized light passes through an optically active medium, one of the circularly polarized component will be absorbed to a greater extent than the other, or will be reflected while the other is transmitted. The phenomenon in the former case is called normal CD while in the latter case it is called apparent CD or circular reflectance (CR). The selective reflection of circularly polarized light by chiral nematic phases makes it possible for the

chiral nematic structure to be characterized by means of CD spectroscopy provided that its pitch falls into the spectral region. The resultant circular polarized dichroic ratio D is defined as

$$D = (I_R - I_L) / (I_R + I_L) \qquad [15]$$

where I_R and I_L are the optical intensities of the transmitted right- and left-handed circularly polarized light.

A negative apparent CD signal means that the right-handed circularly polarized light is reflected and the left-handed circularly polarized light is transmitted, indicating that the corresponding mesophase is right-handed. A chiral nematic phase giving a positive apparent CD corresponds to a left-handed structure. A typical shape for the apparent CD peak of a left-handed chiral nematic sample with a planar texture is shown in Figure 1.8. The position of maximum intensity in the apparent CD peak corresponds to the reflection wavelength of the mesophase. Therefore CD measurements can provide information on both pitch and handedness for a chiral nematic phase. Commercial CD spectrometers can only be used to study samples with pitches falling in the UV-visible region of light.

ii. Optical rotatory dispersion (ORD) spectroscopy. The ORD spectrometer is designed to produce plane (linearly) polarized light components consisting of two circularly polarized light that have equal phase and amplitude, and to measure the optical rotation as a function of wavelength. The magnitude of the optical rotation is proportional to the difference in the refractive index for the right- and left-handed circularly polarized light. When a plane polarized beam passes through an optical active medium containing a chromophore, the refractive index for the two circularly polarized components will differ and thus result in a rotation of the plane polarized beam away from its original position. The resultant ORD spectrum consist of a feature known as a Cotton effect (positive or negative) in the region of absorption, that is, the sign for the optical rotation is changed as the wavelength crosses over the absorption band. As a dispersive phenomenon, optical rotation is also observed at wavelengths far away from the absorption region. This feature gives ORD a distinct advantage over CD for the study of chiral media in the absence of chromophores. On the other hand, it also makes the ORD spectrum more complicated because of the superimposition of different chiral sources.

In the case of a chiral nematic phase containing no chromophores, a positive or negative pseudo Cotton effect may be observed in the ORD spectrum if the reflection band falls into the spectral range. According to de Vries' theory (equation 2), a chiral nematic phase exhibiting a positive pseudo Cotton effect is a left-handed helicoidal structure whereas a chiral nematic phase exhibiting a negative pseudo Cotton effect corresponds to a right-handed structure. A typical ORD spectrum for a left-handed chiral nematic sample with planar texture is shown in Figure 1.8. The observed cross-over wavelength, for which the optical rotation is zero, corresponds to the maximum reflection for the mesophase and to the maximum CD peak (Figure 1.8).

Unlike CD, ORD spectra also provide information on the optical activity for the chiral nematic phase at wavelengths other than the reflection band because of its dispersivity. As a result, the ORD technique may be applied to those samples with a reflection beyond the UV-visible region provided that (1) there is no chromophore within the mesophases and (2) the intrinsic contribution to the optical rotation is negligible with respect to the optical activity arising from the helicoidal structure. The assignment of the handedness is based on de Vries' equation for the case of $\lambda_0 \gg \lambda$ (equation 3). When the optical rotation of the mesophase in the UV-visible region is positive or negative, the corresponding mesophase is either right- or left-handed, respectively. For samples with very long pitches, the determination may become difficult due to scattering interference.

iii. Induced circular dichroism. The extrinsic optical activity exhibited by achiral chromophore molecules intercalated into a chiral nematic phase provides an alternative way to access the helicoidal structure, since the optical activity can be observed in induced CD (ICD) spectra[39]. The ICD signals appearing in the absorption region of chromophores are a result of differential absorption of right- and left-handed circularly polarized light. The chromophores in this case act as a probe of the chiral nematic structure. According to theories[61-63], the sign of the ICD is related to the handedness of the host mesophase, the relative position of the pitch-band of the host mesophase to the absorption bands of the guest chromophores and to polarization of the electronic transition of the chromophores. In principle, the handedness of a chiral nematic phase can be inferred from the ICD guest chromophores regardless of the range of the pitch for the mesophase, provided that the electronic transition of the chromophores are well characterized, the relative pitch-band position of the mesophase is known and an uniform planar texture is formed in the sample to be measured[39]. In practice, however, the existence of linear birefringence (LB) and linear dichroism (LD) may affect to various extents the resultant ICD behaviour[64-65]. Therefore the macroscopic LB and LD must be

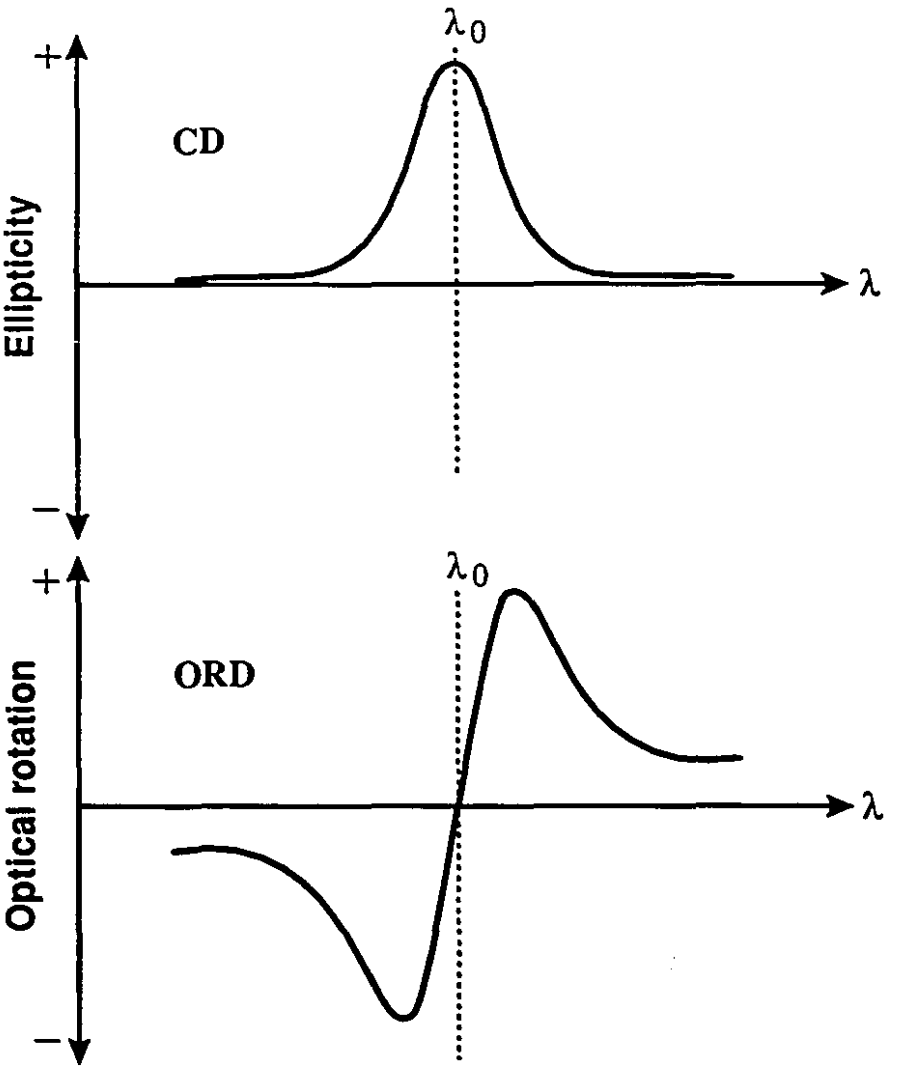


Figure 1.8. An apparent CD and an ORD spectra for a left-handed chiral nematic liquid crystal with a reflection band maximum at λ_0.

minimized during sample preparation and measurement, when this technique is to be applied. The handedness of a chiral nematic phase containing chromophores may also be assigned using a spectrophotometer with a circular polarizer[66].

iv. Other techniques. Several other techniques, such as measuring the retardation of light passing through a chiral nematic phase with a reflection band by use of a polarizer and Berek compensator[67], or analysis of polarizing scattering patterns for a light passing through a chiral nematic phase with pitches ranging from 0.8-10 μm by use of a laser beam with a polarizer and an analyzer have been used to determine handedness[68] . These methods are neither as convenient nor conclusive as CD and ORD, and thus are not widely employed. In the case of solid films with chiral nematic structures, the pitch and handedness of the chiral nematic can be determined using a transmission electronic microscope if oblique sections of the films are available[69].

The above techniques for characterization of the pitch and handedness of a chiral nematic liquid crystal are summarized in Table 1.1.

1.3. Liquid crystals in living systems

It has been recognized that many biological structures exhibit similar morphology and optical properties as liquid crystals. Living tissues such as muscle, tendon and nerve show birefringence characteristic of liquid crystals[3,5,70]. Massive deposits of mesomorphic cholesterol derivatives have been found in kidneys, liver, brain, etc. Solutions of viruses, collagen, native proteins, nucleic acids and fibrinogen exhibit many resemblanes to the liquid crystalline state. It seems probable that liquid crystallinity has important biological consequences, because of (i) its presence in living materials, (ii) its mobility and self-assembly and (iii) its unusual dependence on slight change in composition or on the physical and chemical environment for its formation, existence and disappearance. The following description of liquid crystals in living systems will focus only on three main biologically occurring polymers *in vitro* and *in vivo*. Emphasis will be placed on their chiroptical properties in the mesophase.

1.3.1. Synthetic polypeptides and native proteins

The most extensively studied class of polymeric liquid crystals is the synthetic polypeptides. These were one of the first groups polymers found to be capable of forming mesophases and also they are analogues of the main component of native silk. Certain

Table 1.1. Techniques for the measurement of the pitch and handedness for chiral nematic liquid crystals

Technique		Measurable pitch range	Handedness assignment
UV-visible spectrophotometer	alone	0.2 ~ 0.6 μm	No
	with a polarizer & addition of chromophores	—	Yes(a)(b)
CD spectropolarimeter	alone	0.2 ~ 0.6 μm	Yes
	with addition of chromophores	—	Yes(a)(b)
ORD spectropolarimeter	alone	0.2 ~ 0.6 μm	Yes
	alone	—	Yes (P »1 μm)
Laser diffractometer	alone	0.8-10 μm	No
	with polarizers	—	Yes
Polarizing microscope	alone	> 1 μm	No
	with a compensator	—	Yes (P=0.2~0.6μm)
Cano-wedge (alone)		up to 300 μm	No
Electron microscope (alone)		down to 0.1 nm	Yes(c)

(a) When the pitch-band from a mesophase does not overlap with the absorption bands of the chromophores.

(b) The handedness can be assigned for those samples with pitch values beyond the visible light.

(c) From oblique sections of solid or cross-linked films with chiral nematic structures.

synthetic polypeptides, e.g. poly-γ-benzyl-L(or D)-glutamate (PBLG or PBDG), are known to exist in stable α-helix conformations in many solvents. As a result of their chain rigidity and chiral chain structures, these polymers can spontaneously form chiral nematic liquid crystals in many concentrated solutions[26]. When viewed in a polarizing microscope, the chiral nematic mesophases are characterized by a region of fingerprint patterns surrounding some uniform domains[71]. Optical rotation measurements on these uniform domains indicate a very high optical rotatory power, suggesting a helicoidal structure whose optical axes are parallel to the incident light. The absence of brilliant iridescent colors for most PBLG liquid crystals is because the helicoidal pitch is beyond the visible light region. Robinson[33] applied de Vries' equation to these long-pitch PBLG mesophases and obtained a birefringence value for the nematic-like layer in a helicoidal structure. These calculated results are in good agreement with the experimental results obtained for a racemic mixture of PBLG and PBDG.

The most striking feature of PBLG mesophases is that their handedness is strongly solvent dependent. For example, a PBLG solution in dichloromethane (DCM) forms a left-handed liquid crystal while in dioxane it forms a right-handed one, although the PBLG preserves the same α-helix conformation in both achiral solvents[72]. In an appropriate mixture of dioxane and DCM (2:8), the resultant PBLG mesophase changes from a chiral nematic structure to a compensated nematic structure in which the pitch is infinite and the macroscopic chirality disappears. Samulski and Samulski[49] have proposed a theory to account for this solvent-induced compensation phenomenon. They predicted that the handedness of lyotropic phase would be determined by a dielectric constant of the solvents. The change in the dielectric constant of the solvent would results in reversing the handedness (equation 6). This prediction is consistent with the solvent-induced handedness inversion observed for PBLG in non-interactive single solvent and mixtures of solvents, in spite of some discrepancies[49,73,74].

The nature of the solvent also strongly influences the temperature dependence of pitch for lyotropic PBLG mesophase. The pitch of PBLG anisotropic solutions in dioxane (right-handed) increases with an increase in temperature whereas the pitch of PBLG anisotropic solutions in dichloroethane (DCE) (left-handed) decreases with increasing temperature. An approximately linear relationship is observed between the inverse pitch and temperature in both cases. Depending on the ratio of dioxane and EDC, mixtures of these two mesophases exhibit compensated behavior at a different temperature T*. Similar phenomena were also observed for PBLG in other solvent systems, namely m-cresol-DCE, m-cresol-trichloropropane (TCP) and TCP-tetrachloroethane (TCE)[26]. Strangely, the thermally-induced compensation was also found for PBLG dissolved in a

single solvent, m-cresol, (17%) at 60°C[73]. The thermally-induced compensation has been explained by Kimura's statistical theory[51] where both attractive and repulsive intermolecular interactions were believed to be responsible for the helicoidal ordering. The compensated temperature observed for some PBLG mesophases fits semiquatitatively equation 7, derived from his model. Considering that neither Samulski's nor Kimura's theory can explain both solvent and thermally-induced compensation, Osipov[52] developed a theory combining the above two models and applied it to PBLG liquid crystals. Qualitatively, both compensation phenomena can be interpreted by Osipov's theory.

In order to understand the above chiroptical behaviour, many experimental efforts have also been made using IR and NMR spectroscopy. IR evidence[73] suggests that the formation of hydrogen bonding between C=O in PBLG and the solvent m-cresol may result in breaking down the aggregates of PBLG α-helices and thus lead to some unusual optical properties when m-cresol mixes with other solvents such as TCP and TCE. Deuterium NMR studies[75,76] on a PBLG sample with deuterium labeled benzyl in the side chain have shown that the average orientation of the label changes substantially with temperature and solvent. The solvent- and thermally-induced compensations may be considered to result from a change in surface chirality from sidechain winding α-helix chain at a compensated temperature or composition. However further examination of deuterium quadruple splitting patterns of labeled PBLG in mesophase leads to the conclusion that handedness inversion may not be a consequence of the backbone or sidechain chirality, but a result of intermolecular interaction between PBLG helices via the solvent dielectric medium[77].

In the absence of solvent, the poly(-L-glumates) with long sidechain are also able to form thermotropic mesophases. Watanabe and his coworker have reported that a polypeptide-based copolymer, poly[(γ-benzyl-L-glutamate) co-(γ-dodecyl-L-glutamate)][37], exhibits handedness inversion with temperature in the mesophase. Although the thermotropic phase is not so important in living systems, it does demonstrate the sensitivity of the macroscopic chirality to chemical structure.

Achiral chromophore molecules such as anthracene and pyrene dissolved in PBLG lyotropic mesophase were reported to show CD signals in the absorption region[78,79]. The induced CD of the chromophores has been attributed to the optical activity induced by the asymmetric environment of PBLG chiral nematic phases since the ICD disappears when the anisotropic phase changes to the isotropic phase upon heating or dilution. The induced CD was also observed for phenyl groups on PBLG sidechain

when the mesophase is formed[74,80]. The sign of the ICD is related to the handedness of the PBLG mesophase.

Many native proteins have been reported to exhibit mesomorphic properties. Tobacco mosaic virus (94% proteins) suspensions were the first native protein to exhibit birefringence characteristic of liquid crystals[81]. The same birefringent feature was later found in suspensions of other viruses such as cucumber virus[82]. Hemoglobin, trypsin and other proteins in organisms have been reported to exhibit liquid crystalline textures[83,84]. Narcissus mosaic virus solutions behave like chiral nematic phases[85].

1.3.2. Nucleic acids

The nucleic acids include deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Both DNA and RNA are long chains of alternating sugar and phosphate groups. The common feature among them is their rigid chains resulting from a double helix secondary structure. The first liquid crystalline phase of DNA in aqueous NaCl solution was observed by Robinson in 1961[72]. Microscopic observation indicates the existence of equidistant dark and light lines with a spacing of 1 μm, characteristic of chiral nematic phases. Soon after, Spencer et al.[86] found that the solutions of baker's yeast transfer RNA also formed a liquid crystalline phase. Currently the formation of mesophases has been recognized as a common phenomena exhibited by nucleic acids *in vitro* and *in vivo*.

Basically the formation of lyotropic mesophase of nucleic acids *in vitro* is divided into two classes[87]. First, the nucleic acids dissolved in an aqueous salt solution of moderate or high ionic strength form a self-ordering phase at a critical concentration[87-89]. The second occurs when the ordered phase of nucleic acids is separated from an aqueous polymer solution such as polyethene glycol (PEG)[87,90]. Based on the results of x-ray and microscopic observation, multiple liquid crystalline phases existing in DNA solutions have been identified as precholesteric, chiral nematic or columnar, depending on the concentration[91]. ^{23}Na NMR studies on solutions of DNA also confirmed the existence of the multiple ordered phases[92]. In these chiral nematic phases, the pitch range from 0.2 to 5 μm. A left-handed helicoidal structure of the DNA chiral nematic phase has been suggested on the basis of the negative sign of liquid crystal induced CD from the ordered chromophores on the DNA chain in mesophase[91].

Yevdokimov et al.[87,93,94] reported that the helicoidal structure of DNA lyotropic phase can be changed when the DNA complexes with anti-tumour compound or antibiotics. The formation of the complexes of DNA with cis-Pt(II) results in a phase transition from chiral nematic to isotropic. A handedness inversion also occurs when

DNA-antibiotic (daunomycin) complexes have a molar ratio of daunomycin and DNA over 0.165. In addition, as a chromophore, the daunomycin also exhibit induced CD in the absorption region. The sign for the induced CD is reversed as the handedness of the DNA mesophase is changed.

Liquid crystal analogues are also widely observed for DNA and RNA *in vivo*. A comparison of DNA supermolecular organization in vitro with that observed for chromatin *in vivo* has been made by Livolant[91], as shown in Table 1.2. This parallelism in the table strongly suggests that the DNA liquid crystals are involved in the process of condensation of chromatin *in vivo*. The mesomorphic behaviour exhibited by the mesophases of DNA *in vivo* is a little different from (but analogous to) that *in vitro*, e.g. ordered phase structure, pitch range and texture defects, because the DNA in nature often associates with other compounds such as proteins and their concentrations are different from each other in local domains[91].

1.3.3. Polysaccharides

Polysaccharides, one of the most abundant classes of biopolymers, play an important role in the development of structure support and the transformation of energy in living organisms. The main polysaccharides include cellulose, chitin, starch and glycogen. Similar to proteins and nucleic acids, most polysaccharides are able to form ordered phases. Among these, cellulosic mesophases are the most extensively investigated and will be separately described in detail in the next section.

A component of starch, amylose, is composed of α-linked 1,4 anhydrogluose units. The only difference in structure between amylose and cellulose is that the glucosidic linkage has an α configuration in the former and β in the latter. This difference makes the amylose chain less rigid than the cellulose chain. So far, only triethyl and trimethyl amylose in chloroform have been reported to form liquid crystalline phases[95]. Xanthan, a β-linked 1,4 glucopyranosyl main-chain with branches can form liquid crystals in concentrated salt solutions, and exhibit chiral nematic features[96,97].

Schizophyllan and scleroglucan belong to another class of polysaccharides, β-linked 1,3 glucans. The rigidity of the glucans arises from their triple helical conformation[4]. Consequently, a relative low critical concentration is required to form ordered phase (10-14% by weight). The ordered phases show fingerprint textures and exhibit high optical rotatory power, and thus belong to typical chiral nematic liquid crystals[98-100].

Table 1.2. Comparison of DNA organization between *in vitro* and *in vivo*

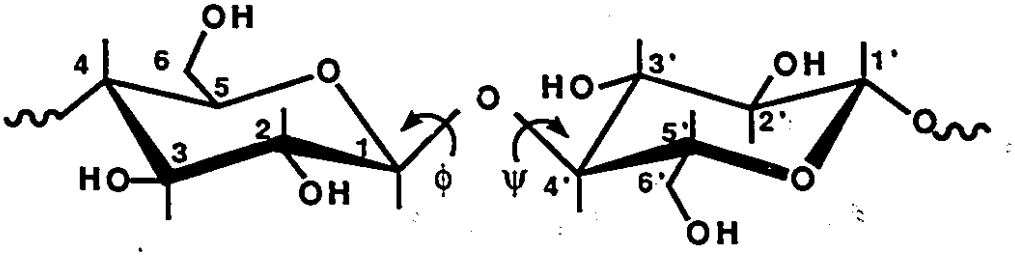
			IN VITRO			
isotropic	↔	precholesteric helical organization (only for long DNA fragments > 500 Å)	→	cholesteric phase (P = 0.2-5 μm)	↔	columnar hexagonal phase
		An increase in DNA concentration →				
decondensed chromatin in the interphase nucleus		decondensed chromosomes	←	dinoflagellate chromosomes (P = 700-4500 Å)		bacteriophages
		eucaryotic chromosomes with a helical shape (*Tradescantia*)		bacterial nucleoids (P = 1000-8000 Å)		
				mitochondrial DNA sperm nuclei (stallion) (P = 500-700 Å)		sperm nuclei (trout, salmon)
			IN VIVO			

An aminopolysaccharide, chitin, is the main component of decalcified crab shells and insect cuticles. Thin samples of outer exocuticle of some beetles reflect lights that is circularly polarized in the direction opposite to that of the transmitted light in the reflection band, a behaviour characteristic of chiral nematic phases[70]. A twisted fibrous arrangement has also been observed for a thin section of insect cuticle[6,101]. These observations provide a strong implication of the biological consequence of chiral nematic ordering. *In vitro*, only partially deacetylated chitin microfibrils suspended in water were found to show birefringence in 1959[102]. Recently, unequivocal evidence of chiral nematic structure exhibited by acid-treated chitin microfibrils suspensions was observed by Revol et al[13]. This significant observation further suggests the involvement of liquid crystalline states in some bioprocess in nature.

1.4 Cellulosic liquid crystals

1.4.1. Chemical characteristics and conformation of cellulosics

Cellulose is the most abundant natural polysaccharide. Chemically it is a linear condensation polymer consisting of D-anhydroglucopyranose units linked together by β-1,4-glucosidic bonds. The pyranose residues in cellulose chain assume the energetically favourable $^4C_1$ chair conformation as in the β-D-glucopyranose molecule, and thus are inflexible. As the result, the conformation of the cellulose chain is determined largely by the relative orientation of the adjacent residues, defined by two dihedral angles ϕ and ψ, between C(1)-H(1) and O(4')-C(4') and C(4')-H(4') and O(4')-C(1) bonds, respectively, as shown below.



Although it may seem that the rotation about these angles could generate numbers of possible conformations, in fact many conformations are forbidden by steric repulsion between atoms on the adjacent residues and intrahydrogen bonding. Results of energy calculation[103-105] suggest that the cellulose chains adopt an extended conformation where ϕ and ψ are energetically favorable and the repetition along the chain of a

preferred angle between adjacent inflexible residues may generate a helix in which each residue lies near the helix axis, but is twisted relative to the previous one. Such conformation render the cellulose chains relatively rigid. Apparently the helical conformation of cellulose chains differ in origin from that of polypeptides since the helix of the polypeptides in solution results from hydrogen bonding between adjacent residues and can be converted into a coiled conformation upon heating or changing pH[106]. Osipov has proposed such a twisted belt model describing the conformations of cellulosics that distinguishes it from the helix of polypeptides as shown in Figure 1.8 (b).

Conformational analysis based on energy calculations is in general agreement with experimental results obtained by means of x-ray and electron microscopy for crystalline cellulose[107-110]. Recently CP/MAS ^{13}C NMR measurements of native cellulose by Horii et al.[111] indicate that the chemical shifts of C(2), C(3), and C(6) on anhydroglucose residue are correlated to the torsion angles ϕ and ψ. A narrow distribution of ϕ and ψ inferred from their NMR results corresponds to an extended cellulose chain in crystalline state. In solution, cellulose also exhibits high degrees of the chain extension as characterized by its high characteristic ratio (the ratio of the mean square and end-to-end distance of a real polymers to that of the corresponding ideal freely jointed chain)[112-115]. A helical conformation of cellulose oligomers in solution has been suggested by ^{13}C-^{1}H coupling[116] and induced CD results[117].

Another chemical characteristic of cellulose is that one primary hydroxyl group and two secondary hydroxyl groups are located at C(6), and C(2) and C(3) positions of each anhydroglucose unit, respectively, leading to the formation of large numbers of intra and intermolecular hydrogen bonds. The resulting intrahydrogen bonds of C(3')OH-O(5) and C(6')OH-O(2)OH are one of main sources of the rigidity of the cellulose chain and the interhydrogen bonds render cellulose insoluble in water and common solvents despite the hydrophilic nature of the hydroxyl groups. On the other hand, the hydroxyl groups provide convenient sites for substitution reaction, leading to a variety of cellulose derivatives. Introduction of the substituents to the hydroxyl must result in disrupting the intra and interhydrogen bonds and introducing new steric effects and interaction between the substituents to various extents, depending on the degree of substitution (DS) (defined as the average number of substituted OH per anhydroglucose unit) and the size and the nature of the substituents. As a consequence, most cellulose derivatives, in general, have a better solubility in a wider range of solvents, and while they may have differ in degree of flexibility from each other, they retain a similar extended chain conformation to cellulose due to the resistance of the inflexible anhydroglucose residues to large changes in the torsion angles ϕ and ψ.

Several cellulose derivatives have been found to exist in crystals or crystal solvates as a helical chain conformation, based on electron microscopic and x-ray analysis[118,119]. The hydrodynamic behaviour of cellulose derivatives in solution suggests an extended conformation[112,120]. Induced CD studies of carboxymethylcellulose (CMC)[121] and methylcellulose (MC)[117] , dyed with acridine orange and congo red, respectively, give a evidence of helical conformation for these two derivatives in solution. Harkness and Gray also observed an exiton split band in a CD spectrum for 6-O-a-(1-methylnaphthalene)-2,3-pentylcellulose solution in cyclohexane, indicative of a helical arrangement of the side-chain chromophores[122].

For partially substituted cellulose derivatives, distribution of the substitution along cellulose chain or among C(2), C(3), and C(6) positions per anhydroglucose unit may affect their conformation. Schweiger[123] has demonstrated a significant difference in solution properties for samples of cellulose sulphate prepared by homogeneous and heterogeneous methods. Recent IR work on specifically substituted cellulose ethers by Kondo and Gray reveals that the ether group on C(2), C(3), or C(6) position strongly influences intra and interhydrogen bonding[124]. The effects of substituent distribution on physical and commercial properties have not yet been explored effectively.

1.4.2. Cellulosic mesophases

Because of their extended chain conformation, cellulosic polymers have been predicted by Flory in 1956 to be able to from liquid crystalline phase, on the basis of his lattice theory[22]. The first observation of this ordered phase in cellulosics was almost twenty years later than the prediction[8]. As discussed in the introduction, liquid crystals are characterized by their mobility and orientational order. The large numbers of hydrogen bonds in cellulose generate such strong intermolecular forces that the cellulose chains lack mobility and will decompose on heating before reaching a melting temperature at which the cellulose chains might start to move and form an ordered phase. Therefore cellulose itself does not spontaneously form a mesophase in spite of its semirigid chain. Most cellulosic liquid crystals reported so far are either cellulose derivatives in bulk or solution, or solutions of cellulose in polar solvents, in which the hydroxyl groups are blocked by substituents or associated with solvent so as to prevent hydrogen bond formation and to achieve mobility and orientation.

1.4.2.1. Lyotropic mesophases of cellulose derivatives

Hydroxypropylcellulose (HPC) is the first cellulose derivative reported to form liquid crystalline phase in concentrated aqueous solution. Werbowyj and Gray[8] observed that a phase separation spontaneously takes place as the HPC concentration increases over a specific range (critical concentration V_C^*). Since then numerous cellulose esters and ethers have been reported to form the anisotropic phases in a variety of solvents[125-127]. In general, the measured critical concentration for phase separation is much higher than theoretical prediction from Flory's rod-like model for polymers (equation 1). As a result, a freely jointed chain model[27] has been proposed to describe semirigid polymers such as cellulosics, in which the axial ratio x = L/d in rod-like model is replaced by x = L'/d, where L' is segment length of a freely jointed chain and d is the chain diameter. Considering that real cellulosic chains are not freely jointed, the Kuhn segment length for a random flight chain or the equivalent segment length for a warm-like chain of persistence length q has been suggested to be taken as the L' in freely jointed chain model, L' = k or $x = k_w/d = 2q/d$. The resultant calculation seems to be closer to line with experimental data despite some deviations[126,128-131]. This general agreement further suggests that the critical concentration for phase separation is determined to a large extent by the stiffness of semirigid cellulosic chain since the persistence length is a measure of chain stiffness.

The fact that the observed values of the critical concentration for mesophase formation in cellulosic system are subject to the type of substituents and solvents implies that the change in chain stiffness may result from the chemical characteristics of cellulosic and solvents. This is evident by recent studies of DS effects on the rigidity of cellulose acetate (CA) in dilute solution and on mesophase formation of some derivatives in concentrated solution. Kamide and Saito[113,132] have shown that the unperturbed chain dimension of CA in dilute solution increase with DS, corresponding to a increase in the chain rigidity. Critical concentration for mesophase formation for (carbamoylethyl)cellulose (CBEC) solutions has been reported to decrease from 50% to 35% by weight as the DS of CBEC increases from 1.0 to 2.3[133]. Similar relationship was also observed for cellulose cinnamate (CC)[134] and nitrocellulose (NC)[135] solutions. Although the cause of the change of chain stiffness with DS is not clear, especially in concentrated solutions, the results for CA in dilute solution[113] did lead to a plausible explanation that the stiffness of cellulose derivatives in solution is a result of total contribution from (1) steric interactions between adjacent pyranose residues with or without substituents, (2) intrahydrogen bonding and (3) steric hindrance of solvating solvent molecules. In other words, stiffness of cellulosics depends on the nature of both substituents and solvents and on the content of hydroxyl groups or DS. The solvent effect

is clearly demonstrated by the fact that CA in dilute solution is more rigid in polar solvent than in less polar solvent[113, 132], and that highly polar or acidic solvents generally favor mesophase separation at lower critical concentration than simple organic solvents[136,137]. Comparison of esters with ethers of cellulose with respect to the critical concentration does not give any simple relation. In fact the chain stiffness of cellulosics is not simply additive but is a complicated balance of the above three contributions. This is illustrated by CMC solution, in which the critical concentration for phase separation increases with DS[133], different from that observed for CC[134], NC[135], CBEC[133]. In light of the different reactivity among three hydroxyl groups and the existence of intrahydrogen bonds formed mainly between C(3')OH and O(5)[138], the distribution of substitution for partially substituted derivatives of cellulose may also play a role in governing the mesophase formation.

It has been reported that an increase in molecular weight results in decreasing the critical concentration for some cellulose derivatives such as CA[137,139], but it does not affect the critical concentration for some other polydisperse cellulosics such HPC with main chains much larger than their persistence length[128,129,140]. The reason for the appearance of these two types of molecular weight effects on critical concentration for high molecular weight polymers remains unclear. The phase separation is also affected by temperature. The higher temperature often leads to a higher critical concentration for the mesophase separation in cellulosic system, presumably as a result of the decrease in chain stiffness[140a].

In principle, all cellulose derivatives are able to form liquid crystalline phase in suitable solvents due to their semirigid structure. However crystallization, gel formation, aggregation and other factors may be favored over mesophase formation. To form liquid crystalline phases, the intermolecular attractive forces must be weak enough to allow mesogens to move and achieve orientational order. Hydroxyl-rich or lightly substituted derivatives such as commercial hydroxyethylcellulose (HEC) and methylcellulose (MC) aqueous solution often form gels or aggregates prior to forming mesophase as the polymer concentration increases, possibly due to strong hydrogen bonding between cellulosic chains. Some highly substituted derivatives have been reported to form stable crystalsolvates from liquid crystal phases[135,141,142], presumably because the symmetry in the shape of the resulting cellulose-solvent solvates under certain circumstances favours packing as a highly ordered crystalline structure.

1.4.2.2. Lyotropic mesophases of cellulose

The discovery of the self-ordering of cellulose derivatives has stimulated considerable interest in investigating the possibility of forming mesophases of cellulose itself in solution, because of the potential for making high strength and high modulus regenerated cellulose fibres. As mentioned earlier, however, the main problem facing the formation of an ordered phase of cellulose is its limited solubility in common solvents. Fortunately, great progress in the search for new solvents for cellulose has been achieved in the last decade[143]. In general these new solvents consist of at least one polar component that complexes with or solvates the hydroxyl groups of the cellulose chains, leading to dissolution. Unlike the conventional solvents, these new solvents cause less degradation to cellulose, especially the non-aqueous solvents, and they have relatively highly dissolving ability. The latter feature makes it possible to access the region of high concentrated solution of cellulose.

The first observation of lyotropic cellulose mesophase in a mixture of water and N-methyl-morpholine-N-oxide (MMNO) was claimed by Chanzy and Peguy in 1980[9]. Concentration of cellulose up to 20% by weight gives strong birefringence under a polarizing microscope. The critical concentration for mesophase formation depends on molecular weight, water content and temperature. A rheological study also gave evidence for mesophase formation[144].

Gilbert and his colleagues[10] have found that mixtures of trifluoroacetic acid (TFA) and chlorinated alkanes are excellent solvents for cellulose. Their initial report showed that anisotropic phases of cellulose solution in TFA/DCM or 1,2-dichloroethane (DCE) are separated at a concentration over 20% by weight. Their recent results[145] indicate that the critical concentration can be as low as 4%, depending on the solvent composition. However the system is subject to a strong aging effect, suggesting the occurrence of some degradation of the cellulose.

The development of the LiCl/dimethylacetamide (DMAC) system, a nondegrading solvent, immediately led to attempts to obtain anisotropic solution in the hope of producing high performance fibers[11,115,146,147]. Microscopic and optical evidence indicate that the formation of mesophase occurs at 10-15% by weight, depending on the ratio of LiCl/DMAC. However a stable pure anisotropic solution seems unlikely to be obtained due to limited solubility at high concentration (>15%)[115,147].

Another solvent system for cellulose is a mixture of liquid NH_3 and NH_4SCN, which has been extensively investigated by Cuculo and his coworkers[12,148]. The critical concentration for mesophase formation is found to change from 3.5% to 8.5% (g/ml), depending on the solvent composition and molecular weight of the cellulose. In general, the critical concentration for cellulose solutions for mesophase formation is relatively low

in comparison with that for solutions of cellulose derivatives, presumably because of (1) the existence of the intrahydrogen bonds along cellulose chains and (2) the small size of hydroxyl groups relative to other substituents. As a result of these differences, the cellulose may have a high segmental axial ratio and thus form an ordered phase at a lower critical concentration, according to Flory's lattice theory. In fact, measurements of the persistence length of cellulose in dilute solutions in LiCl/DMAC[115] and NH_3/NH_4SCN[114] have indicated that the cellulose chains are stiffer than the those of cellulose derivatives. It has been suggested that the formation of complexes of cellulose with solvents such as LiCl/DMAC may enhance the stiffness of the resulting cellulose complex chains[115].

Efforts to make high performance films and fibres from anisotropic solutions of cellulose have been made by several research groups[144,148-150]. The results seem to give some properties superior to commercial products but not as promising as expected. This is probably attributed in part to the fact that the ordered structures are not well preserved during the process of the regeneration of cellulose in the presence of the nonsolvents.

More recently, a significant finding was reported by Revol at al.[13] that acid-treated cellulose microfibrils suspended in water can form chiral nematic phase at concentrations lower than 3% by weight. Different from cellulose solution, the cellulose in the suspensions exists as crystallites, crystalline aggregates of cellulose chains. The low critical concentration for the phase separation in this system may related to the shape and charged surface of the microfibrils. Although the mechanism for this type of mesophase formation is not understood yet, this significant finding may provide the insights into the correlation of chirality on a molecular level to macroscopic chirality displayed by cellulose-based biostructures in nature.

1.4.2.3. Thermotropic mesophases of cellulose derivatives

In the absence of solvents, the nature, size and quantity of substituents become the most important factors in governing mesophase formation by cellulose derivatives. Highly substituted derivatives with large and flexible substituents seem to favour formation of mesophases, presumably because such substituents act as 'solvents', disrupting hydrogen bonding between the cellulose chains, preventing crystallization and allowing the cellulosic main chain to have sufficient mobility to achieve orientational order. HPC is a typical example[151-153]. The majority of thermotropic cellulose derivatives reported so far belong to the family of HPC derivatives[154-161]. The larger ester or ether groups HPC-based polymers seem to favour mesophase formation at lower

temperatures. It has been reported that HPC itself form mesophases at 160-205°C[151], while the acetic acid ester of HPC form them at 90-160°C[155]. In extreme cases, the long chain phthalic ester of HPC and cyanoethylated O-(2,3-dihydroxypropyl)cellulose (CEDHPC)[162] exhibit mesomorphic behaviour at room temperature. Like HPC, the hydroxyalkyl celluloses, hydroxyethylcellulose (HEC) and hydroxybutylcellulose (HBC), also form thermotropic mesophases[163]. Bulky cellulose esters, phenyl-, 4-methoxyphenyl- and p-tosyl-acetoxylcelluloses have been reported to show thermotropic characteristics and to be readily regenerated under mild conditions[164]. Recently a specifically substituted derivative, 6-O-α-(1-methynathalene)-2,3-O-pentylcellulose was shown to form a mesophase at 90-110°C[122]. Most of the above thermotropic derivatives are also able to form lyotropic phase in suitable solvents.

In addition to the size, the chemical nature of substituents also strongly influence mesomorphic properties of their derivatives. Yamagishi et al.[165] have shown the phase transition temperature of a series of cellulose esters and ethers varies from 100°C to 180°C, even though these polymers have same DS and approximately same length of substituents and DP. The molecular weight effect seems to be more straightforward. An increase in phase transition temperature with increasing molecular weight has been observed for HPC and acetoxypropylcellulose (APC)[166]. However when the DP of cellulosic chain is small, other unusual liquid crystalline behaviors may be displayed. Long chain alkyl ethers of cellulose oligomer (DP = 11) have reported to form thermotropic chiral nematic liquid crystals whose handedness is temperature dependent[38]. On the other hand, long chain aliphalic esters of cellulose oligomers form columnar liquid crystals in spite of the same chiral cellulosic chain[167]. These observations demonstrate the importance of chemical structure in the cellulosic liquid crystals.

Ethylcellulose (EC) also form another type of thermotropic mesophase[152,168]. Formation of the mesophase in such short substituent derivative is probably related to the content of hydroxyl groups remaining in the cellulosic chain since the thermotropic mesophase is only observed for EC with a certain range of DS[168].

1.4.3. Chiroptical properties in mesophase

In light of the existence of optically active centers along the cellulose backbone, it is not surprising that most cellulosics form chiral nematic mesophases. Chiroptical behaviours exhibited by these cellulosic mesophases are similar to those observed for chiral nematic phases of small molecules or of polypeptides. The iridescent colours observed accidentally by Werbowyj and Gray[8] for samples of concentrated aqueous HPC

solutions were the first indication of chiral nematic phase formation in cellulosic system. Later, optical characterization of a series of HPC solutions confirmed that anisotropic HPC solutions are right-handed chiral nematic liquid crystals and the iridescent colors are the result of selective reflection of light by a helicoidal structure[128,169].

Early investigations on solutions of HPC and its esters and ethers showed that in most cases, they form right-handed mesophases at high concentration. The first left-handed cellulosic liquid crystal was observed by Vogt and Zugenmaier[141] for ethylcellulose solutions in acetic acid (AA). It appears that majority of the cellulose derivatives form right-handed chiral nematic phases, especially those with bulky substituents such as hydroxypropyl and its derivatives. On the other hand, a left-handed helicoidal structure is often found for the mesophases of those derivatives with small substituents such as cellulose acetate (CA)[170], cellulose triacetate (CTA)[171], MC[172] and EC[141,173]. However, two bulky derivatives, (acetoactoxypropyl)cellulose (AAPC)[174] and 6-O-trityl-2,3-O-hexylcellulose (TrHC)[122], were recently reported to form left-handed mesophases in AA and THF, respectively. Exhibition of both right- and left-handed structures in cellulosic liquid crystals implies that the nature of the substituent play an important role in determining the macroscopic chirality, since all cellulose derivatives share the same chiral backbone. A further typical example is that cellulose tricarbanilate (CTC) in triethylene gylcol monomethyl ether form left-handed mesophase while 3-chlorophenylurethane of cellulose (3-ClPC) in the same solvent form right-handed mesophase[160,175]. The only difference between these two derivatives is one chlorine on the substituent.

As in the case of lyotropic polypeptide liquid crystals, solvent for cellulosics surprisingly strongly influence the handedness of their mesophases even though the solvents are all achiral. Ethylcellulose was the first cellulose derivative reported to show a solvent dependence of handedness. EC solutions in AA form a left-handed mesophase but in dichloroacetic acid (DCA) a right-handed one[176]. Further examination of EC in a variety of other solvents except for DCA gave left-handed structures[173]. A similar solvent dependence of handedness was also observed for CTC[177] and TrHC[178]. Anisotropic solutions of cellulose itself were also reported to exhibit both handedness, depending on the solvent system[10,145,147]. It is obvious that the different handedness observed for the same cellulose derivatives must be related to the nature of the solvents. The dielectric constant of solvent has been suggested by Samulski and Samulski[49] to be a key factor in governing handedness of lyotropic mesophase, as mentioned previously. This theory has successfully been applied to some polypeptide mesophases. However the solvent dependence of handedness observed for anisotropic EC solutions in a series of solvents

seems not to be simply related to the dielectric constant of the solvent[173]. In addition to the physical properties, reactivity of the solvent with cellulosics may affect their handedness as the case of CA in TFA[179]. Fresh anisotropic solutions of CA in TFA form a left-handed mesophase while the same solutions after few-days standing become a right-handed mesophase, presumably due to the occurrence of trifluoroacetylation, transesterification or degradation[179].

In the absence of solvent, the handedness of thermotropic mesophases of cellulose derivatives is mainly determined by the substituents. So far most thermotropic cellulosic liquid crystals reported are right-handed except for tri-O-heptylcellulose (THC), tri-O-butoxyethylcellulose (TBC) and tri-O-2-(2-methoxyethoxy)ethyl) cellulose oligomer (O-TMEC)[165]. Moreover, the O-THC and O-TMEC (DP=11) derivatives change the handedness from left to right upon heating[38]. Strangely, this thermally-induced handedness inversion was not observed for the same derivatives with a high DP (210). This has been attributed to a high compensated temperature beyond the clearing temperature. From a chemical point of view, hemiacetal groups at the end of the cellulosic chain may also play a role in contributing to the asymmetric intermolecular forces determining chirality, especially in such samples with low DP and with long side chain. So far, no thermally-induced compensation has been observed in lyotropic system of cellulosics. A solvent-induced handedness inversion does occur in anisotropic solutions of EC in mixtures of AA and DCA[176] and CTC in mixtures of methyl propyl ketone (MPK) and diethylene glycol monomethyl ether (DEME)[177].

The cause of both thermally- and solvent-induced handedness inversion is not well understood although currently existing chiral nematic theories can provide some qualitative interpretations. One may expect that the change in the handedness of cellulosic mesophases may be a result of a change in their chain helical conformation in solution or melt. However, no direct evidence of the correlation between the helicity of cellulosic chains and the chirality of their mesophase has appeared to date. A recent effort was made by Harkness and Gray to prepare special cellulose derivatives with chromophores as substituents and investigate their chiroptical activity in dilute solution and in mesophase by means of CD spectroscopy[122,178,180,181]. The results suggest that the conformations of these polymers in dilute solution are not correlated to the handedness of their concentrated mesophases. However, whether the conformation of cellulosic chains in dilute and concentrated solution remains the same is unknown.

Another important optical characteristic of cellulosic mesophases is the pitch. In general, an increase in concentration leads to a decrease in pitch for most lyotropic cellulosic liquid crystals; only CTC in ethyl methyl ketone (EMK) or in 2-pentanone[141]

and CIPC in DEME[175] are exceptions. The dependence of pitch on concentration can be expressed by an empirical relationship, $1/|P| \propto \phi^{\alpha}$, where ϕ is concentration of cellulosics and α is a coefficient and varies from 1.8 to 4, depending on the type of cellulose derivative and solvent and on temperature etc[182]. The pitch for cellulosic mesophases also varies with their molecular weight. An increase of pitch with increasing molecular weight has been observed for lyotropic solutions of CA/TFA[183] and CTC/2-pentanone[141,184]. The reverse is observed for lyotropic solution of HPC[185] and APC[155].

The most sensitive factor controlling the pitch is temperature. Like other polymeric chiral nematic phases, majority of cellulosic mesophases show a positive temperature dependence of pitch. For lyotropic cellulosics, EC is only cellulose derivative reported so far to display both negative and positive temperature dependence of pitch in mesophase, e.g. anisotropic EC solutions in chloroform show a negative temperature dependence of pitch whereas the EC solutions in DCA a positive temperature dependence of pitch[173].

A summary of the chiroptical properties of cellulosic liquid crystals, particularly their handedness and the temperature dependence of pitch, is given in Figure 1.9. It appears from this survey that commercial EC is an unusual cellulose derivative with respect to the chiroptical behaviour of its liquid crystalline phase, in that it displays a solvent dependence of the handedness and a negative temperature dependence of the pitch. This raise questions about the role of the ethyl groups and solvents in the unusual mesomorphic behaviour. An initial attempt to address the question was to acetylate commercial EC with a DS of 2.5 and to investigate the chiroptical behaviour of the resultant derivative, (acetyl)(ethyl)cellulose (AEC), in mesophase. Surprisingly, the anisotropic AEC solutions in chloroform form a right-handed helicoidal structure and show a positive temperature dependence of pitch, opposite to that exhibited by the unacetylated EC mesophases in the same solvent[186,187]. The general objective of this research is to further explore the chiroptical properties of AEC liquid crystals in other solvents and to provide insight into the factors that are responsible for the handedness inversion for AEC mesophase, in the hope of establishing the some relationships between the molecular structure of cellulosics and their chiroptical behaviour in liquid crystalline phase.

1.5. Introduction to remaining chapters

Chapter 2 describes the preparation and characterization of (acetyl)(ethyl)cellulose polymers with acetyl DS' values ranging from 0 to 0.5, and also

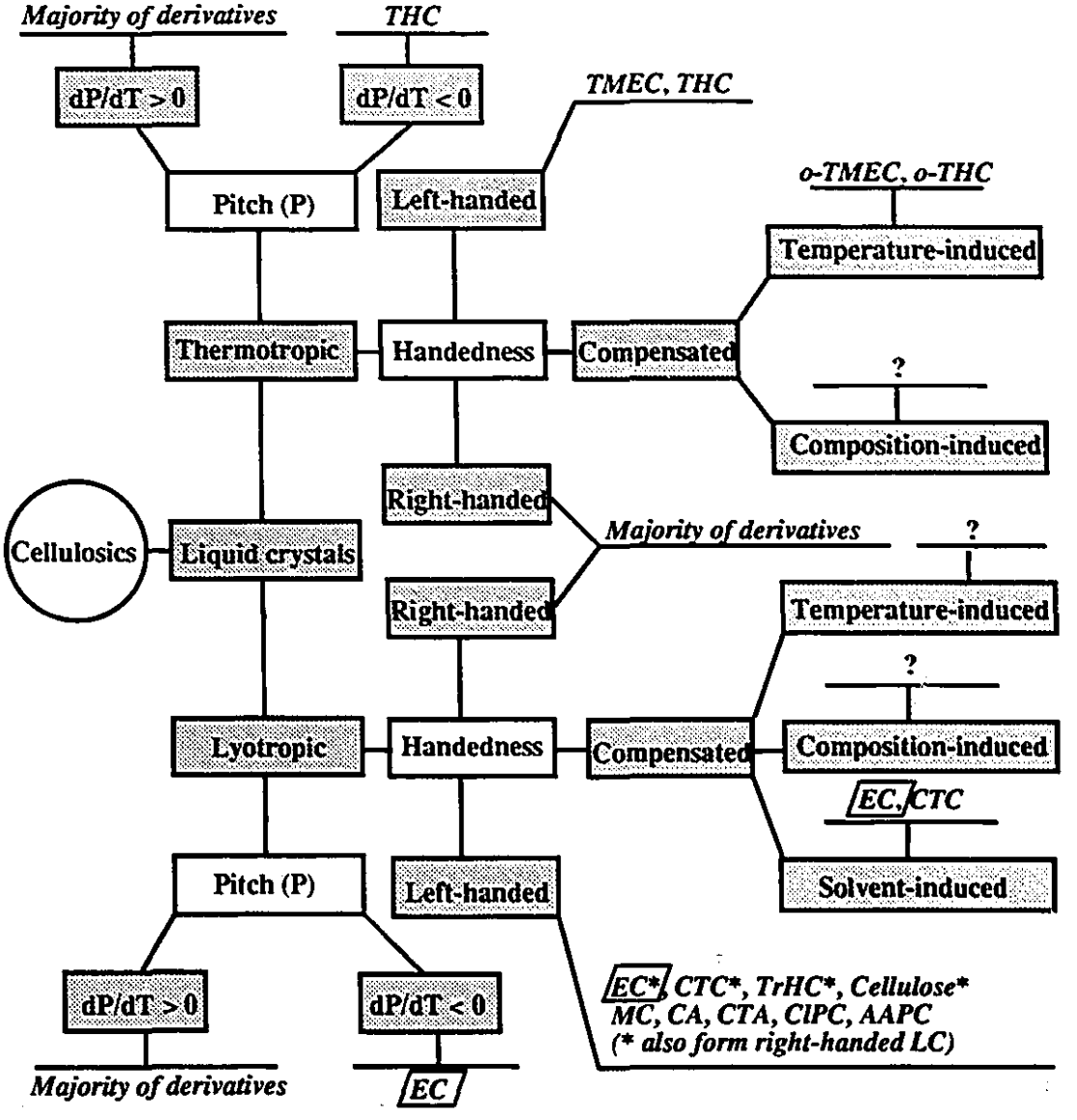


Figure 1.9 Outline of chiroptical properties exhibited by cellulosic liquid crystals.

other polymers, (acetyl)(methyl)cellulose (AMC) and (propionyl)(ethyl)cellulose (PEC). The chiroptical properties of lyotropic AEC solutions in a variety of organic solvents are examined in Chapter 3. The results of the effects of acetyl content on the handedness, pitch and flow time of the AEC mesophase are presented in detail. The compensated AEC mesophases are characterized by means of microscopy, laser diffractometry and ORD. In Chapter 4 the optical activity of dye molecules dissolved in isotropic and anisotropic solutions of AEC are investigated by means of CD and ORD spectroscopy. Orientational behaviour of the dyes in left- and right-handed helicoidal structure are discussed on the basis of their ICD spectra. The factors influencing the ICD of the dyes in the AEC mesophase are also presented in this chapter. In Chapter 5 some mechanisms for the handedness inversion for AEC mesophases with changing acetyl DS are discussed. Some experimental evidence and theoretical consideration are both presented. The conclusions drawn from this study and suggestions for further research are presented in the last chapter.

1.6. References

1. R.A. Hegstrom and D.K. Kondepudi, Scientific American, January 1990, pp. 108
2. M. Gardner, in The Ambidextrous Universe, Scribner, New York, 1979, Chapter. 8-9
3. G.H. Brown and J.J. Wolken, Liquid Crystals and Biological Structures, Academic Press, 1979
4. T. Norisuye, T. Tanaki and H. Fujita, J. Polym. Sci. Phys. Ed. 18, 547(1980)
5. Y. Bouligand, in Liquid Crystlline Order in Polymers, Ed. A. Blumstein, Academic Press, 1978, pp. 261
6. Y. Bouligand, Tissue Cell, 4(2), 189(1972)
7. B.A. Meylan and B.G. Butterfield, Wood Sci. Technol., 12, 219(1978)
8. R.S. Werbowyj and D.G. Gray, Mol Cryst. liq. Cryst. (Letter), 34, 97(1976)
9. H. Chanzy and A. Peguy, J. Polym. Sci. Polym. Phys. Ed., 8, 1137(1980)
10. D.L. Patel and R.D. Gilbert, J. Polym. Sci. Polym. Phys. Ed., 19, 1231(981)
11. G. Conio, P. Corazzo, E. Bianchi, A. Teoldi and A. Ciferri, J. Polym. Sci.Polym. Lett. Ed., 22, 273(1984)
12. Y.S. Chen, J.A. Cuculo, J. Polym. Sci. Polym. Chem. Ed., 24, 2075(1986)
13. J.-F. Revol, H. Bradford, J. Giasson, R.H. Marchessault and D.G. Gray, Int. J. Biol. Macromol., 14, 170(1992)
14. G. Charlet and D.G. Gray, Macromolecules, 20, 33(1987)
15. J. Giasson, J.-F. Revol, A.M. Ritcey and D.G. Gray, Biopolymers, 27, 1999(1988)

16. J. Giasson, J.-F. Revol, D.G. Gray and J. St-Pierre, Marcomolecules, 24, 1694(1991)
17. F. Reinitzer, Monatsh, 9, 421(1888)
18. H.W. Gibson, in Liquid Crystals: The Fourth State of Matter, Ed. F.D. Saeva, Marcel Dekker, New York, 1979, Chapter 3
19. S. Chandrasekhar, in Liquid crystals, Cambridge University Press, Cambridge, 1977, Chapter 1
20. G. Vertogen and W.H. DeJeu, Thermotropic Liquid Crystals: Fundamentals. Springer-Verlag Berlin Heidelberg, 1988
21. P.A. Crooker, Liq. Cryst., 5, 751(1989)
22. P.J. Flory, Proc. R. Soc. London Ser. A. 234, 73(1956)
23. H. Yanakawa and M. Fujii, Macromolecules, 7, 128(1974)
24. A.Yu, Grosberg and A.R. Khokhlov, Adv. Polym. Sci., 41, 53(1981)
25. S.P. Papkov, Adv. Polym. Sci. 59, 75(1984)
26. I. Uematsu and Y. Uematsu, Adv. Polym. Sci., 59, 37(1984)
27. P.J. Flory and A. Abe, Macromolecules, 11, 1119(1978)
28. P.J. Flory, Adv. Polym. Sci., 59, 1(1984)
29. T. Hongu and G.O. Phillips, New Fibers, Ellis Horwood, 1990, Chapter 2
30. D. Demus and L. Richter, Textures of liquid crystals, Verlag Chemie, 1978
31. H. Keller and R. Halz, in Handbook of liquid crystals, Verlag Chemie, 1980, Chapter 6
32. Hl. de Vries, Acta, Cryst., 4, 219(1951)
33. C. Robinson and J.C. Ward, Nature, 180, 1183(1957)
34. F.D. Saeva, in Liquid Crystals: The Fourth State of Matter, Ed. F.D. Saeva, Marcel Dekker, New York, 1979, Chapter. 2
35. E.Sackmann, S. Meiboom, L.C. Snyder, A.E. Meixner and R.E. Dietz, J. Amer. Chem. Soc.,90, 3576(11968)
36. H. Baessler, F.M. Larnge and M.M. Labes, J. Chem. Phys. 51, 3213(1969)
37. J. Watanabe and T. Nagase, Macromolecules, 21, 171(1988)
38 T. Yamagishi, T. Fukuda, T. Miyamoto, T. Ichizhuka and J. Watanabe, Liq. Cryst. 7, 155(1990)
39. F.D. Saeva, in Liquid Crystals: The Fourth State of Matter, Ed. F.D. Saeva, Marcel Dekker, New York, 1979, Chapter 6
40. M. Hatano, Adv. Polym. Sci., 77, 1(1986)
41. P.N. Keating, Mol. Cryst. Liq. Cryst., 8, 315(1969)
42. W.J.A. Goosens, Mol. Cryst. Liq. Cryst., 12, 237(1971)
43. H. Finkelmann and H. Stgemeyer, Ber. Bunsenges. Phys. Chem., 82, 1302(1978)
44. Y.R. Lin-Liu, Y.M. Shih and C.-W. Woo, Phys. Rev. A, 15, 2550(1977)
45. B. Böttcher, Chem. Ztg, 96, 214(1972)
46. A. Wulf, J. Chem. Phys., 59, 1487(1973)

47. B.W. Van de Meer, G. Vertogen, A.J. Dekker and J.G.J. Ypma. J. Chem. Phys. 65, 3935(1976)
48. G.S. Chillaya and L.N. Lisetski, Mol. Cryst. Liq. Cryts. 140, 243(1986)
49. T.V. Samulski and E.T. Samulski, J. Chem. Phys. 67, 824(1977)
50. A.D. Mclachlan, Discuss. Farad., Soc. 40, 239(1965)
51. H. Kimura, M. Hoshino and H. Nakana, J. Phys. Soc. (Japan), 51, 1584(1982)
52. M.A. Osipov, Chem. Phys. 96, 259(1985)
53. M.A. Osipov, Nuovo Cimento Soc., Ital. Fis, 10D, 1249(1988)
54. M.A. Osipov, in Liquid Crystal and Mesomorphic Polymers Ed., V. Shibaev and L. Lam, Springer, New York, 1991 in press.
55. L. Varichon, A.Ten Bosch and P. Sixou, liq. Cryst. ,9, 701(1991)
56. L. Varichon and A.Ten Bosch, Macromolecules, 25, 3812(1992)
57. J.L. Fergason Appl. Optics, 7, 1729(1968)
58. R.S. Werbowyj and D.G. Gray, Macromolecules, 17, 1512(1984)
59. R. Cano. Bull. Soc. Franc. Miner. Cryst., 91, 20(1968)
60. L.M. Blinov, in Electro-Optical and Magneto-Optical Properties of Liquid Crystals, John Wiley and Sons Limt., 1983, Chapter 6.
61. E. Sackmann and J. Voss, Chem. Phys. Lett., 14, 528(1972)
62. G. Holzwarth and N.A.W. Holzwarth., J. Optic. Soc. Am., 63, 324(1973)
63 S. Chandrasekhar, in Liquid Crystals , Cambridge University Press, 1977, Chapter 4
64. H.P Jensen, J.A. Schellman and T. Troxell, Appl. Spectrosc., 32, 92(1978)
65. Y. Shindo and Y. Ohmi, J. Am. Chem. Soc. 107, 91(1985)
66. F.D. Saeva, Mol. Cryst. Liq. Cryst., 18, 375(1972)
67. H. Kozawaguchi and M. Wada, Mol. Cryst. Liq. Cryst.. 45,55(1978)
68. T. Hashimoto, S. Ebisu and H. Kawai, J. Polym. Sci. Polym. Lett. Ed., 18, 569(1980)
69. F. Livolant, M.-M. Giraud and Y.Bouligand, Biol. Cell. 31, 159(1978)
70. H. Keller and R. Halz, in Handbook of Liquid Crystals, Verlag Chemie, 1980, Chapter 12
71. C. Robinson, Trans. Farad. Soc., 52, 571(1956)
72. C. Robinson. Tetrahedron, 13, 219(1961)
73. H. Toriumi, S. Minakuchi, I, Uematsu and Y. Uematsu, Polym. J., 11.863(1979)
74. H. Toriumi, S. Minakuchi, I, Uematsu and Y. Uematsu, Mol. Cryst. Liq.Cryst., 94, 267(1983)
75. E.T. Samulski, J. Phys. (Paris), 40, C-3, 471(1979)
76. K. Czarniecka and E.T. Samulski, Mol. Cryst. Liq. Cryst., 63, 205(1981)
77. H. Toriumi, T. Yamazaki, A. Abe and E.T. Samulski, Liq. Cryst., 1, 87(1986)
78. F.D. Saeva and G.R. Olin, J. Amer. Chem. Soc., 95, 7882(1973)
79. F.D. Saeva, P.E. Sharpe and G.R. Olin, J. Amer. Chem. Soc., 95, 7656(1973)

80. H. Toriumi and I. Uematsu, Mol. Cryst. Liq. Cryst., 116(1984)
81. F.C. Bawden and N.W. Pirie, Proc. R. Roc. London, Ser. B, 123, 274(1937)
82. J.D. Bernal and I. Fankuchen, J. Gen. Physiol, 25, 111(1941)
83. M.F. Perutz, A.M. Liquori and S. Eirich, Nature, 167, 929(1951)
84. E. Iizuka, Mol. Cryst. Liq. Cryst., 42, 67(1977)
85. H.R. Wilson and P. Tollin, J. Ultrastruct. Res., 33, 550(1970). CA, 74, 121606p(1971)
86. M. Spencer, W. Fuller, M.H.F. Wilkius and G.L. Broon, Nature, 194, 1014(1962)
87. Yu.M. Yevdokimv, S.G. Skuridin and V.L. Salyanov, Liq. Cryst., 3, 1443(1988)
88. E. Iizuka. Polym. J., 15, 525(1983)
89. F. Livolant. Europ. J. Cell. Biol., 33, 300(1984)
90. L.S. Lerman, Proc. Natn. Acad. Sci. U.S.A. 68, 1886(1971)
91. F. Livolant, Physica A, 176, 117(1991)
92. R.L. Rill, T.E. Strzelecka, M.W. Davidson and D.H. Van Winkle, Physica A, 176, 87(1991)
93. Yu.M. Yevdokimov, V.I. Salyanov, A.T. Dembo and H. Berg, Biomed. Biochim. Acta, 42, 855(1983)
94. Yu.M. Yevdokimov, V.I. Salyanov, and M. Palumbo, Mol. Cryst. Liq. Cryst. 131, 285(1985)
95. P. Zugenmaier and M. Voihsel. Makromol. Chem. Commun., 5, 245(1984)
96. G. Maret, M. Milas and M.Rinaudo, Polym. Bull., 4, 291(1981)
97. Y. Bouligand and F. Livolant, J. de Phys. 45, 1899(1984)
98. K. Van, T. Norisuye and A. Teramoto. Mol. Cryst. Liq. Cryst. 78, 123(1981)
99. K. Van and A. Teramoto. Polym. J., 14, 999(1982)
100. K. Van, T. Asakwa and A. Teramoto, Polym. J. 16, 16 61(1984)
101. Y. Bouligand, J. Phys. (Paris) C-1, 36, 331(1975)
102. R.H. Marchessault, F.F. Moreheed and N.M. Walter, Nature, 184(1959)
103. D.A. Rees and R.J. Skerret, Carbohyd. Res. 7, 334(1968)
104. A. Pizzi and N. Raton, J. Marcomol. Sci. Chem. A22, 105(1985)
105. I. Simon, H. Scheraga and R.St. Manley, Macromolecules, 21, 983(1988)
106. D. Poland and H.A. Scheraga, Theory of Helix-Coil Transition in Biopolymers, Academic Press, New York, 1970
107. K.H. Gardner and J. Blackwell, Biopolymers, 13, 1975(1974)
108. A. Sarko and R. Muggli, Macromolecules,7, 486(1974)
109. R.St.J. Manley, Nature (London), 204, 1155(1964)
110. R.St.J. Manley, J. Polym. Sci. Polym. Phys. Ed., 9, 1025(1971)
111. F. Horii, A. Hirai and R. Kitamaru, in The Structures of Cellulose: Characterization of the Solid States, Ed. R.H. Atalla, ACS Symp. Ser. 340,1987, p. 119

112. S.B. Ross-Murphy, in Cellulose Chemistry and its Application, Eds. T.P. Nevell and S.H. Zeronian, John Wiley & Sons, 1983, Chapter 8
113. K. Kamide and M. Saito, Adv. Polym. Sci., 83, 1(1987)
114. S.M. Hudson and J.A. Cuculo, J. Polym. Sci. Polym. Chem. Ed., 18, 3469(1980)
115. C.L. McCormick, P.A. Callais and B.H. Hutchinson Tr., Macromolecules, 18, 2394(1985)
116. A.S. Perlin, N. Cyr. R.G.S. Ritchie and A. Parfondry, Carbohydr. Res. 37, C-1, (1974)
117. A.M. Ritcey and D.G. Gray, Biopolymers, 27, 479(1988)
118. P. Zugenmaier, J. Appl. Polym. Sci. Appl. Polym. Symp., 37, 223(1983)
119. H. Steinmeier and P. Zugenmaier, Carbohydr. Res. 164, 97(1987)
120. W. Brown, in Cellulose and Cellulose Derivatives, Eds. N.M. Bikales and L. Segal, Wiley-Interscience, New York, 1971, Part IV, p. 557
121. K. Nishida and A. Iwasaki, Kolloid-Z. u Z. Polmere, 251 136(1973)
122. B.R. Harkness, Ph.D. Thesis, McGill, Montreal, 1990
123. R.G. Schweiger, Carbohyd. Res., 70, 185(1979)
124. T. Kondo and D.G. Gray, unpublished results
125. R.D. Gilbert and P.A. Patton, Prog. in Polym. Sci., 9, 115(1983)
126. D.G. Gray, J. Polym. Sci., Appl. Polym. Symp., 37, 179(1983)
127. B.R. Harkness and D.G. Gray, in Liquid Crystal and Mesomorphic Polymers Ed., V. Shibaev and L. Lam, Springer, New York, 1991 in press
128. R.S. Werbowyj and D.G. Gray, Macromolecules, 13, 69(1980)
129. G.V. Laivins and D.G. Gray, Macromolecules, 18, 1753(1985)
130. E. Bianchi, A. Ciferri, G. Conio, L. Lanzavecchia and M. Terbojevich, Macromolecules 18, 973(1985)
131. J.M. Mays, Macromolecules, 21, 3179(1988)
132. K. Kamide and M. Saito, Eur. Polym. J. 20, 903(1984)
133. S. Takahashi, H. Susuki, T. Miyamoto and H. Inagaki, in Cellulose:Structural and Functional Aspects, Eds. J.F. Kennedy, G.O. Phillips and P.A. Williams, Ellis Horwood, 1989, p. 403
134. K. Arai and H. Satoh, J. Appl. Polym. Sci. 45, 387(1992)
135. C. Viney and A. H. Windle, Liq. Cryst., 1, 379(1986)
136. S.M. Aharoni, Mol. Cryst. Liq. Cryst. (Lett.), 86, 237(1980)
137. P. Navard, J.M. Haudin, S. Dyan and P. Sixou, J. Polym. Sci. Polym. Lett. Ed., 19, 379(1981)
138. J. Blackwell and R.H. Marchessault, in Cellulose and Cellulose Derivatives, Eds. N.M. Bikales and L. Segal, Wiley-Interscience, New York, 1971, Part IV, p.1
139. D.P. Patel and D.G. Gilbert, J. Polym. Sci. Polym. Phys. Ed. 21, 1079(1983)
140. G. Canio, E. Bianchi, A. Ciferri, A. Tealdi and M.A. Aden, Macromolecules, 16, 1264(1983)

140a. G.V. Laivins and D.G. Gray, Macromolecules, 18, 1746(1985)
141. V. Vogt and P. Zugenmaier. Ber. Bunsenges Phys. Chem., 89, 1217(1985)
142. P. Zugenmaier, in Cellulose: Structure, Modification and Hydrolysis, Eds.R.A. Young and R.M. Rowell, John Wiley & Sons,1986, p.221
143. D.G. Johnson in Cellulose Chemistry and its Application, Eds. T.P. Nevell and S.H. Zeronian, John Wiley & Sons, 1983, Chapter 7
144. P. Navard and J. Haudin. Br. Polym. J., 120, 174(1980)
145. Y.K. Hong, D.E. Hawkinson, E. Kohout, A. Garrard, R.E. Fornes and R.D. Gilbert in Polymer Association Structures, Ed. El-Bokaly, ACS Symp. Ser. 384, 1989, p. 184
146. M. Terbojevick, A. Coseni, G. Conio, A. Ciferri and E. Bianchi, Macromolecules, 18, 640(1985)
147. E. Bianchi, A. Ciferri, G. Conio, A. Coseni and M Terbojevick. Macromolecules, 18, 646(1985)
148. K.S. Yang, M.H. Theil and J.A. Cuculo, in Polymer Association Structures, Ed. El-Bokaly, ACS Symp. Ser. 384, 1989, p. 156
149. E. Bianchi, A. Ciferri, G. Conio and A. Teoldi, J. Appl. Polym. Sci. 27, 1477(1989)
150. K.S. Yang, M.H. Theil and J.A. Cuculo, Polymers, 33, 179(1992)
151. K. Shimamura, J.L. White and J.F. Fellers, J. Appl. Polym. Sci. 26, 2156(1981)
152. S. Suto, J.L, White and J.F. Fellers. Rhelogica. Acta, 21, 62(1982)
153. G. Charlet and D.G. Gray, Macromolecules, 20, 33(1987)
154. S.-L. Tseng, A. Valente and D.G. Gray, Macromolecules, 14, 715(1981)
155. G.V. Laivins and D.G. Gray, Polymers, 26, 1435(1985)
156. S.-L. Tseng, G.V. Lavins and D.G. Gray, Macromolecules, 15, 1262(1982)
157. S.N. Bhadani and D.G. Gray, Mol. Cryst. Liq. Cryst., 99, 29(1983)
158. S.N. Bhadani and D.G. Gray, Mol. Cryst. Liq. Cryst., 102, 255(1984)
159. A.M. Ritcey and D.G. Gray, Macromolecules, 21, 1251(1988)
160. H. Steinmeier and P. Zugenmaier, Carbohydr. Res. 173, 75(1988)
161. S.M. Aharoni, J. Polym. Sci., Polym. Lett. Ed., 19, 495(1981)
162. T. Sato, Y. Tsujii, M. Minoda, Y. Kita and T. Miyamoto, Makromol. Chem. 193, 647(1992)
163. H. Yokota, Cellul. Technol. 20, 478(1986)
164. W.P. Pawlowski, R.D. Gilbert, R.E. Fornes and S.T. Purrington, J. Polym. Sci.:, Polym. Phys. Ed., 26, 1101(1988)
165. T. Yamagishi, T. Fukuda and T. Miyamoto, in Cellulose: Structural and Functional Aspects, Eds. J.F. Kennedy, G.O. Phillips and P.A. Williams, Ellis Horwood, 1989, p. 391
166. S. Ambrosino and P. Sixou, in Polymer Association Structures, Ed. El-Bokaly, ACS Symp. Ser. 384, 1989, p. 142

167. T. Yamagishi, T. Fukuda, T. Miyamoto, Y. Yakoh, Y. Takashina and J. Watanabe, Liq. Cryst., 11, 467(1992)
168. J. Chen, Y. Huang, J. Yuan, S. Lu and S. Yun, J. Appl. Polym. Sci. 42, 3263(1990)
169. R.S. Werbowyj and D.G. Gray, Macromolecules, 17, 1512(1984)
170. J. Lematre, S. Dayan and P. Sixou, Mol. Cryst. Liq. Cryst., 84, 267(1982)
171. G. H. Meeten and P. Narvard, Polymers, 23, 1727(1982)
172. J.X. Guo, D.G. Gray, unpublished result.
173. D.R. Budgell, Ph.D. Thesis, McGill, Montreal, 1989
174. W.P. Pawlowski, R.D. Gilbert, R.E. Fornes and S.T. Purrington, J. Polym. Sci.:, Polym. Phys. Ed. 25, 2293(1987)
175. M. Siekmeyer, H. Steinmeier and P. Zugenmaier, Makromol. Chem. 190, 1037(1989)
176. P. Zugenmaier and P. Haurand, Carbohydr. Res., 160, 369(1987)
177. M. Siekmeyer and P. Zugenmaier, in Cellulose: Structural and Functional Aspects, Eds. J.F. Kennedy, G.O. Phillips and P.A. Williams, Ellis Horwood, 1989, p. 347
178. B.R. Harkness and D.G. Gray, Can. J. Chem., 68, 1135(1990)
179. A.M. Ritcey, and D.G. Gray, Macromolecules, 21, 2914(1988)
180. B.R. Harkness and D.G. Gray, Macromolecules, 23, 1452(1990)
181. B.R. Harkness and D.G. Gray, Liq. Cryst., 8, 237(1990)
182. P. Sixou and A. Ten Bosch, in Cellulose: Structure, Modification and Hydrolysis, Eds. R.A. Young and R.M. Rowell, John Wiley & Sons, 1986, p.205
183. P. Sixou, J. Lematre, A. Ten Bosch, J.M. Gilli and S. Dayan, Mol. Cryst. Liq. Cryst., 91, 277(1983)
184. M. Siekmeyer and P. Zugenmaier, Makromol. Chem., Rapid., Commun.8, 511(1987)
185. S. Fortin and G. Charlet, Macromolecules, 22, 2286(1989)
186. J.X. Guo and D.G. Gray, Macromolecules, 22, 2082(1989)
187. J.X. Guo and D.G. Gray, Macromolecules, 22, 2086(1989)

Chapter 2.

Preparation, Characterization and Mesophase Formation of (Acetyl)(ethyl)cellulose and Other Cellulose Derivatives

2.1. Introduction

Physical properties of cellulose derivatives are strongly influenced by both main chain properties, e.g. the degree of polymerization (DP) and the distribution of molecular weight, and by their side chain properties, e.g. the nature of substituents, degree of substitution (DS) and the distribution of substituents along the cellulosic chains and among C(2), C(3) and C(6) positions in an anhydroglucose unit of the cellulose[1]. A survey of the literatures on cellulosic liquid crystals in Chapter 1 also indicates that their chiroptical properties depend to a large extent on the nature of substituent and solvent. For example, cellulose tricarbanilate (CTC) forms a right-handed liquid crystal in methyl propyl keton (MPK)[2] but a left-handed liquid crystal in triethylene glycol monomethyl ether (TEME)[3]. An additional chlorine atom on the benzyl ring of each CTC substituent leads the corresponding cellulose derivative, 3-chlorophenylurethane of cellulose (3-ClPC), to form a right-handed mesophase in the same solvent (TEME)[3]. It is still unknown why and how the achiral substituents and solvent influence the chirality of mesophases formed by cellulose derivatives in mesophase.

Ethylcellulose (EC) is a non-ionic cellulose derivative. Commercial EC products with DS around 2.3-2.6 have excellent solubility in a wide range of organic solvents. The mesomorphic properties of EC in solution have been widely investigated, e.g. dielectric[4], rheological[5,6], orientational[7] and optical behaviour[8-10]. Perhaps most striking observation are the chiroptical properties exhibited by the lyotropic EC liquid crystals, which display a solvent dependence of handedness and a negative temperature dependence of pitch in many solvents. In a previous paper[11], it has also been shown that the introduction of acetyl group into free hydroxyl group on commercial EC (ethyl DS = 2.5) results in a reversal of handedness for the resultant (acetyl)(ethyl)cellulose (AEC) polymers in the same solvent. In this chapter, a series of AEC polymers with small variations in acetyl content are prepared and characterized. Acetylation of EC was studied because it is a simple organic reaction and easily controlled in terms of the extent of reaction. Two new cellulose derivatives, (propionyl)(ethyl)cellulose (PEC) and (acetyl)(methyl)cellulose (AMC), are also prepared and characterized for the study of the mechanism for the handedness inversion of AEC liquid crystals with acetyl DS in the following chapters.

2.2. Experimental section

Materials. Ethylcellulose and methylcellulose were purchased from Aldrich Co. and Fisher Scientific Co., respectively. The ethoxyl content of the commercial EC is 48% and the viscosity (5% in solution) is 22 cp. The DS of the commercial MC is 1.6[12] and the viscosity is 15 cp. Reagent-grade acetic and propionic anhydrides and pyridine (Aldrich Co.) were used without further purification.

Preparation of (acetyl)(ethyl)cellulose polymers with acetyl DS ranging from 0 to 0.5. 8 grams EC was dissolved in 120 ml of pyridine in a 250-ml three-neck flask to give a clear, homogeneous and viscous solution. Acetic anhydride was added dropwise to the solution with stirring under nitrogen atmosphere. The acetylated products were isolated by pouring the reaction mixture into a large amount of cooled water, filtering, and washing several times with distilled water to remove excess reagent and solvent. The products were redissolved in tetrahydrofuran (THF) and reprecipitated in distilled water. Final products were dried under vacuum at 65°C. The acetyl content of the products depended on the reaction time, temperature, and amount of reagent and catalyst, as shown in Table 2.1.

Preparation of fully substituted (acetyl)(methyl)cellulose. A mixture of 4 grams of methylcellulose, 30 ml of pyridine and 15 ml of acetic anhydride in a 150-ml three-neck flask was stirred and heated to reflux for three hours under nitrogen. The product was isolated by slowly pouring the mixture into a large amount of cooled distilled water, filtering, and washing several times with distilled water. The product was redissolved in acetone and reprecipitated in distilled water. Final products were dried under vacuum at 65°C.

Preparation of fully substituted (propionyl)(ethyl)cellulose. A mixture of 4 grams of ethylcellulose, 30 ml of pyridine and 20 ml of propionic anhydride in a 150-ml three-neck flask was stirred and heated to reflux for three hours under nitrogen. The product was precipitated by slowly pouring the mixture into a large amount of hexane. The precipitates were obtained by centrifugation and washed several time with hexane. The dried product was redissolved in THF and reprecipitated in distilled water. Final product was dried under vacuum at 65°C.

General analysis: Infrared spectra of thin polymer films were recorded with a Mattson Polaris FT-IR spectrophotometer. The AEC and PEC films cast from THF solution (5% by weight) and AMC film cast from acetone solution (5% by weight).

The ^{13}C spectra were recorded with a JEOL CPF-270 spectrometer at a frequency of 67.80 MHz. The samples are dissolved in deuterated chloroform ($CDCl_3$) and polymer concentration is approximately 5% (w/v). The ^{13}C NMR spectra were obtained at 40°C with a complete decoupling mode (a flip angle of 45°and a pulse repetition time of 2.0

Table 2.1. Acetylation Conditions for Ethylcellulose

Sample	Regent (ml)	Temperature (°C)	Time (hr)	Catalyst (ml)	Acetyl DS[a]
AEC-33	10	30	0.5	0	0.09
AEC-21	20	30	1.0	0	0.13
AEC-22	20	30	2.5	0	0.16
AEC-23	30	30	4.0	0	0.18
AEC-24	30	30	5.5	0	0.21
AEC-25	40	30	7.0	0	0.24
AEC-26	40	30	8.5	0	0.26
AEC-34	45	30	9.0	0	0.29
AEC-27	45	30	10.0	0	0.31
AEC-30	50	30	12.0	0	0.35
AEC-28	50	20	10.0	0.5	0.44
AEC-29	50	20	12.0	1.0	0.48
AEC-36	60	30	12.0	1.5	0.50

(a) Measured by FT-IR spectroscopy

second) and with transients 18000-20000. The chemical shifts of the above polymers were referenced to $CDCl_3$ (77.0 ppm).

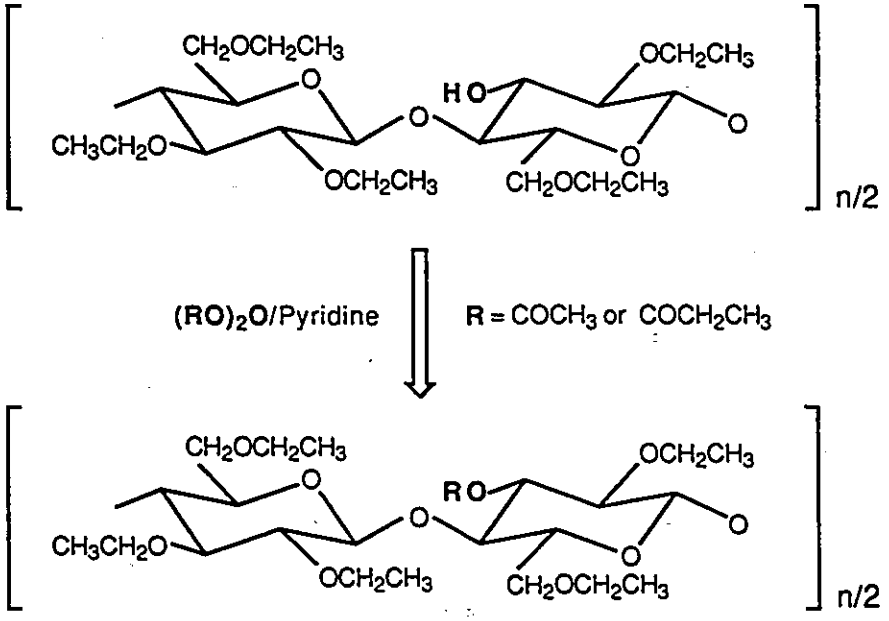
Gel permeation chromatograms (GPC) for EC and AEC polymers in THF were obtained with a Waters model 6000A pump with a refractive index detector and 10^5, 10^4, 10^3, 500 and 100 Å μ-Styragel Columns (Waters) in series. The retention volume of EC and AEC polymers were approximately evaluated from their GPC elution curves.

The microscopic observation and photograph of liquid crystalline samples were made on a polarizing microscope (OPTIPHOT-POL) with a camera. The samples were prepared between microscope slide and cover glass and sealed with epoxy resin to prevent solvent loss.

2.3. Results and discussion

2.3.1. Characterization of AEC polymers

The commercial EC before further chemical modification in this study has an ethyl content of 48%, corresponding to a degree of substitution of 2.5. It means that there are about five hydroxyl groups every two anhydroglucose units being substituted by ethyl groups and one free hydroxyl group every two anhydroglucose units available for further acetylation or propionylation as shown below:



The extent of acetylation was controlled by the reaction time and the quantity of reagent (Table 2.1). In order to obtain highly acetylated samples, perchloric acid was used as a catalyst.

Figure 2.1 shows the FI-IR spectra for EC and three AEC polymers obtained under different reaction conditions. The absorption bands around 3650-3350 cm^{-1} and 1850-1700 cm^{-1} are due to hydroxyl and carbonyl stretching vibrations, respectively. The intensity of the hydroxyl absorption peak decreases and that of carboxyl absorption peak increases with increasing the extent of acetylation. Apparently, there are no other significant absorption bands appearing in the spectra for the acetylated samples, suggesting that side reactions are negligible during acetylation. The absence of hydroxyl peak in the FT-IR spectrum for AEC-36 indicates that the free hydroxyl groups of the commercial EC were completely acetylated.

If the acetyl degree of substitution (acetyl DS) of product AEC-36 is taken as 0.5, the relative acetyl DS of other AEC products can be calculated according to the following equation[11]:

$$(DS)_X = \frac{0.5 \times (I^{CO} / I^{OH})_X}{(I^{C=O} / I^{OH})_{AEC\text{-}36}} \qquad [1]$$

where $I^{C=O}$ and I^{OH} are the maximum intensities of carboxyl and hydroxyl peaks, respectively, and subscript X indicates the sample to be calculated. The calculated relative acetyl DS of the series of AEC products are listed on Column 6 of Table 2.1.

Analysis of the AEC products by means of NMR spectroscopy provides more details of the structural features. Figure 2.2 is the ^{13}C NMR spectra for the same EC and AEC polymers as in Figure 2.1. The signals appearing around 15-17 ppm and 66.5-69.5 ppm are assigned to the methyl carbons and methylene carbons in the ethyl substituents, respectively. The signals for methyl carbons in the acetyl substituents of AEC polymers are located around 21 ppm and the corresponding carbonyl carbons resonance around 170-171 ppm. The intensity of both peaks increase with increasingly severe acetylation. It has been reported that the chemical shifts of carbon six positions (C(6)) bearing free hydroxyl groups of cellulose or partially substituted cellulose derivatives are located around 62 ppm[13,14] and that of the sugar carbons bearing ethoxyl substituents of EC shifts down field about 7-8 ppm with respect to the same carbons of unsubstituted cellulose[15-17]. The absence of peaks from 66 ppm down to below 30 ppm in the spectra for EC and AEC is an indication that the hydroxyls at C(6) in the commercial EC is completely ethylated and no deethylation occurs at C(6) during acetylation. The

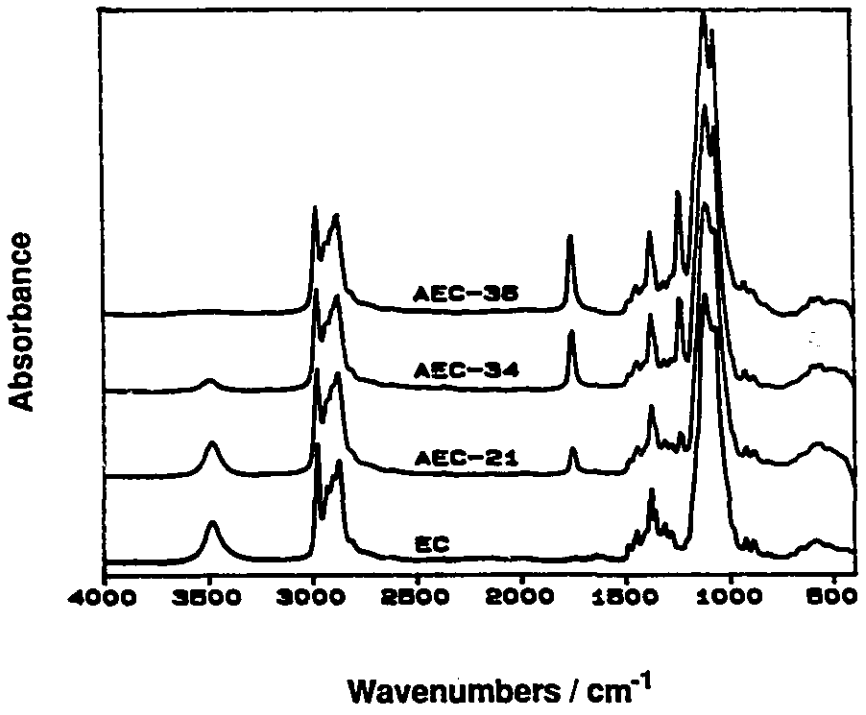


Figure 2.1. FT-IR spectra for ethylcellulose and (acetyl)(ethyl)cellulose polymers.

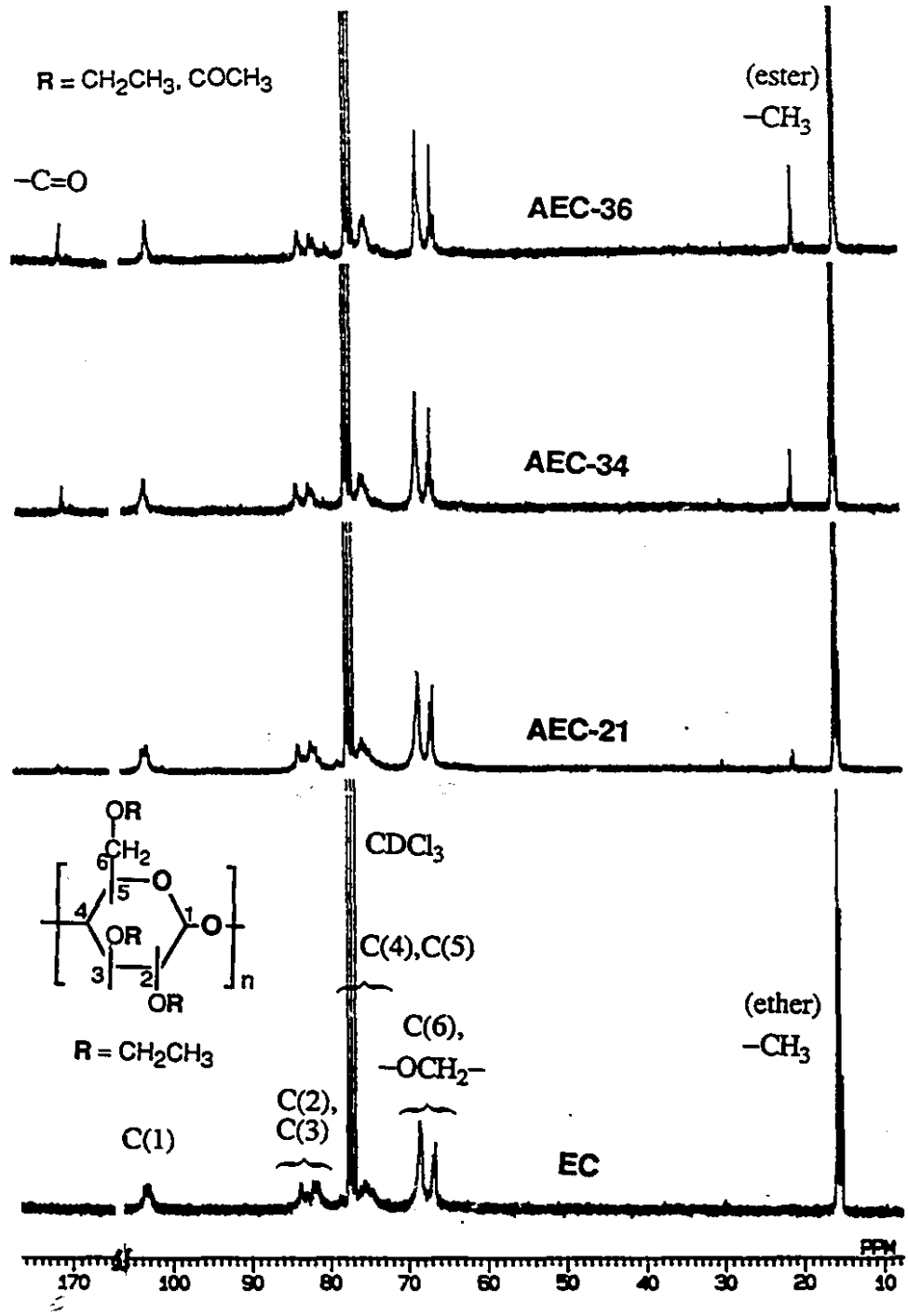


Figure 2.2. ^{13}C NMR spectra for ethylcellulose and (acetyl)(ethyl)cellulose polymers in $CDCl_3$.

preference for substitution at the sterically-favoured hydroxyls at C(6) of cellulosic anhydroglucose units has been observed for many cellulose derivatives[1]. The signal for C(6) bearing the ethoxyl groups overlaps with their methylene carbons peaks. The C(1) in anhydroglucose unit gives a resonance around 103 ppm and C(4) and C(5) around 74-79 ppm. The signals for C(2) and C(3) positions substituted by ethoxyl groups are located around 81.5-85 ppm. Compared with EC, a small additional peak appears in the region of 80-81.5 ppm for AEC products and increase in intensity with the extent of acetylation. This may represent C(2) and C(3) atoms substituted by acetyl groups.

GPC measurements of EC and the series of AEC products reveal that there is no significant degradation occurring during acetylation, as indicated by approximately constant retention volumes as shown in Figure 2.3.

2.3.2. Characterization of PEC and AMC.

Figure 2.4 is the FT-IR spectra for PEC and AMC polymers. As for the AEC polymers, strong absorption peaks characteristic of carboxyl vibrations appear at 1750 cm^{-1} in the FT-IR spectra of both polymers. The absence of a hydroxyl absorption peak for PEC and AMC in the region of 3400-3600 cm^{-1} in Figure 2.4 suggests that both cellulose derivatives are fully substituted.

In the ^{13}C NMR spectrum of PEC, the methyl and methylene carbons in the propionyl substituents are located at 10 ppm and 28 ppm, respectively. The chemical shift of the corresponding carbonyl carbons are around 173-174 ppm, a shift of 3 ppm down field in comparison with the same carbons in AEC polymers, as shown in Figure 2.5. The chemical shifts of other carbons of PEC are almost identical to that of AEC.

In the ^{13}C spectrum of AMC (Figure 2.6), the peaks around 58-61 ppm are assigned to the methoxyl carbons of the AMC, similar in chemical shift to the methoxyl carbons of trimethylcellulose[17]. The signals of methyl and carbonyl carbons in acetyl substituents of AMC appear almost same positions as in AEC polymers (21 ppm and 170-171 ppm, respectively). The other assignments of the chemical shifts of sugar carbons in AMC polymer are shown in Figure 2.6.

2.3.3. Mesophase formation in concentrated solutions

Ethylcellulose with a DS of 2.5 is soluble in many organic solvents. Its acetylated products, AEC, with acetyl DS ranging from 0 to 0.5 were found to retain good solubility in these solvents. The excellent solubility exhibited by these series of AEC polymers

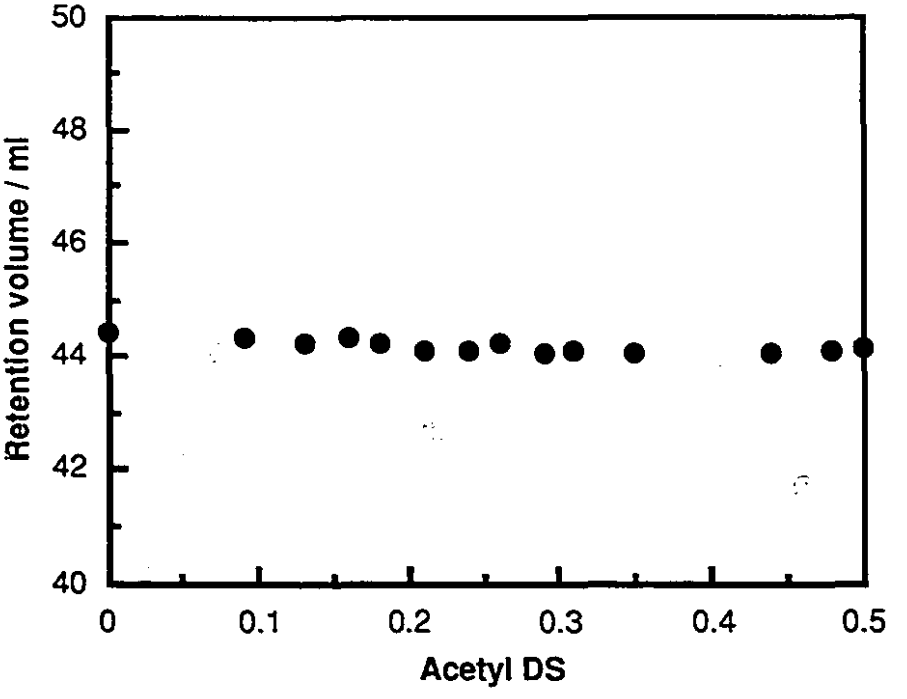


Figure 2.3. Variation in retention volume as a function of acetyl DS for AEC polymers in tetrahydrofuran.

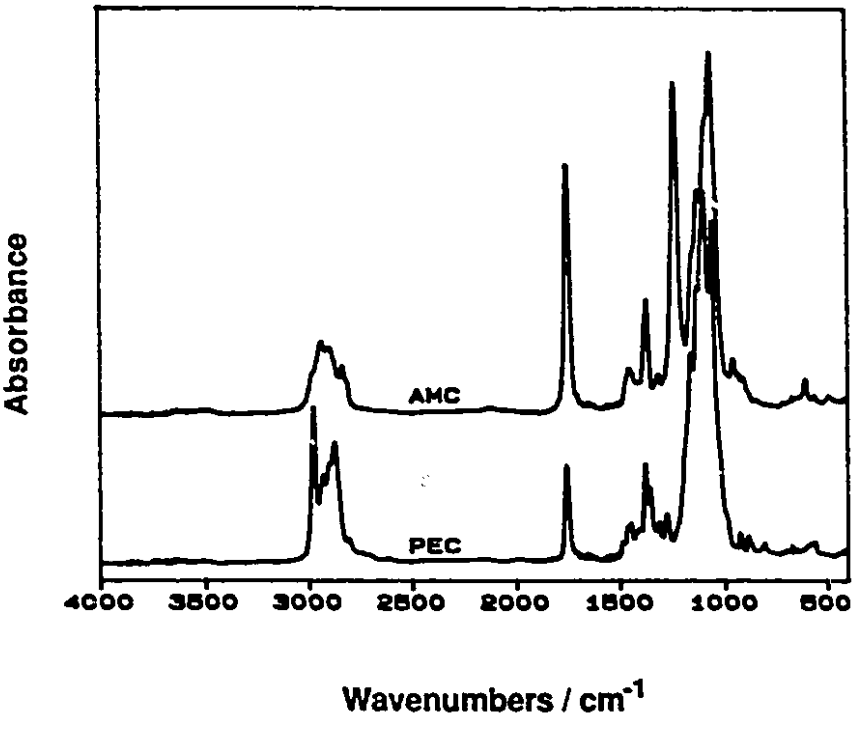


Figure 2.4. IR spectra for (acetyl)(methyl)cellulose and (propionyl)(ethyl)cellulose polymers.

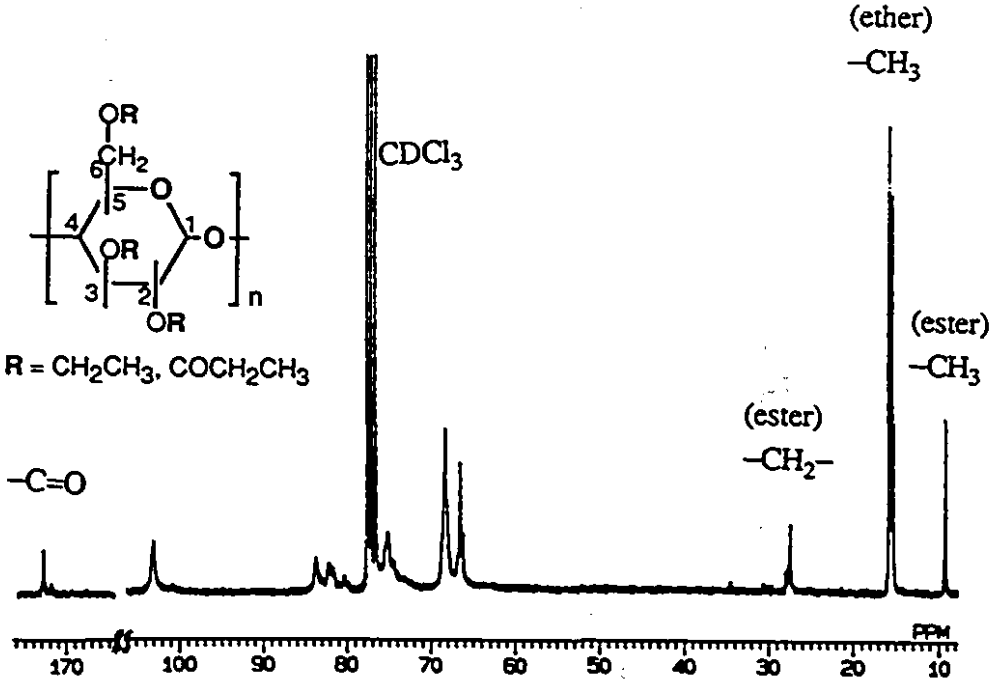


Figure 2.5. ^{13}C NMR spectrum for (propionyl)(ethyl)cellulose polymers in $CDCl_3$.

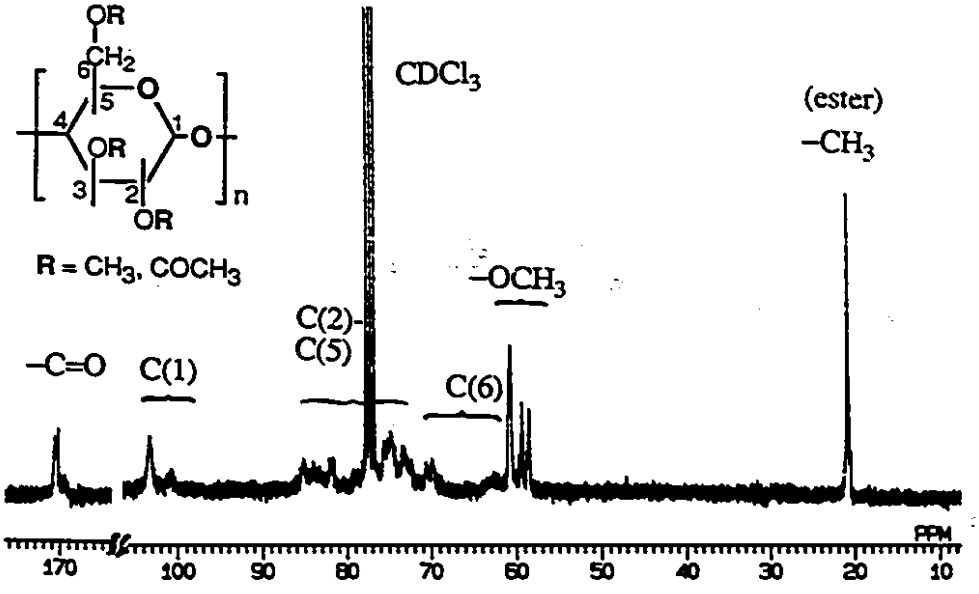
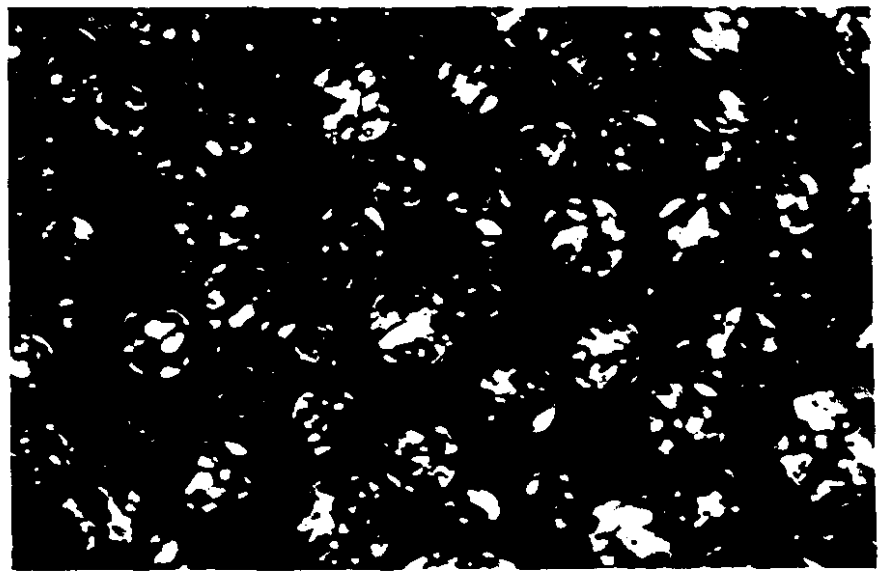


Figure 2.6. ^{13}C NMR spectrum for (acetyl)(methyl)cellulose polymers in $CDCl_3$.

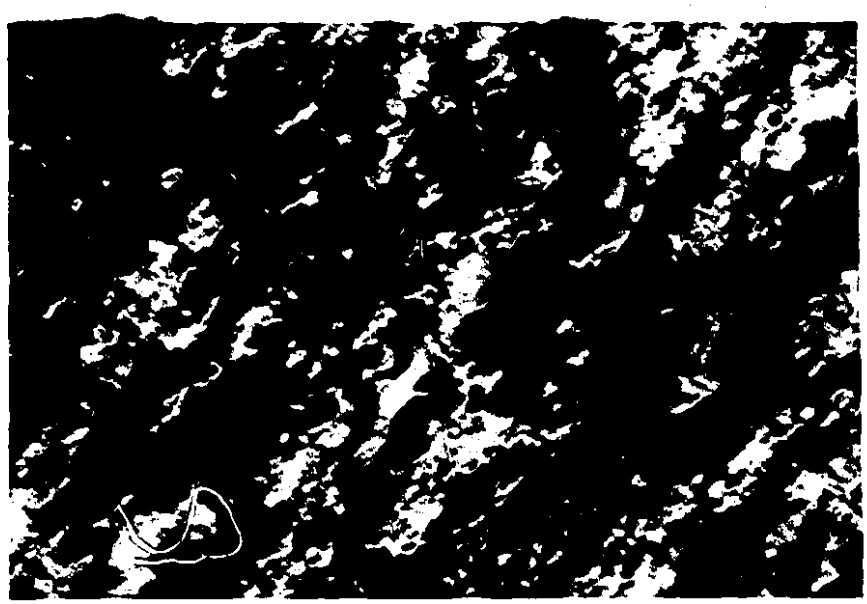
facilitates the study of DS effects on liquid crystalline properties in the following chapters. So far only a few reports on the relation between chiroptical properties of cellulose derivatives and their DS have appeared. This lack of activity may be due to the lack of solubility of most cellulose derivatives in a single solvent when the range of DS is wide.

EC form liquid crystals in acetic acid (AA), dichloroacetic acid (DCA), chloroform, bromoform, dichloromethane (DCM), dibromomethane (DBM), aqueous phenol (AP) and m-cresol[8-10]. Concentrated solutions of acetylated EC in these solvents are also found to form mesophases, regardless of acetyl DS. Figure 2.7 shows two photomicrographs of AEC-36 solutions in m-cresol at concentrations of 31% and 40% by weight, taken between crossed polars with a microscope at room temperature. The dark domains in the Figure 2.7(a) represent an isotropic phase where AEC molecules orient randomly. The strong birefringence exhibited by the bright domains indicates that the AEC molecules in these domains form an ordered phase. Thus two phases of the AEC solution at this concentration are in equilibrium at room temperature. The critical concentration, C*, for the separation of an anisotropic phase from an isotropic phase for AEC solution was found to depend on the acetyl DS. In general, the value of C* for AEC polymers in a given solvent decreases as the acetyl DS increases. For instance, the values of C* for lyotropic solutions of AEC polymers with an acetyl DS of 0, 0.21 and 0.5 in chloroform is around 29.0%, 25.5% and 23.0% by weight, respectively, at room temperature. This observation is similar to that observed for lyotropic (carbamoylethyl)cellulose (CBEC)[18], cellulose cinnamate (CC)[19] and nitrocellulose (NC)[20] liquid crystals. The critical concentration for AEC solutions also depends on the solvent system. For example, the value of C* for AEC-36 solution in m-cresol is about 30% by weight while that of the same polymer in bromoform is only 18% by weight. The decrease in C* with an increase in acetyl DS and with a change in solvent system from m-cresol to bromoform suggests that the AEC polymer chains become stiffer according to Flory's lattice theory. A further increase in the concentration of AEC solution results in the formation of a pure ordered phase. As shown in Figure 2.7 (b), no isotropic phase was observed for AEC-36 solution at a concentration of 40% at room temperature.

Anisotropic solutions of AEC polymers in the above solvents all show typical characteristics of a chiral nematic liquid crystal, e.g. reflection colors or fingerprint texture, depending on the solvent system, acetyl content, concentration and temperature. In the following chapters (3-5), the concentrations of all samples to be studied are carefully selected and varied for a given solvent so that the pure anisotropic phases are



(a)



(b)

Figure 2.7. Polarizing micrographs of AEC-36 solutions in m-cresol at a concentration of (a) 31% and (b) 40% (by weight) at room temperature (x 400)

formed and their pitch values are measurable by a UV-visible spectrophotometer, circular dichroism spectrometer or optical microscope.

Concentrated solutions of PEC in the above solvents and of AMC in DCA and TFA also form chiral nematic mesophases, similar to the unmodified EC and MC in the same solvents.

2.4. Conclusion

The ^{13}C NMR analysis of commercial ethylcellulose with a DS of 2.5 indicates that the hydroxyl groups at carbon six of anhydroglucose units are completely substituted. Acetylation of the ethylcellulose under different conditions yields (acetyl)(ethyl)cellulose (AEC) polymers having acetyl DS ranging from 0 to 0.5. Fully substituted (propionyl)(ethyl)cellulose (PEC) and (acetyl)(methyl)cellulose (AMC) were successfully prepared. Chiral nematic liquid crystals are formed in these mixed ester/ether of cellulose at high concentration, similar to their precursors in the same solvents. The critical concentration for phase separation for AEC solutions depends on acetyl DS and solvent system at a given temperature.

2.5. References

1. L. Segal, G.D. Hiatt, W.J. Rebel, A.B. Savage, N.M. Bikales, et al., in Cellulose and Cellulose Derivatives, Eds. N.M. Bikales and L. Segal, Wiley-Interscience, New York, 1971, Part V, Chapter XVII
2. M. Siekmeyer and P. Zugenmaier, in Cellulose: Structural and Functional Aspects, Eds. J.F. Kennedy, G.O. Phillips and P.A. Williams, Ellis Horwood, 1989, pp. 347
3. M. Siekmeyer, H. Steinmeier and P. Zugenmaier, Makromol. Chem. 190, 1037(1989)
4. K. Araki, Y. Iida and Y. Imamura, Makromol. Chem. Rapid Commun. 5, 99(1984)
5. S. Suto, J. Polym. Sci. Polym. Phys. Ed. 22, 637(1984)
6. S. Suto, M. Ohshiro, W. Nishibori, H. Tomita and M. Karasawa, J. Appl. Polym. Sci. 35, 407(1988)
7. S. Suto, S. Kimura and M. Karasawa, J. Appl. Polym. Sci., 33, 3019(1987)
8. P. Zugenmaier and P. Haurand, Carbohydr. Res., 160, 369(1987)
9. V. Vogt and P. Zugenmaier. Ber. Bunsenges Phys. Chem., 89, 1217(1985)

10. D.R. Budgell, Ph.D. Thesis, McGill, Montreal, 1989
11. J.X. Guo and D.G. Gray, Macromolecules, 22, 2086(1989)
12. A.M. Ritcey and D.G. Gray, Biopolymers, 27, 479(1988)
13. S. Takahashi, T. Fujimoto, B.M. Barua, T. Miyamoto and H. Inagaki, J. Polym. Sci. Polym. Chem. Ed., 24, 2981(1986)
14. T. Miyamoto, Y. Sato, T. Shibata and H. Inagaki, J. Polym. Sci. Polym. Phys. Ed., 22, 2363(1984)
15. J. Reuben, Carbohydr. Res. 161, 23(1987)
16. P. Zadorecki, T. Hjertberg and M. Arwidsson, Markrol Chem., 188, 513(1987)
17. A. Isogai, A. Ishizu and J. Nakano, J. Appl. Polym. Sci., 31, 341(1986)
18. S. Takahashi, H. Susuki, T. Miyamoto and H. Inagaki, in Cellulose: Structural and Functional Aspects, Eds. J.F. Kennedy, G.O. Phillips and P.A. Williams, Ellis Horwood, 1989, pp. 391
19. K. Arai and H. Satoh, J. Appl. Polym. Sci. 45, 387(1992)
20. C. Viney and A. H. Windle, Liq. Cryst., 1, 379(1986)

Chapter 3

Effect of Degree of Acetylation and Solvent on the Chiroptical Properties of Lyotropic (Acetyl)(Ethyl)cellulose Solutions

3.1. Introduction

Cellulose is the naturally occurring homopolymer of β-D-glucopyranose. As a result of the semi-rigid and chiral nature of the cellulose backbone, cellulose and its derivatives can form liquid crystalline phases that show chiral nematic behaviour[1-8]. Stable colloidal dispersions of cellulose crystallites also show chiral nematic properties[9]. The chirality of the cellulosic mesophases depends on temperature, on the nature of solvent (in case of lyotropic liquid crystals) and on the chemical structure of substituents on the cellulose chains. Most cellulose derivatives in mesophase form right-handed helicoidal structures. Ethylcellulose (EC) was the first derivative found to form a left-handed lyotropic liquid crystal and to display a solvent dependence of handedness[4,10,11]. Although a large numbers of cellulosic liquid crystals have been reported[12-14], only a few cellulose derivatives showed the solvent dependence of handedness[10,11,15,16].

The nature of the (achiral) substituents on the cellulose chain strongly influences the chiroptical properties of the mesophases. In a previous paper[17], it has been shown that the introduction of acetyl group on the ethylcellulose can result in a large change of chiroptical properties of the product, (acetyl)(ethyl)cellulose (AEC), in liquid crystalline solutions. For example, AEC with ethyl DS of 2.5 and acetyl DS above 0.2 in chloroform exhibits a handedness and temperature dependence of the pitch opposite to that for the unacetylated EC in the same solvent, in spite of the observation that both polymers have apparently similar conformations in dilute solution as indicated by means of optical rotatory dispersion (ORD). The reversal of handedness is observed in many systems where a continuous change in some variable (composition, temperature, degree of substitution, etc.) leads to a divergence in the pitch, which increases to infinity to give a compensated nematic phase, then reverses handedness and decreases again. In thermotropic mesophases, the compensation may occur at an appropriate mixture of two liquid crystalline optical isomers or at a compensated temperature. In lyotropic mesophases, the compensation may also occur at an appropriate mixture of two solvents in which the handedness of the individual lyotropic solutions is opposite. A solvent-induced compensation has been observed for ethylcellulose (EC) in a mixture of acetic acid (AA) and dichloroacetic acid (DCA)[10] and for cellulose tricabanilate (CTC) in a mixture of methyl propyl ketone (MPK) and diethylene glycol monomethyl ether (DEME)[18], and a thermally-induced compensation is reported for oligomers of tri-O-2(2-methoxyethoxy)ethylcellulose (O-TMEC) and tri-O-heptylcellulose (O-THC)[8]. By analogy, the compensation is expected to occur at a specific acetyl DS for the AEC

mesophases as the acetyl DS is varied. In this chapter, the previous work[17] is extended to other organic solvents. Optical microscopy, laser diffraction and optical rotatory dispersion are employed to characterize the nematic and chiral nematic phases.

3.2. Experimental Section

Ethylcellulose (EC) with an ethoxyl content of 48% and a viscosity of 22 cp (5%) was purchased from Aldrich Co. AEC polymers with an acetyl DS ranging from 0 to 0.5 were prepared from this EC, and characterized as in chapter 2. Organic solvents; dichloromethane (DCM), dibromomethane (DBM), acetic acid (AA), dichloroacetic acid (DCA), m-cresol and bromoform from Aldrich Co. and aqueous phenol (AP) from Anachemia were used without purification.

The lyotropic liquid crystal samples for optical characterization were prepared by placing polymer and solvent in rectangular glass capillary tubes, 0.4-mm path length (Vitrodynamic Inc.), to give a desired polymer concentration. The capillaries were then sealed by flaming. The solutions were well mixed by centrifuging back and forth in the capillaries and were allowed to equilibrate for at least two weeks. The liquid crystalline samples for some measurements were also prepared between microscope slide and cover glass as described in Chapter 2. For a given solvent, a fixed value of polymer concentration was employed, and samples with acetyl DS ranging from 0 to 0.5 were examined. In order to make samples with pitch values accessible by measuring reflection band wavelengths, commercial circular dichroism (CD) or by optical microscopy. The value of the concentration was selected to bring the pitch values into an experimentally convenient range for measurements. The pitch of the liquid crystals was determined by means of optical microscopy, laser diffractometry, UV-visible spectrometry or CD spectrometry, depending on the range of their pitches. The polarizing microscope (OPTIPHOT-POL) was equipped with a video camera (Cohu); the spacings between striation lines (half the pitch) were recorded on video tape and analyzed by Java video analysis software. The value of the pitch was taken from the average of at least three measurements. Optical diffraction measurements were carried out by photographing the diffracting rings produced when the beam from a Helium-Neon laser (λ = 6328Å) impinged at right angle on a mesophase sample. The pitch was calculated from Bragg's diffraction equation, $m\lambda = (|P|/2)\sin\varphi$, where λ is the wavelength of the laser light, φ is the scattering angle, m is an integer and P is the pitch. The CD and UV-visible spectra for those AEC mesophases with a reflection band in the wavelength region of UV-visible light were recorded with a Jasco-500c spectropolarimeter and a Pye Unicam SP8-150

spectrophotometer, respectively. The corresponding pitches were calculated from the wavelength of maximum reflection λ_0 and mean refractive index according to de Vries' equation[20], $|P| = \lambda_0 / \bar{n}$. The mean refractive index $\bar{n}$ of the AEC liquid crystals was measured with an Abbé refractometer (Carl Zeiss Model 44159). For those mesophases with pitch values beyond the order of visible light, the handedness can be assigned by the sign of ORD curve. The assignment is based on the de Vries' equation[19] for $\lambda \ll \lambda_0$ as follows:

$$\alpha = \pi (\Delta n)^2 P / 4 \lambda^2 \qquad [1]$$

where α is the optical rotation at a wavelength λ, P is the pitch (taken to be a pseudoscalar that is positive for a right-handed helicoid and negative for a left-handed helicoid) and Δn is the birefringence of the pseudonematic layer. The sign of α for $\lambda \ll \lambda_0$ thus indicates the handedness of the helicoidal structure, with $\alpha > 0$ for a right-handed twist, and $\alpha < 0$ for a left-handed twist. For measurements as a function of temperature, the samples were placed in a hot stage (Mettler FP52) mounted in the sample stage of the microscope or in the spectrometer beam, and heated at a rate of 0.2°C / min.

Optical rotation was also measured with a Jasco DP-140 digital polarimeter. The relative fluidity of the AEC lyotropic solutions was estimated from the time required for the meniscus to move a given distance when the vials were tilted through 30°.

3.3. Results and Discussion

3.3.1. Solvent dependence of handedness

It has been shown in Chapter 2 that the AEC solutions form chiral nematic liquid crystals, regardless of acetyl DS. The reflection band at λ_0 observed for samples whose pitches are of the order of the wavelength of UV or visible light is most readily detected by the apparent circular dichroism spectra (which gives λ_0 and is positive for left-handed and negative for right-handed helicoidal structures). For samples with longer pitch values, the magnitude may be estimated from optical microscopy or optical diffraction, and the sign from optical rotatory dispersion measurements and equation 1.

Figure 3.1 shows the apparent CD spectra for lyotropic AEC solutions in DCM, DBM, AA, and bromoform. Positive CD bands were observed for the AEC samples with an acetyl DS of 0.13 in DCM, DBM, AA, and bromoform, indicating reflection of

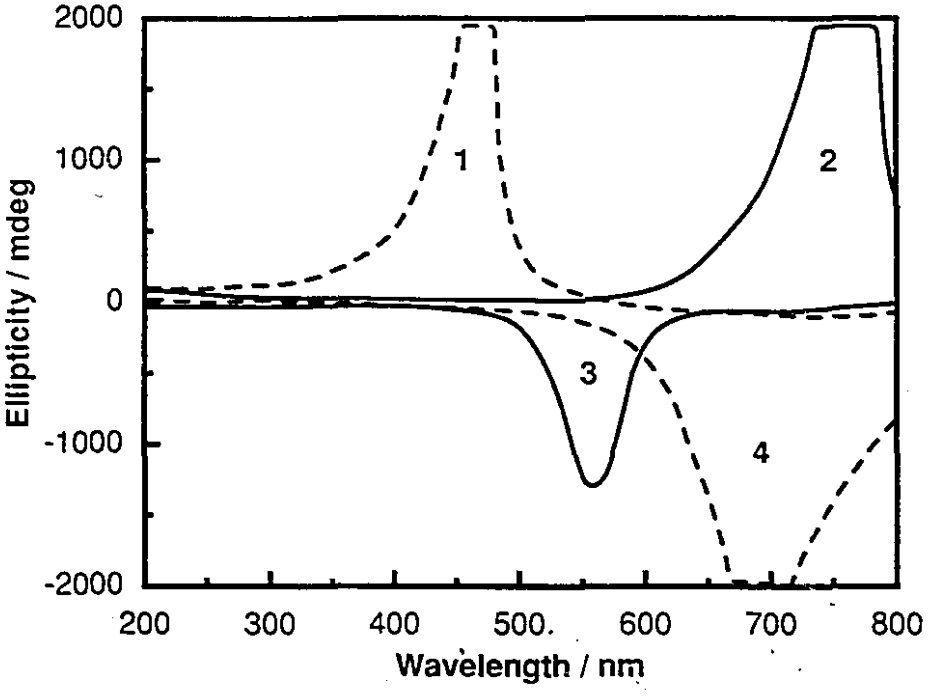


Figure 3.1. Apparent CD spectra of anisotropic AEC solutions in DCM (solid lines) and DBM (dashed lines) at room temperature. The acetyl DS of samples in curves 1 and 2 is 0.13 and that of samples in curves 3 and 4 is 0.5.

circularly polarized light by a left-handed liquid crystal. The negative CD bands observed for the fully acetylated AEC mesophases in DBM and DCM are an indication of the presence of a right-handed helicoidal structure. Since the pitch values of the fully acetylated AEC mesophases in AA and bromoform are beyond visible light wavelength, the handedness of the samples was determined by ORD according to equation [1]. These lyotropic solutions display a positive optical rotation and are thus assigned as a right-handed liquid crystal. The same ORD approach was taken to other long-pitch systems such as AEC/AP and AEC/m-cresol anisotropic solutions. Based on the CD and ORD results, the apparent handedness of the series of AEC lyotropic solutions in different solvents is summarized in Table 3.1. It can be seen from the table that AEC with low acetyl content is a left-handed liquid crystal in all the listed solvents except for DCA, while the AEC with high acetyl DS (> 0.4) is right-handed, independent of solvent. In other words, the handedness inversion takes place for AEC solutions in all the listed solvents except for DCA in which the AEC liquid crystals all form a right-handed helicoidal structure, independent of acetyl DS.

The solvent dependence of handedness was first found for polypeptide liquid crystals[20]. A few cellulose derivatives also show the feature, e.g. ethylcellulose[4], cellulose tricarbanilate[15] and 6-O-trityl-2,3-O-hexylcellulose[16]. Samulski and Samulski[21] predicted that the reversal of handedness for a given polymer occurs at a critical dielectric constant of a solvent, ε^*. This prediction satisfies the observation of the solvent-induced handedness inversion in some mixtures of solvents[21,22] and in some non-interactive solvents[24] for polypeptides, although there is some discrepancy. As shown in Table 3.1, the solvent dependence of handedness was found for the AEC with low acetyl content, but not for the AEC with an acetyl DS over 0.40, even though the same series of solvents are used. Furthermore, a minor change in acetyl DS gives rise to a reversal of the handedness, in spite of sharing the same chiral mainchain in an achiral medium of the same dielectric constant.

It is evident that some other factors are operative here. It seems likely that strong and specific solvent-polymer interactions must play a role in addition to substituent effects on the main-chain conformation.

3.3.2. Effect of acetyl DS on pitch

As reported previously[17], the pitch of chiral nematic AEC liquid crystalline solutions in chloroform shows a strong dependence on acetyl DS. The same AEC

Table 3.1. Handedness dependence of acetyl DS for AEC anisotropic solutions in various organic solvents

Solvent	ε	C(wt%)	Acetyl DS				
			0.1	0.2	0.3	0.4	0.5
m-cresol	11.8[a]	42%	left	right	right	right	right
Chloroform	4.86[b]	45%	left	left	right	right	right
DCM	9.08[b]	45%	left	left	right	right	right
DBM	7.77[c]	33%	left	left	right	right	right
Bromoform	4.39[b]	24%	left	left	left	right	right
AP	9.78*	40%	left	left	left	right	right
AA	6.16[b]	42%	left	left	left	right	right
DCA	8.20[d]	30%	right	right	right	right	right

(a) 25°C, (b) 20°C, (c) 10°C, (d) 22°C

* Phenol at 60°C

polymers in DCM, DBM, AA, AP, bromoform and m-cresol also show a similar relation between pitch and acetyl content in a given solvent, concentration and temperature.

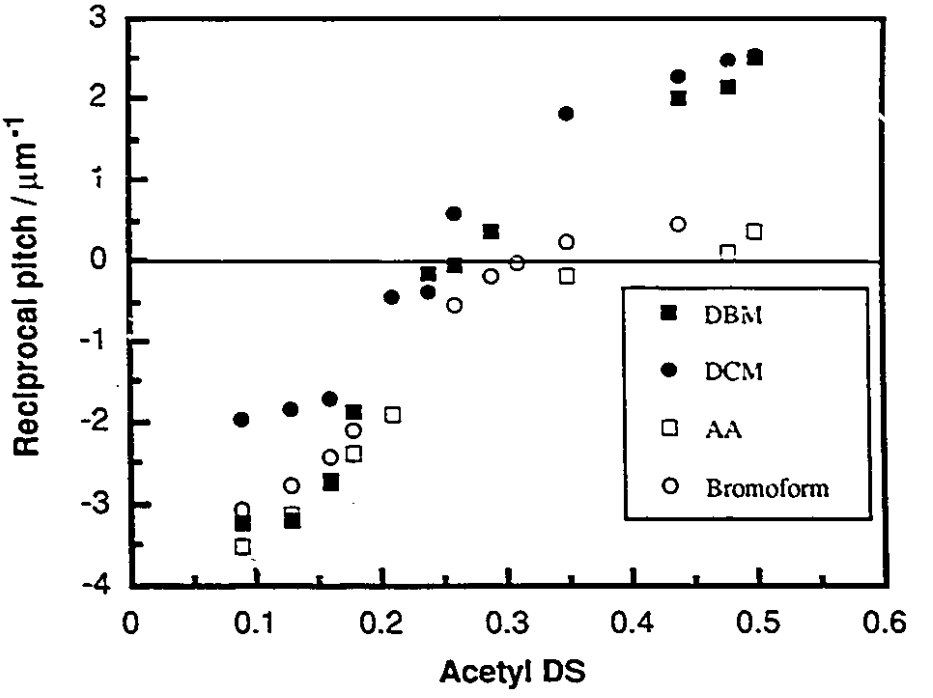
Figure 3.2 shows typical plots of reciprocal pitch against acetyl DS for AEC lyotropic solutions in these solvents. In general, the magnitude of inverse pitch decreases with increasing acetyl DS, falls to zero at a certain acetyl DS, and increases with further increasing acetyl DS. The negative and positive inverse pitch values represent left- and right-handed liquid crystals, respectively. The same trend of acetyl DS dependence on pitch was observed for all solvent systems, but the acetyl DS corresponding to zero inverse pitch varies with the individual solvent. At this DS, the pitch P becomes infinite, and an untwisted nematic-like structure replaces the helicoidal ordered structure. As defined in a previous paper[17], the acetyl DS corresponding to the appearance of the nematic-like mesophase is referred to as the compensated degree of acetylation, DA*.

It is striking that the DA* shows a strong solvent dependence even though the polymers are the same. The approximate DA* for the AEC polymers in different solvents, estimated as illustrated in Figure 3.2(b), is given in Table 3.2. The values of DA* in this series of solvents vary from 0.19 to 0.37. Again, it can be seen that the value of DA* bears no relation to the dielectric constant of the solvents employed, indicating that specific interactions between AEC polymers and solvent are involved in the handedness inversion.

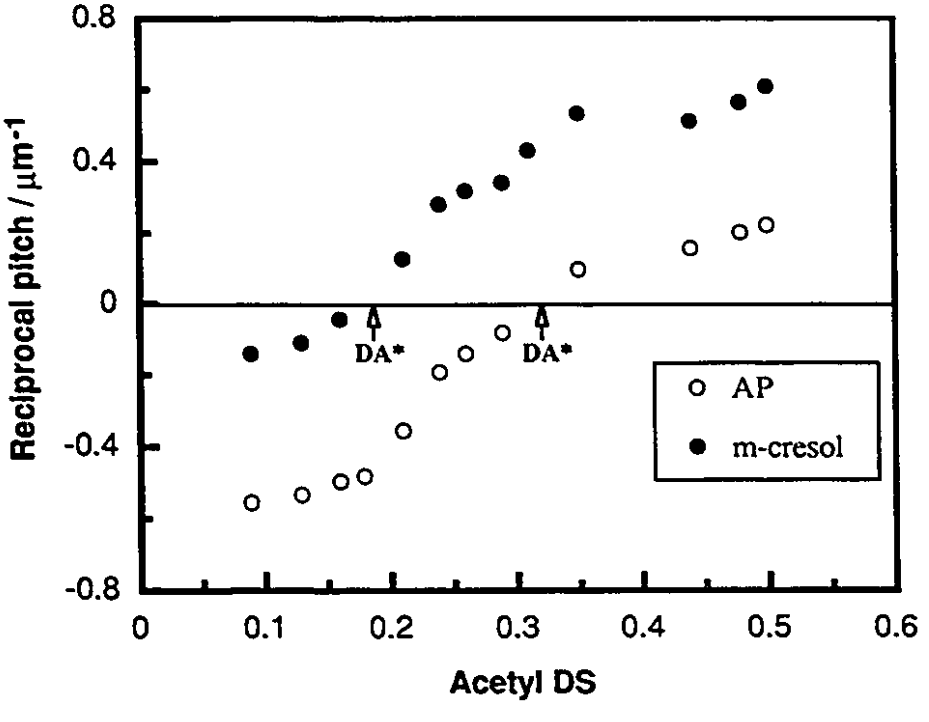
It should be mentioned here that the AEC mesophases show right-handed helicoidal structures in DCA, regardless of acetyl DS; solutions in DCA display a weak acetyl DS dependence with values for the pitch decreasing approximately linearly from around 445 nm at an acetyl DS of 0.16 to around 425 nm at an acetyl DS of 0.5, as shown in Figure 3.3.

3.3.3. Optical phenomena close to the compensated condition

When the degree of acetyl DS that produces the compensated structure is approached, either from higher or lower acetyl DS, the bright iridescent colours move from blue to red, and then give cloudy opalescent solution. Close to DA*, the turbidity drops markedly to give an almost transparent solution. The appearance in the optical microscope is shown in Figure 3.4. The parallel lines in the photographs result from the periodic arrangement of pseudonematic molecular layers of the chiral nematic structure with the helicoidal optical axis perpendicular to the incident light beam. The lines were observed for samples with acetyl DS larger or smaller than 0.31. The spacing between the



(a)



(b)

Figure 3.2. Reciprocal pitch as a function of acetyl DS for AEC anisotropic solutions in (a) DCM , DBM, bromoform and AA (b) AP and m-cresol at room temperature. Negative values of the pitch correspond to left-handed helicoidal structures.

Table 3.2. Compensated degrees of acetylation (DA*) and temperature dependence of pitch for lyotropic AEC liquid crystals

Solvent	Conc. (wt%)	DA*	dP/dT (DA<DA*)	dP/dT (DA>DA*)
m-Cresol	42%	0.19	-	+
DCM	45%	0.25	-	+
DBM	33%	0.27	-	+
Bromoform	24%	0.32	-	+
Phenol (aq.)	40%	0.32	+	-
Acetic acid	45%	0.37	-	+
DCA	30%	RH	+	

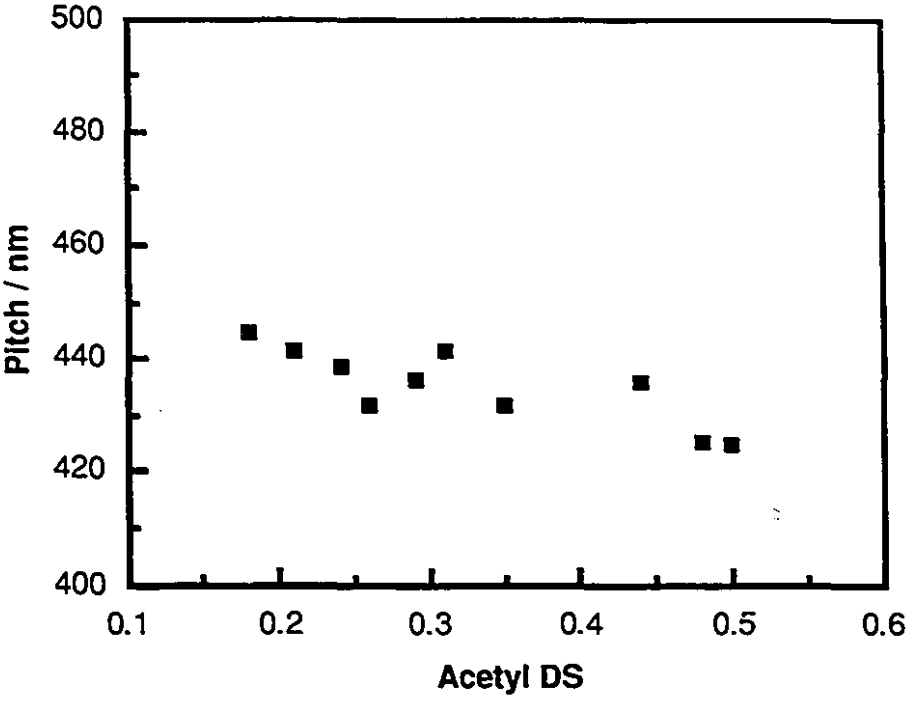


Figure 3.3. Pitch as a function of acetyl DS for AEC anisotropic solutions in DCA at room temperature.

(a) (b) (c) (d) (e)

Figure 3.4. Polarizing micrographs of anisotropic AEC solutions (40%) in aqueous phenol (AP). The acetyl DS' of samples (a)-(e) are 0.26, 0.29, 0.31, 0.35, 0.44, respectively. (x 400)

lines, equal to half of the pitch depends on the acetyl DS: the samples with acetyl DS closer to 0.31 have a longer pitch. Instead of the equidistant striations, the sample with an acetyl DS of 0.31 shows a thread-like texture characteristic of a nematic liquid crystal, implying that the helicoidal ordering structure no longer exists in this mesophase. These microscopic observations indicate that the compensation occurs in aqueous phenol at an acetyl DS around 0.31.

The periodicity observed normal to the optic axis of the chiral nematic helicoid under crossed polars also corresponds to periodicity in refractive index. This gives rise to diffraction of light at an angle that depends on the magnitude of the spacing. The diffraction angle decreases as the pitch goes to infinity; this method has been used to determine the existence of compensated mesophases[22,24]. Figure 3.5 shows diffraction rings for AEC mesophases in aqueous phenol as the acetyl DS is varied. The pitch values calculated from the diffraction rings are very close to those measured microscopically, with the sample with an acetyl DS of 0.31 showing only a diffuse central spot, as expected as the pitch becomes infinite.

The microscopic and diffraction measurements do not indicate the handedness of the mesophase. Well away from DA*, where the pitch is short enough to cause reflection of visible light, the handedness is readily inferred from the sign of the apparent CD peak, as described above. For longer pitch samples, a direct CD measurement is not applicable. However, optical rotatory dispersion from the mesophase may be used to assign the handedness in this region, according to the amplified form of de Vries' equation for the case of $\lambda \ll \lambda_0$ (equation 1). Figure 3.6 shows ORD curves for AEC lyotropic solutions in aqueous phenol as a function of acetyl DS. The high rotatory power observed for these samples is evidence of their chiral nematic supermolecular order. The handedness can be inferred from the sign of the ORD curves because optical microscopy clearly shows that they have long pitch values. The AEC samples with an acetyl DA* below 0.29 all show negative ORD curves, an indication of the presence of left-handed helicoidal structures. On the other hand, positive ORD signals were observed for those AEC samples with an acetyl DS above 0.35, suggesting that right-handed helicoidal structures are present in these mesophases. In addition, plots of the α against $1/\lambda^2$ in Figure 3.7 also give straight lines as predicted from equation 1. These ORD results provide a further proof of handedness inversion for AEC lyotropic solutions with changing acetyl content at a given concentration and temperature.

By analogy with the compensated temperature, composition, or mixture of solvent, there must exist a compensated degree of acetylation, DA*, falling between 0.29 and 0.35 for the AEC/AP system, and the corresponding mesophase must have an infinite

(a) (b) (c) (d) (e)

Figure 3.5. Optical diffraction patterns of anisotropic AEC solutions (40%) in AP. The acetyl DS' of samples (a)-(e) are 0.24, 0.29, 0.31, 0.35, 0.44, respectively.

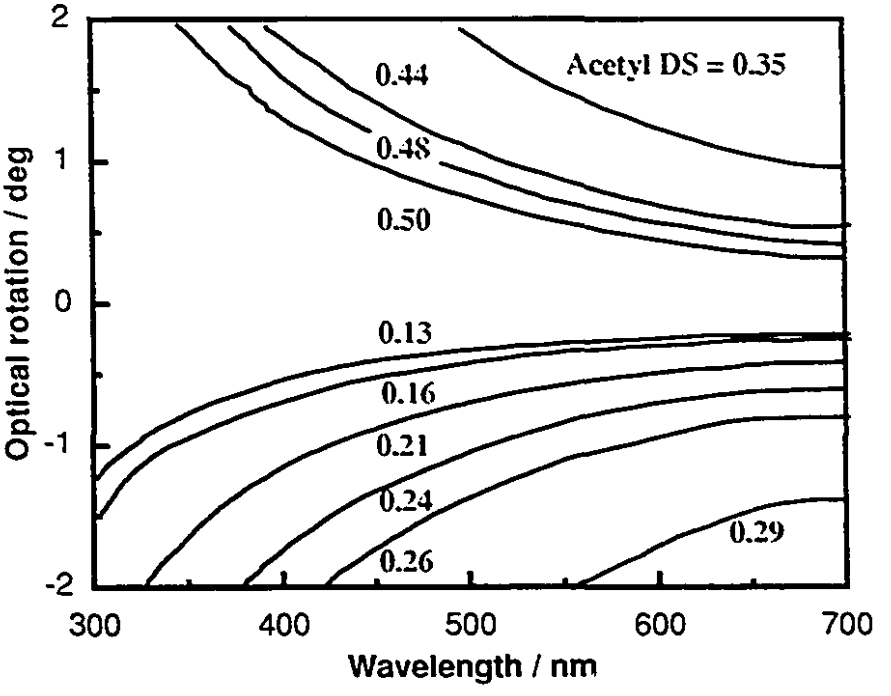


Figure 3.6. ORD curves for anisotropic AEC solutions (40%) in aqueous phenol. The thickness of the samples is 10 μm.

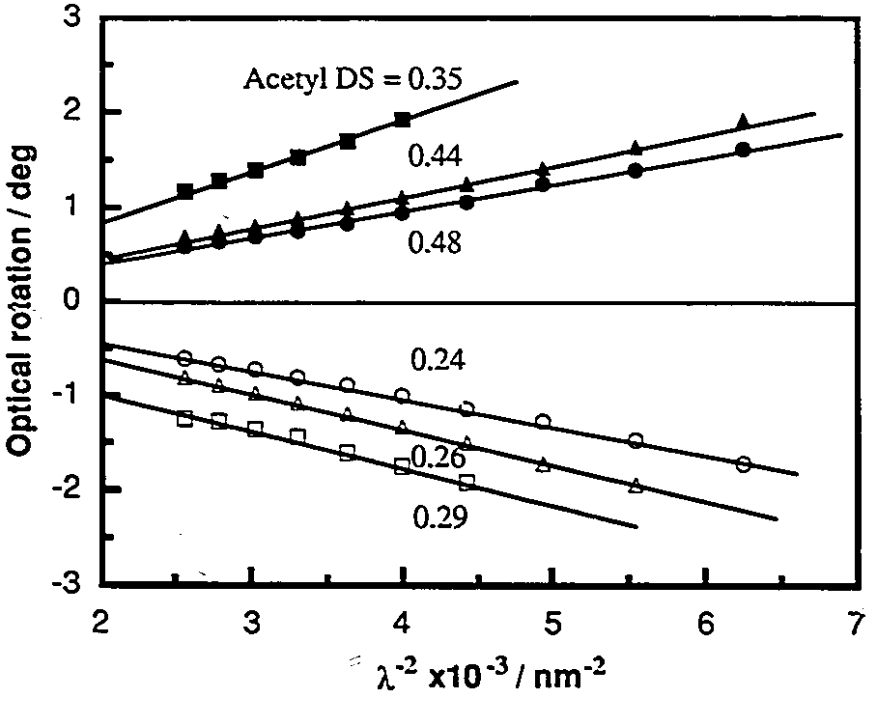


Figure 3.7. Plots of optical rotation against $1/\lambda^2$ for anisotropic AEC solutions (40%) in aqueous phenol. The thickness of the samples are 10 μm.

pitch and behave optically inactive. Since optical microscopy and optical diffraction indicate that the AEC sample with an acetyl DS of 0.31 has an almost infinite pitch, exhibition of nematic-like optical behavior is expected for the sample. Figure 3.8 shows the rotatory power (optical rotation per unit of thickness) at λ = 589 nm of AEC anisotropic solutions in AP as a function of acetyl DS. Perhaps counterintuitively, the rotatory power becomes increasingly negative as the acetyl DS increases and the chiral nematic pitch increases. The magnitude of the rotatory power then decreases sharply for the sample with an acetyl DS of 0.31, and changes sign, eventually decreasing with further increase in acetyl DS. The change in sign and discontinuity in the rotatory power as the acetyl DS is increased again indicates that there exists a specific acetyl DS close to 0.31 where the solution behaves as a compensated nematic. Similar observations have been made for a mixture of cholesteryl chloride and cholesteryl myristate; where a reversal of handedness and a compensation occur as the temperature is changed[25,26]. In our case, the compensation is a function of acetyl content, concentration and the nature of the solvent, in addition to temperature.

3.3.4. Temperature dependence of pitch.

A positive temperature dependence of pitch has been observed for most cellulosic liquid crystals. However, ethylcellulose liquid crystalline solutions have been found to show a positive or negative temperature[4,11] dependence of pitch, depending on the solvent. It has been shown previously[17] that the temperature dependence of pitch for EC/chloroform mesophases can be reversed by introducing acetyl group into the free hydroxyl group on EC chains (acetyl DS > 0.2), implying that the effect of temperature on pitch is also sensitive to the chemical structure of side chain. The effect is also observed for other solvents. A negative temperature dependence of the wavelength of maximum reflection, λ_0 ($\lambda_0 = \bar{n}/P$), was observed for the anisotropic solutions of AEC with an acetyl DS below DA* in DBM and DCM (Figure 3.9). The solutions of AEC with an acetyl DS above DA* display a positive temperature dependence of λ_0 in the same solvents. This pattern was observed for all the solvents with one exception, where the pitch increased with increasing temperature for a low-acetyl DS AEC sample in aqueous phenol (a left-handed mesophase), and decreased with increasing temperature for a right-handed highly acetylated sample in the same solvent (Figure 3.10). The reason for this optical behaviour is not known. Thus the temperature dependence of pitch remains solvent dependent for the lyotropic AEC liquid crystals, irrespective of the acetyl content. The results are summarized in Table 3.2. The reversal of handedness with acetyl content

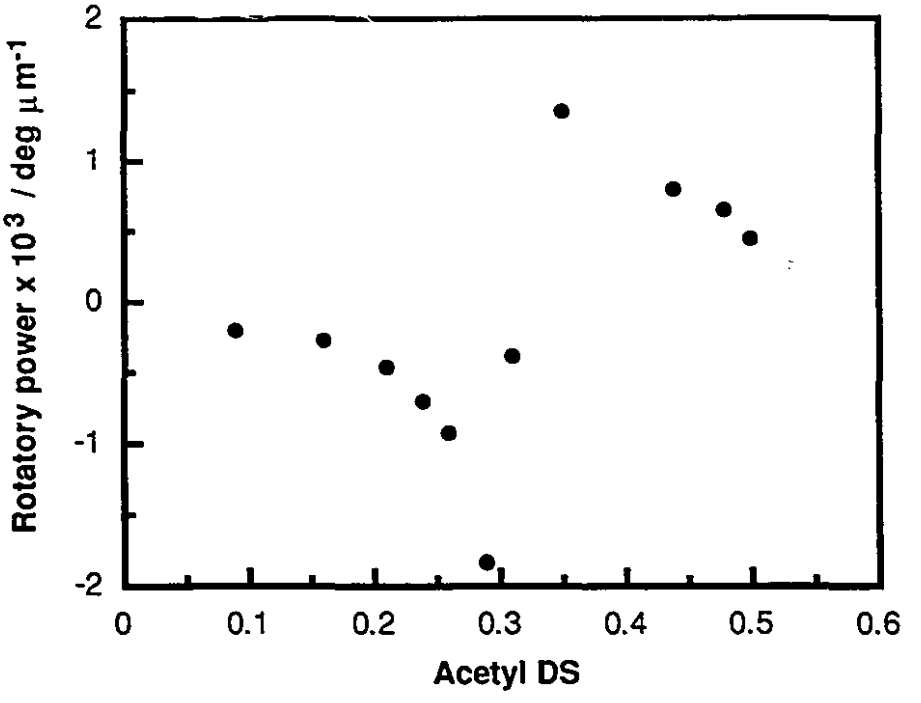


Figure 3.8. Rotatory power at λ = 589 nm as a function of acetyl DS for anisotropic AEC solutions (40%) in aqueous phenol.

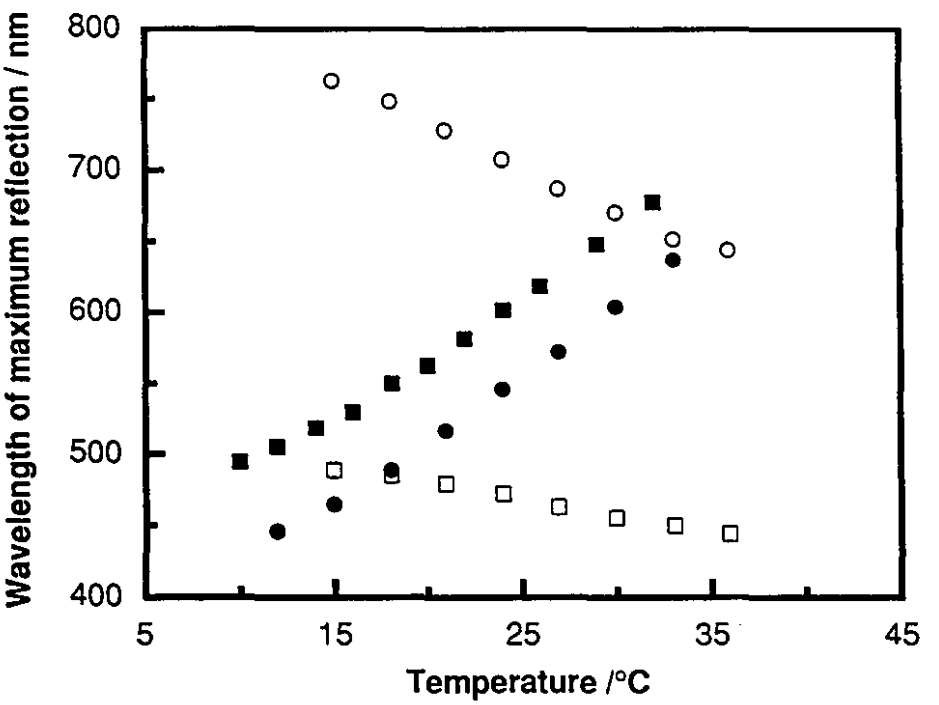


Figure 3.9. Temperature dependence of the wavelength of maximum reflection for liquid crystalline AEC solutions in DCM (circle symbols) and DBM (square symbols). The samples of the unfilled and filled plots are left- and right-handed liquid crystals, respectively.

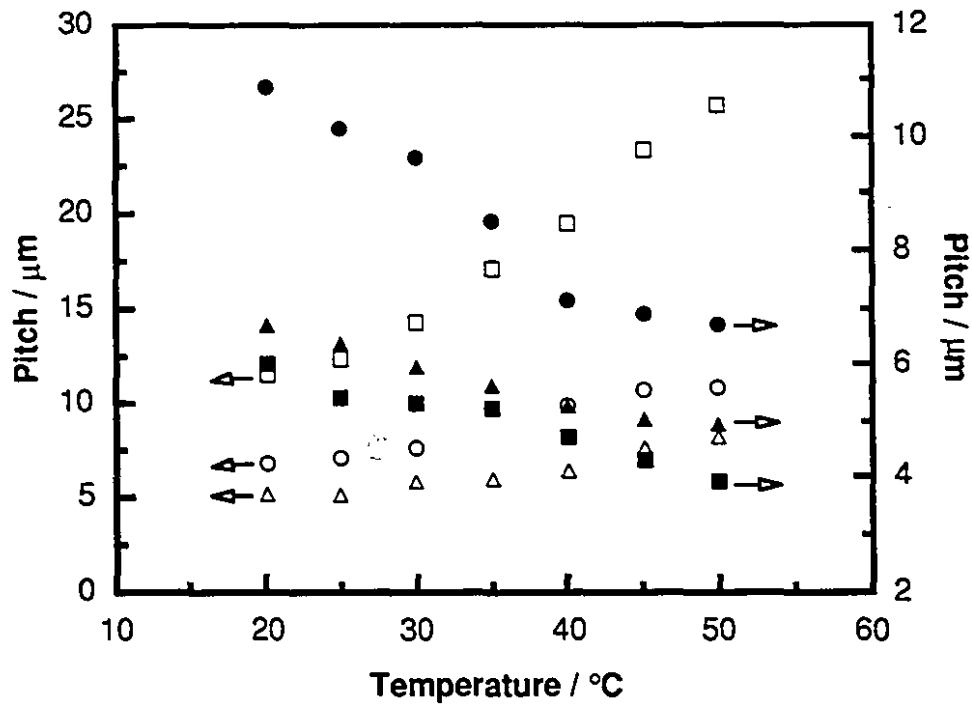


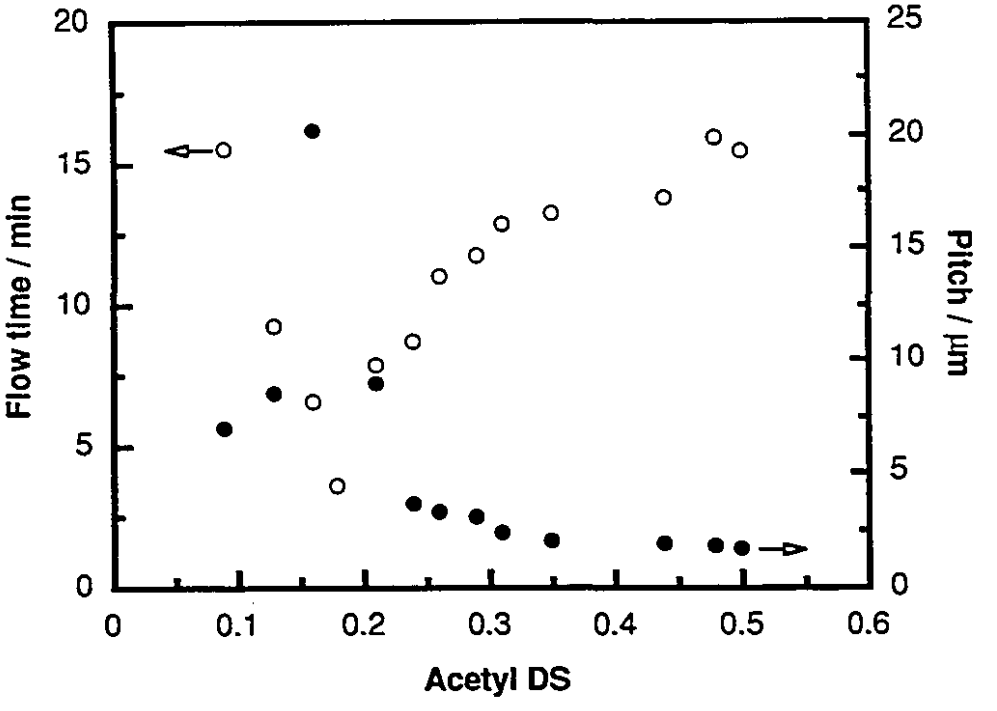
Figure 3.10. Temperature dependence of the magnitude of pitch for anisotropic AEC/AP solutions with different acetyl DS'. (△) 0.24, (○) 0.26, (□) 0.29, (●) 0.35, (▲) 0.44, (■) 0.48. The samples of the unfilled and filled plots are left- and right-handed liquid crystals, respectively.

is accompanied by a change in the temperature dependence of pitch for these AEC mesophases .

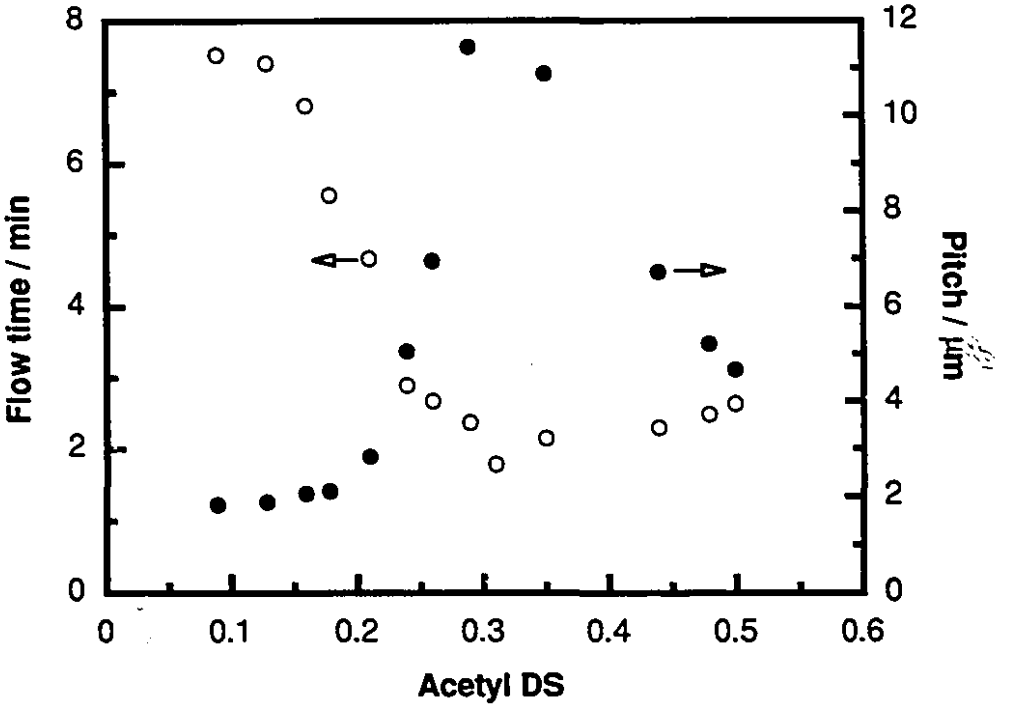
3.3.5. Pitch effects on flow behavior

The flow properties of chiral nematic liquid crystals are different from those of regular nematics in that they have a high apparent viscosity at low shear rate[27] and a pitch dependence of the viscosity[10,28,29] Helfrich[30] proposed a permeation mechanism to explain the rheological behavior of low molar mass chiral nematic liquid crystals, in which the flow direction of the mesophase is along the helicoidal optical axis. The theory predicts that the apparent viscosity is slightly pitch dependent. The applicability of this approach to polymeric system is questionable.

The pitch values of lyotropic mesophases depend on temperature and concentration, but of course viscosity is also a sensitive function of these variables, so that in general the effect of pitch on viscosity is difficult to disentangle. In AEC lyotropic systems, the pitch can be readily controlled by a small change in acetyl DS, with concentration and temperature held constant (see Figure 3.2). These mesophases thus appear to serve as good samples to study the pitch effects on the flow behavior. Figure 3.11 shows an empirical flow time as a function of acetyl DS for AEC/AP and AEC/m-cresol mesophases. The flow time decreases rapidly with increasing acetyl DS (and hence with the magnitude of the pitch), reaches a minimum at acetyl DS close to DA*, where the pitch is almost infinite, and then increases with further increase in acetyl DS. As observed for mixtures of a nematic and a chiral nematic phase[28] and a mesophase mixture of left and right optical isomers (PBLG and PBDG)[29] with various composition ratios, there is a general correlation of resistance to flow with the magnitude of inverse pitch for the lyotropic solutions of AEC, irrespective of handedness and solvent. This conclusion is further supported by the measurement of flow time of AEC/DCA mesophases whose handedness is independent of acetyl DS and whose pitches do not show a discontinuity with acetyl DS. Figure 3.12 is a plot of the flow time against acetyl DS. Apparently, there is no minimum flow time observed with increasing acetyl DS in this solvent. Since the same series of polymers were used in Figure 3.11 and 3.12, this is a clear indication that the ordered structure of chiral nematic liquid crystal has a strong effect on the flow properties.



(a)



(b)

Figure 3.11. Flow time (O) and magnitude of pitch (●) as a function of acetyl DS for anisotropic AEC solutions in m-cresol (a) and AP (b) at room temperature.

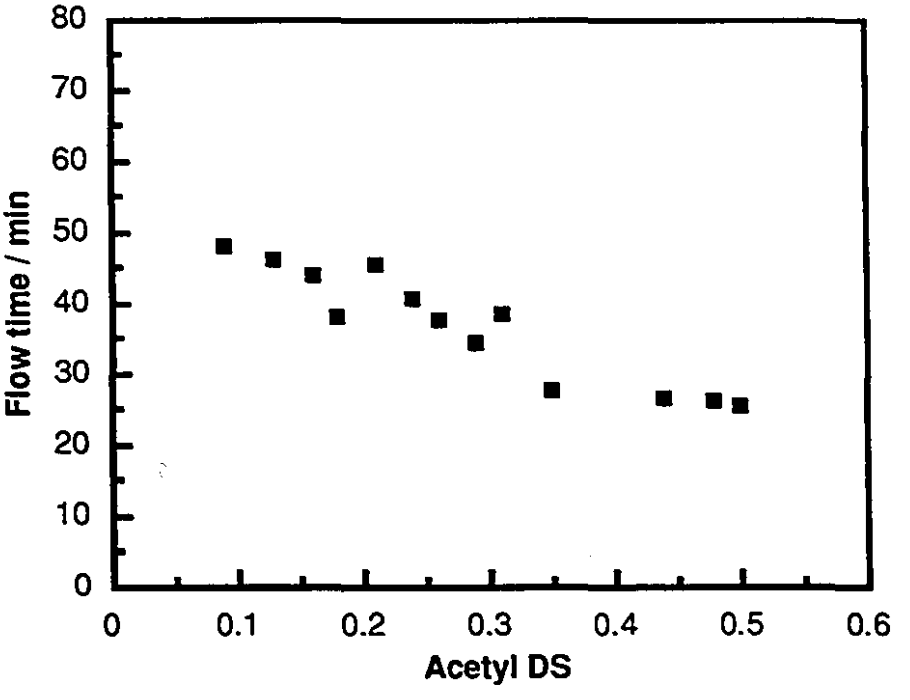


Figure 3.12. Flow time as a function of acetyl DS for anisotropic AEC solutions in DCA at room temperature.

3.4. Conclusion

(Acetyl)(ethyl)cellulose (AEC) polymers with an ethyl degree of substitution (DS) of 2.5 and acetyl DS ranging from 0 to 0.5 dissolve readily in a wide range of organic solvents and form chiral nematic liquid crystalline phases in concentrated solution. Despite the fact that the substituents and solvents are achiral, the chiroptical properties of these liquid crystals are strongly influenced by the acetyl content and solvent. In dichloromethane, dibromomethane, chloroform, bromoform m-cresol, acetic acid and aqueous phenol, the AEC lyotropic mesophases all show a handedness inversion as the acetyl DS of the polymers is increased, changing from left- to right-handed supermolecular helicoidal structures. The temperature dependence of the pitch for these mesophases is also reversed from negative to positive with increasing acetyl DS in all the above solvents except aqueous phenol, in which solvent the corresponding AEC mesophases change from positive to negative. The optical microscopic, optical diffraction and ORD evidence provide a unique indication that the reversal of the handedness and temperature dependence for the AEC mesophases occurs at a compensated degree of acetylation, DA*. The corresponding compensated mesophases show an infinite pitch and behave optically like nematic mesophases. The value of the DA* is dependent on solvent. In dichloroacetic acid, AEC liquid crystals remain right-handed, independent of the acetyl DS. At given concentration and temperature, the long pitch samples flow much more readily than short pitch samples.

3.5. References

1. R.S. Werbowyj and D.G. Gray, Mol. Cryst. Liq. Cryst. (letters), 34, 97(1976)
2. D.L. Patel and R.D. Gilbert, J. Polym. Phys. Ed. 19, 1449(1981)
3. P. Sixou, J. Lematre, A. Ten Bosch, J.M. Gilli and S. Dayan, Mol. Cryst. Liq. Cryst., 91, 277(1983)
4. U. Vogt and P. Zugenmaier, Ber. Bunsenges. Phys. Chem., 89, 1217(1985)
5. G.V. Laivins and D.G. Gray, Polymer, 26, 1435(1985)
6. H. Steinmeier and P. Zugenmaier, Carbohydr. Res., 173, 75(1988)
7. B.R. Harkness and D.G. Gray, Macromolecules, 23, 3449(1990)
8. T. Yamagishi, T. Fukuda, T. Miyamoto, T. Ichizhuka and J. Watanabe, Liq. Cryst. 7, 155(1990)
9. J.-F. Revol, H. Bradford, J. Giasson, R.H. Marchessault and D.G. Gray, Int. J. Biol. Macromol., 14, 170(1992)

10. P. Zugenmaier and Petra Haurand, Carbohydr. Res., 160, 369(1987)
11. D.R. Budgell, Ph.D. Thesis, McGill University, Montreal, 1989
12. R.D. Gilbert and P.A. Patton, Prog. in Polym. Sci., 9, 115(1983)
13. D.G. Gray, J. Polym. Sci., Appl. Polym. Symp., 37, 179(1983)
14. B.R. Harkness and D.G. Gray, in Liquid Crystal and Mesomorphic Polymers Ed., V. Shibaev and L. Lam, Springer, New York, 1991, in press.
15. M. Siekmeyer and P. Zugenmaier, Makromol. Chem., Rapid., Commun. 8, 511(1987)
16. B.R. Harkness and D.G. Gray, Can. J. Chem., 68, 1135(1990)
17. J.X. Guo and D.G. Gray, Macromolecules, 22, 2086(1989)
18. M. Siekmeyer and P. Zugenmaier in Cellulose Structural and Functional Aspects, Eds. J.F. Kennedy, G.O. Phillips and P.A. Williams, Ellis Horwood, 1989, P347
19. Hl. de Vries, Acta., Crysta., 4, 219(1951)
20. C. Robinson, Tetrahedron, 13, 219(1961)
21. T.V. Samulski and E.T. Samulski, J. Chem. Phys. 67, 824(1977)
22. H. Toriumi, S. Minakuchi, I, Uematzu and Y. Uematzu, Polym. J., 11, 863(1979)
23. H. Toriumi, S. Minakuchi, I, Uematzu and Y. Uematzu, Mol. Cryst. Liq. Cryst., 94, 267(1983)
24. E. Sackmann, S. Meiboom, L.C. Snyder, A.E. Meixner and R.E. Dietz, J. Am. Chem. Soc., 90, 3567(1968)
25. G.S. Rarganath, S. Chandrasekhar, U.D. Kini, K.A. Suresh and S. Romasesh, Chem. Phys. Lett. 25, 12(1974)
26. S. Chandrasekhar, in Liquid Crystals, Cambridge University Press, 1977, chapter 4
27. R.S. Pooter, E.M. Barrall and J.F. Johnson, J. Chem. Phys. 45, 1452(1966).
28. S. Candau, P. Martinoty and F. Debeauvais, C.R. Acad. Sci., B277, 769(1973)
29. D.L. Patel and D.B. Dupré., Rheol Acta., 18, 662(1979)
30. W. Helfrich, Phys. Rev. Letters, 23, 372(1969)

Chapter 4

Induced Circular Dichroism of Dye Molecules in Chiral Nematic Liquid Crystals of (Acetyl)(Ethyl)cellulose Solutions

4.1. Introduction

As discussed in Chapter 1, chiral nematic liquid crystals possess high optical activity and selective reflection of circularly polarized light because of their helicoidal ordering structures. Optically inactive (achiral) chromophore molecules incorporated in these helicoidal structures may also develop an apparent optical activity as a result of the interaction between the guest achiral chromophores and the host chiral matrices[1,2]. The resulting optical activity is called liquid crystal induced optical activity or liquid crystal induced circular dichroism (LCICD) because it is detectable by CD spectrometer. The first observation of this induced optical activity for N-(p-methoxybenzylidene)-p-butylaniline in a thermotropic chiral nematic phase was reported by Saeva and Wysocki in 1971[3]. Since then this optical phenomenon has widely been observed for achiral chromophores dissolved in thermotropic[4-13] and lyotropic[14-19] chiral nematic phases. Other types of the liquid crystal induced optical activity are also exhibited by achiral chromophores either chemically or physically bound to chiral mesogens in mesophase, as observed for benzyl side-chain attached to polypeptide chains[15,20-23] and triphenylmethyl attached to cellulosic chains[24-26], or for acridine orange (AO) and chromophoric antibiotics complexed with polyglutamic acids (PLGA)[27] and DNA[28,29], respectively.

In order to account for the above extrinsic optical activity, several theories have been developed by an extension of de Vries' theory for non-absorbing chiral nematic phases to the absorbing case by adding a frequency-dependent complex distribution to the spiraling dielectric tensor of the mesophases[7,30-32]. The calculations from these theories seem to be in agreement with the experimental observations in terms of the correlation of the sign and magnitude of the LCICD for the ordered guest achiral chromophores with the chirality of the host mesophases and the polarization direction of the electronic transitions of the chromophores, although there are some discrepancies. Chandrasekhar and his colleagues have also developed a rigorous theory to describe optical behaviour for dye molecules incorporated with chiral nematic liquid crystals ($P \gg \lambda$)[33-35]. By assuming a helicoidal arrangement of the dye molecules in the chiral nematic structures and the same principal axes of linear birefringence (LB) and linear dichroism (LD) for any single nematic-like layer of the structure, they derived the following equations,

$$D_0 = \frac{I_R - I_L}{I_R + I_L + 2(I_R I_L)^{1/2}} \qquad [1]$$

$$I_R = |A_1|^2 + |A_2|^2 \qquad I_L = |B_1|^2 + |B_2|^2 \qquad [2]$$

$$\begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \frac{1}{\sqrt{2}} J_m \begin{bmatrix} 1 \\ i \end{bmatrix} \qquad \text{for right circular polarized light} \qquad [3]$$

$$\begin{bmatrix} B_1 \\ B_2 \end{bmatrix} = \frac{1}{\sqrt{2}} J_m \begin{bmatrix} 1 \\ -i \end{bmatrix} \qquad \text{for left circular polarized light} \qquad [4]$$

$$J_m = S^m (GS^{-1})^m$$

$$= \begin{bmatrix} \cos\beta & -\sin\beta \\ \sin\beta & \cos\beta \end{bmatrix}^m x \left\{ \exp(-\alpha) \begin{bmatrix} \exp(-i\gamma) & 0 \\ 0 & \exp(i\gamma) \end{bmatrix} \begin{bmatrix} \cos\beta & -\sin\beta \\ \sin\beta & \cos\beta \end{bmatrix}^{-1} \right\}^{-m} \qquad [5]$$

where D_0 is the quantity evaluated by CD (equation 3), I_R and I_L are the transmitted intensities for right- and left-handed circularly polarized lights incident on the medium, respectively, J_m is net Jones matrix for m layers system (m = d/p, where d is the sample thickness and p is the thickness of a single nematic layer), S represents the rotation of the principal axis by β for a single nematic layer, where β is an angle between the directors of two successive layers and defined as $\beta = 2\pi p/P$ (P is the pitch), G is a complex retardation matrix of any single layer with reference to its principal axis , α is related to phase factor defined as $\alpha = (k_a + k_b)/2p$, where k_a and k_b are the principal absorption coefficients of the layer, and γ is a complex quantity defined as $\gamma = \pi\Delta np/\lambda - i\Delta k/2$, where Δn and Δk are linear birefringence and linear dichroism of the single layer with thickness p, respectively.

In this theory, they conclude that the magnitude of dichroic power D (expressed as D_0/d, where d is the sample thickness) for dye molecules incorporated in a chiral nematic phase is dependent of the pitch as well as the sample thickness. They also predicted that variation of D versus the inverse pitch would exhibit an anomalous behaviour for dye molecules incorporated in a chiral nematic liquid crystal when a compensation occurs. In other words, the dichroic power increases with decreasing inverse pitch and changes the sign on crossing zero inverse pitch. This prediction has been confirmed experimentally by the observation of LCICD as a function of temperature for β-carotene dissolved in a thermotropic liquid crystalline mixture of cholesteryl chlororide (CC) and cholesteryl myristate (CM) (1.64:1 by weight), whose handedness changes from left to right with an increase in temperature[34]. Recently, Sisido and Kishi[36] applied the above equations to calculate LCICD of dye molecules incorporated in chiral nematic polypeptide gel films and obtained a semiquantitative fitting between the

calculations and the experimental observations. However, no application of the theory to the dyes incorporated in lyotropic chiral nematic mesophase has been reported so far.

LCICD displayed by chromophores incorporated in a chiral nematic phase is quite different in origin from the apparent CD of the mesophase: the former results from the chromophore molecules being oriented in a helicoidal arrangement and absorbing differentially right- and light-handed circularly polarized light in their absorption region, whereas the latter is a result of the selective reflection of one hand circularly polarized light by the chiral nematic phase in the region of λ_o, $\lambda_o = \bar{n}|P|$, where $\bar{n}$ is the mean refractive index of the mesophase and P is the pitch. As a consequence, these two effects are distinguishable as follows. (i) The shape of the apparent CD peak intensity against wavelength is Gaussian provided that a perfect planar texture is formed in a thin sample. The shape of the LCICD peak generally follows the shape of the absorption bands of the chromophore (but it may be positive or negative). (ii) The position of the apparent CD reflection band is pitch dependent, while that of the LCICD depends on the absorption energy for electronic transition of the chromophores rather than on the pitch. In addition, the position of the apparent CD of a given sample is a function of angle between incident beam and the chiral nematic optical axis, whereas the LCICD does not depend on geometric factors. (iii) The ellipticity of the apparent CD is much higher than that of LCICD if their optical densities are the same.

It is because of the above characteristics that the LCICD technique has been applied to determine the handedness and existence of chiral nematic liquid crystals[1,14,15,19,25,26,36,37], even for those mesophases whose pitches are beyond wavelength accessible by commercial CD spectropolarimeters. The polarization direction of the electronic transition for chromophores oriented in chiral nematic phases[4,7,10,30,38] has also been characterized on the basis of LCICD spectra. In addition, effects of chemical and geometrical structures of guest chromophores in chiral nematic matrices on their orientation[6,36,38,39] were reported using the LCICD technique. A few applications of LCICD to cellulosic liquid crystals have been reported. LCICD has been observed for AO dissolved in a chiral nematic phase of cellulose acetate solution in trifluoroacetic acid (TFA)[40] and for congo red in a cellulose film with a chiral nematic structure[41]. However, the handedness of these chiral nematic cellulosic solutions or films were not established by the observed LCICD.

In the previous chapter, it has been shown that the chiral nematic (acetyl)(ethyl)cellulose (AEC) solutions in many organic solvents exhibit a change in handedness from left to right with increasing acetyl content. Provided that the handedness inversion of AEC mesophases exists naturally, induced CD signals displayed by suitable

dyes dissolved in these AEC mesophases should be able to be discriminated between left- and right-handed mesophases and the assignment of their handedness from the corresponding LCICD should be in agreement with the apparent CD and ORD results shown in Chapter 3. In this chapter, the chiroptical properties of AEC liquid crystals are investigated by the LCICD technique, and discussed on the basis of the orientational behavior of dye molecules in these mesophases. The main dye used in this study is acridine orange (AO) since the AO is optically achiral and dissolves easily in the organic solvents in which AEC polymers form liquid crystals. Proflavine is selected only for AEC/AP system for comparison.

4.2. Experimental section

The same series of AEC polymers with an ethyl DS of 2.5 and acetyl DS' ranging from 0 to 0.5 and solvents as in Chapters 2 and 3 are used in this study. The dye AO was purified according to the following procedures[42,43]. Excess of 0.1N NaOH was added to an aqueous solution of AO hydrochloride (Aldrich Co.). The free base of the AO was recrystallized twice from an ethanol-water mixture, washed with water and dried under vacuum. The dried AO was dissolved in chloroform and chromatographed on an alumina column. The main band was collected and concentrated. The precipitates were filtered, dried in air and then dried under vacuum at 70°C. The proflavine was purchased from Sigma Chemical Co. and used without further purification.

Dilute AEC/dye solutions were prepared by adding the polymer to dye-containing solvent in glass vials, at desired concentration of polymer and dye. The solutions were transferred to a 1 mm-path length quartz spectrophotometric cell for ORD, CD and UV-visible absorption measurements.

The liquid crystalline samples containing dyes were prepared by mixing the desired weight of AEC polymer and solvent containing dyes in glass vials, which were stored until use. Unless otherwise specified, the AO concentration was 5×10^{-3} mol/L. Once the contents of the vials were homogeneous, the mixture was sandwiched between quartz plates with a Teflon spacer of 10 μm or between glass microslides with Teflon spacers ranging from 20 μm to over 200 μm, measured by micrometer. The error of the thickness measurement is within 5%. In most cases, the sample thickness is 10 mm, otherwise as specified.

The CD and ORD spectra were recorded with a Jasco-500C and Jasco ORD/UV Model-5 spectropolarimeters, respectively. In order to check for LB and LD effects on optical behavior, the samples for CD or ORD measurements were mounted on a rotating

stage in order to record spectra at various sample orientations. UV-visible measurements were carried out with a Pye Unicam SP8-150 spectrophotometer. Linear dichroism was also measured in the UV-visible spectrophotometer by placing a plane polarizer in front of the sample mounted on a rotating stage. For measurements as a function of temperature, the sample was placed in a hot stage (Mettler FP52) mounted in the spectrometer beam and heated at a rate of 0.2°C/min.

4.3. Results and discussion

4.3.1. Absorption and CD spectra of AO dissolved in AEC isotropic solutions

Figure 4.1 shows the absorption spectrum of a dilute solution of AEC in dichloromethane (DCM) containing AO (dashed line). The absorption bands around 497 nm and 295 nm have been assigned to the π-π^* electronic transition of monomeric AO molecules along their long axis (^1L_b) and the band around 470 nm to the ^1L_b transition of dimeric AO[44]. The band around 270 nm corresponds to electronic transition of monomeric AO molecules along their short axis (^1La) (The ^1La band of AO in aqueous phenol (AP) and m-cresol is overlapped by strong absorption bands of these solvents. Hereafter, the absorption and CD spectra of AO in these solvents will be shown only in the visible light region). The CD spectrum for AO in AEC dilute solution is also shown in Figure 4.1 (solid line). Contrary to AO in poly-α,L-glutamic acid (PLGA)[45] and sodium carboxymethylcellulose (CMC) dilute solutions[46], no induced CD band is observed for AO in the AEC solutions, indicating that there is no chiral complex formation between AO and AEC in isotropic solution. No induced CD was observed for the AO dissolved in dilute AEC solutions in any solvents, regardless of acetyl content of AEC and dye content. Obviously, this is a result of random orientation of AO molecules in AEC dilute solutions.

4.3.2. CD spectra of AO dissolved in AEC anisotropic solutions

When the AO was added to a highly concentrated solution of AEC, where an anisotropic phase is formed, strong induced CD bands appear in the absorption region of AO. Figure 4.2 shows the CD spectrum (solid line) in 300-700nm for AO dissolved in AEC (acetyl DS = 0.26) lyotropic solution (40%) in AP. As seen in the spectrum, the induced CD band generally follows the shape of AO absorption bands in the absorption spectrum (dashed line) except for a negative sign. Since the liquid crystal is an

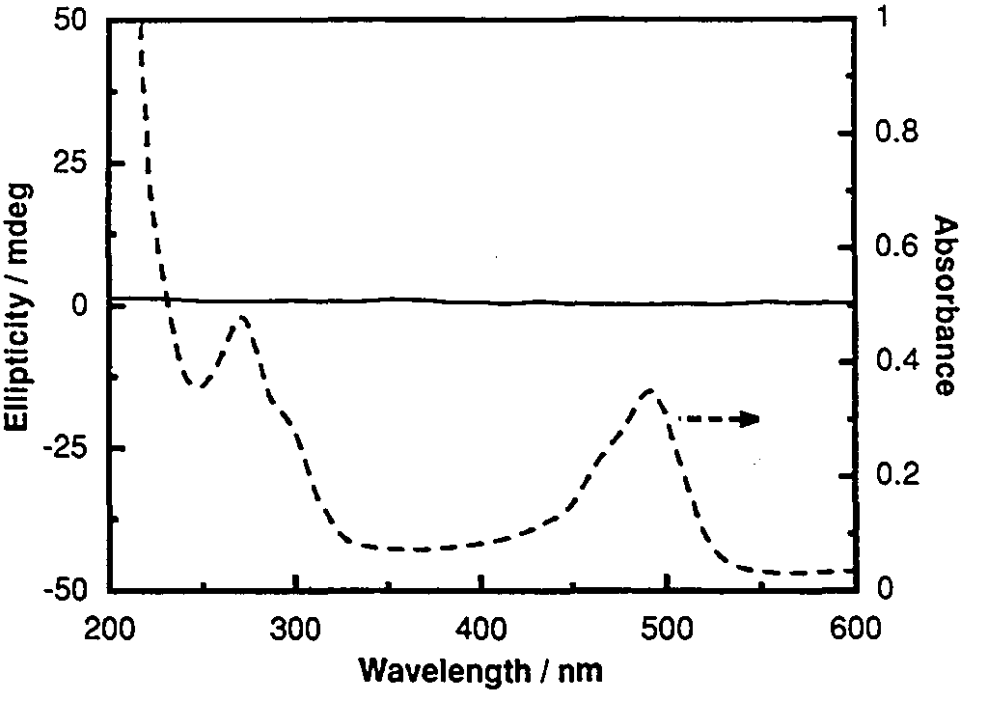


Figure 4.1. UV-visible absorption (dashed line) and CD (solid line) spectra for an AEC dilute solution (2% wt) in dichloromethane (DCM) containing acridine orange ($1x10^{-4}$ mol/L). The acetyl DS of the sample is 0.26.

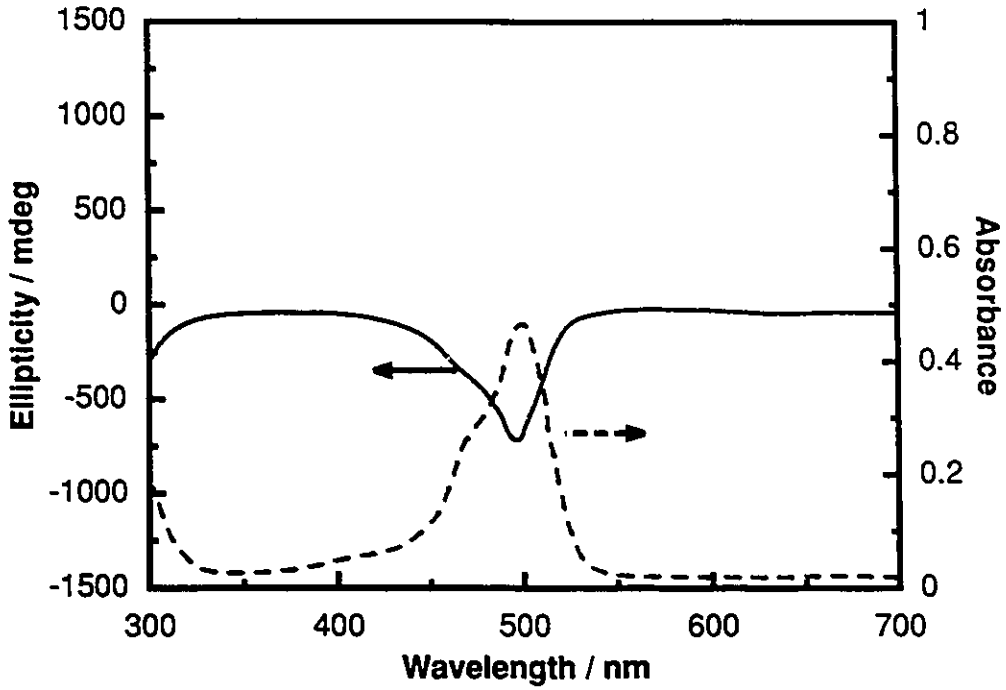


Figure 4.2. Absorption (dashed line) and CD (solid line) spectra for acridine orange dissolved in an AEC anisotropic solution (40% wt) in aqueous phenol (AP). The acetyl DS of the sample is 0.26.

anisotropic ordered medium, possible effects of LD and LB raising from the medium must be considered[47-49]. In order to minimize the LD and LB effects, the experiments in this study were carefully carried out. First, the samples are prepared as thin as possible (10μm) in order to form a planar texture and reduce the potential macroscopic linear birefringence. Secondly, the samples were allowed to equilibrate after sample preparation to minimize the stress-induced birefringence. Thirdly, CD spectra were recorded at 30° interval as the sample was rotated about the light beam from 0° to 180°and were averaged. This process can remove some of the artifacts resulting to the coupling between instrumental imperfections and LD and LB of the sample[4,46,50].

Figure 4.3 shows CD spectra as a function of the rotating angle for the same sample as in Figure 4.2. The spectra recorded at different angles are almost identical in sign, shape and intensity. This suggests that the macroscopic LD in this sample is negligible despite the high circular dichroism. An independent LD measurement of this sample was made with a polarized UV-visible spectrophotometer. Figure 4.4 shows the absorbance of AO at λ = 498 nm as a function of rotating angle of the sample. Again, there is no significant evidence of macroscopic LD existing in such a thin and well-equilibrated liquid crystalline film. The strong induced CD signal is assumed to be due to orientation of the AO molecules by the AEC chiral nematic mesophase to give a helicoidal ordered array. If this is true, then randomizing the orientation of the host molecules in the helicoidal structure may affect the induced CD behavior of their guest AO molecules. This effect can be clearly seen from the change of the LCICD spectra for AO with temperature (Figure 4.5). With an increase in temperature, the intensity of LCICD decreases and finally the ICD disappears around 81°C. Observation with a polarizing microscope shows that the AEC solution shows an anisotropic-isotropic phase transition at this temperature. When the sample is cooled down, the LCICD signal reappears again. A similar temperature dependence of the intensity of LCICD has been observed for pyrene dissolved in a thermotropic cholesteryl nonanoate (CN)-cholesteryl chloride (CC) (70:30) liquid crystal[51] and for AO dissolved in PBLG-EDC lyotropic liquid crystal[15]. The decrease in intensity of LCICD with temperature has been attributed to a reduction on the helicoidal orientational order upon heating.

The disappearance of LCICD around 81°C is a clear indication that AO molecules in a isotropic medium are optically inactive irrespective of polymer concentration. In other words, the helicoidal ordering structure of the host matrix is essential for the observation of ICD.

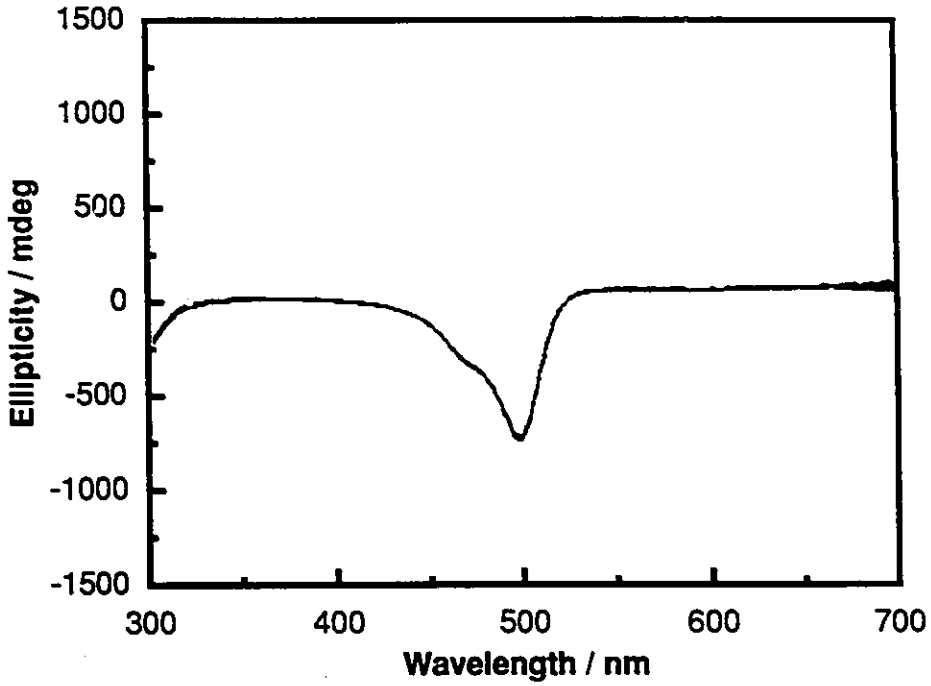


Figure 4.3. CD spectra recorded at 30° intervals for the same sample as in Figure 4.2 as the sample was rotated from 0 to 180°. The seven spectra at different angles superimpose almost perfectly.

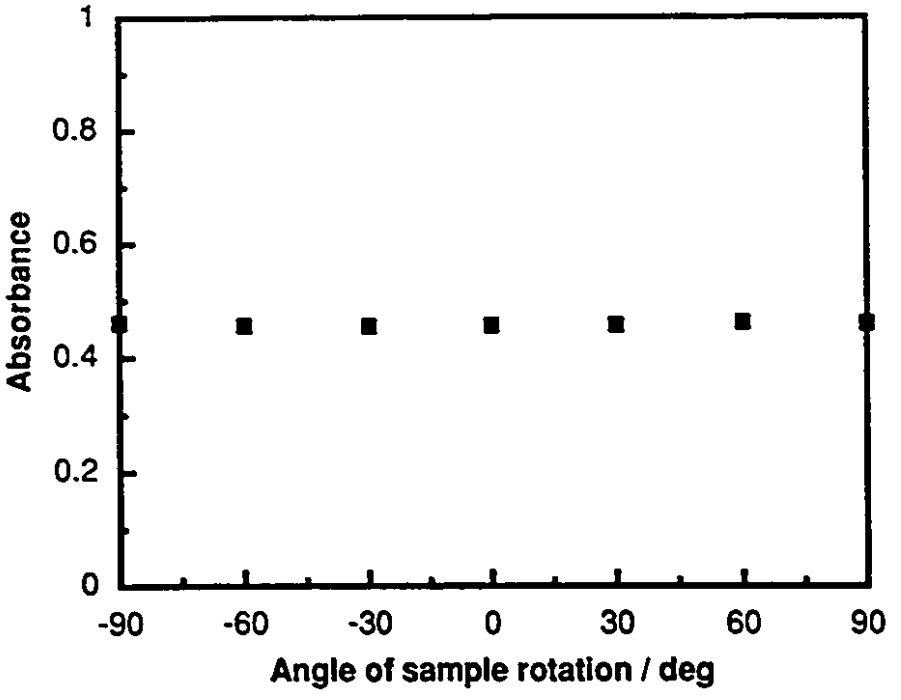


Figure 4.4. The absorbance of plane polarized light at λ = 498 nm as a function of sample rotation angle (about light beam) by acridine orange dissolved in the same sample as in Figure 4.2.

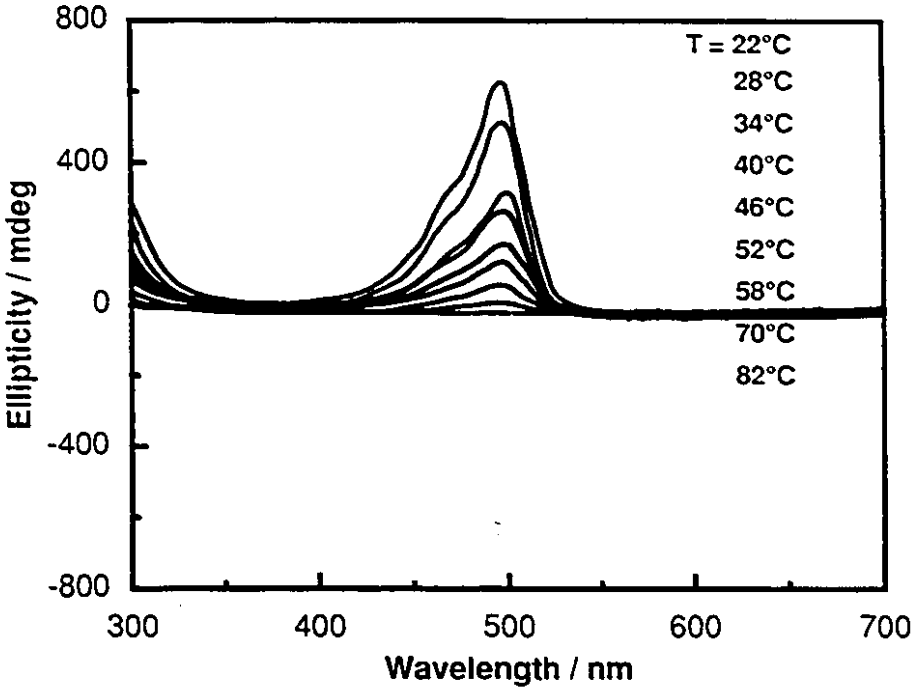


Figure 4.5. Induced CD spectra as a function of temperature for acridine orange dissolved an anisotropic AEC/AP solution (40% wt). The acetyl DS of the sample is 0.44.

4.3.3. LCICD spectra of AO in left- and right-handed AEC lyotropic solutions

In the previous chapter, it has been shown that the handedness of AEC lyotropic solutions in a given solvent depends on the acetyl DS. By adding AO to these solutions, LCICD is observed in the absorption region of AO. These LCICD spectra are divided in two families; a family of negative LCICD peaks for AEC samples with a low acetyl DS and a family of positive peaks for AEC samples with a high acetyl DS. Figure 4.6 shows the LCICD spectra of AO in lyotropic solutions of AEC with an acetyl DS of 0.29 and 0.35, representatives of the two families of LCICD spectra. It can be seen that the shape of the both LCICD spectra are almost identical except for the sign although these two AEC polymers share the approximately same chiral cellulosic chains, have only minor difference in acetyl DS (0.06), and are dissolved in the same achiral solvent. This suggests that the change in sign of ICD is a result of AO molecules being incorporated in two different chiral environments (matrices). By analogy, other kinds of achiral dye dissolved in these two matrices would give the same results. Figure 4.7 is the LCICD spectra of proflavine dissolved in the same polymer solutions as in Figure 4.6. Similar to AO, the proflavine dissolved in the AEC samples with an acetyl DS of 0.29 and 0.35 shows negative and positive LCICD bands in the absorption region of the proflavine, respectively. The exhibition of the same sign of LCICD for the different dyes dissolved in the same matrices further supports the essence of helicoidal ordering structure for the induced CD of achiral dye molecules.

The relation between the handedness of a chiral nematic liquid crystal and its apparent CD due to reflection is well known, so it is of interest to generate a LCICD peak in a sample with a reflection band in the visible range, thus establishing a correlation between the sign of the LCICD and the handedness of the AEC mesophase. In the previous chapter, it has been shown that the pitch of AEC anisotropic solutions in DCM ranges from UV light length to infinite, depending on its acetyl DS. By adding AO to an AEC sample with an acetyl DS of 0.16, both the LCICD and apparent CD may be observed (Figure 4.8). A positive apparent CD band around 700 nm is due to the reflection of left-handed circularly polarized light by the AEC mesophase. The mesophase is thus left-handed. The negative CD bands below 550 nm generally follow the AO absorption bands and are attributed to the LCICD for AO oriented by the AEC mesophase. Therefore, the negative LCICD band of AO corresponds to a left-handed structure of its host matrix. By analogy, a negative and a positive LCICD observed for AO dissolved AEC samples with an acetyl DS of 0.29 and 0.35 in Figure 4.6 suggest that

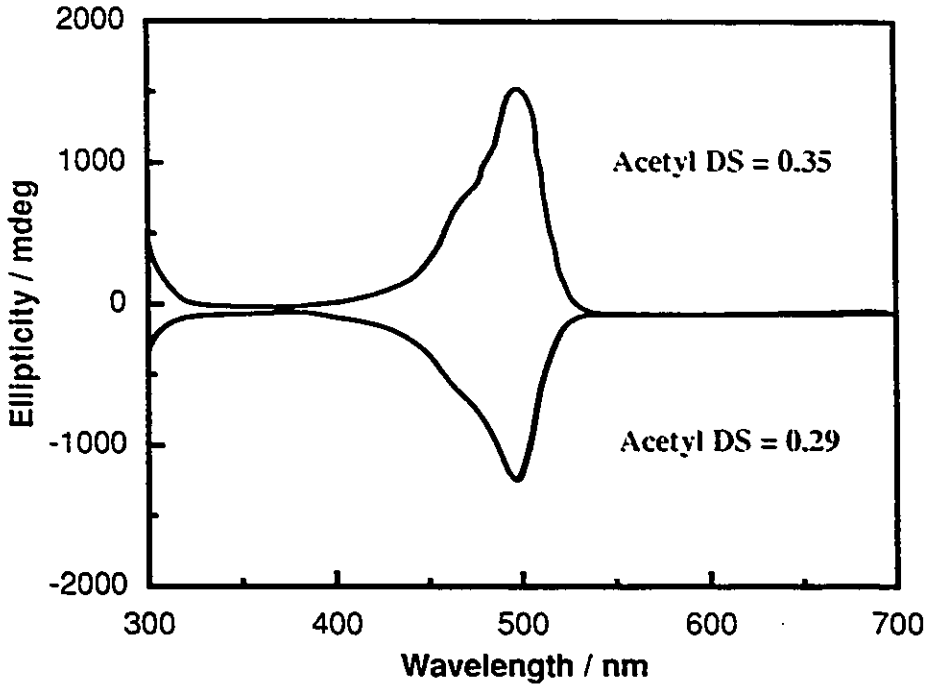


Figure 4.6. Induced CD spectra for acridine orange dissolved in anisotropic AEC/AP solutions (40% wt) at room temperature.

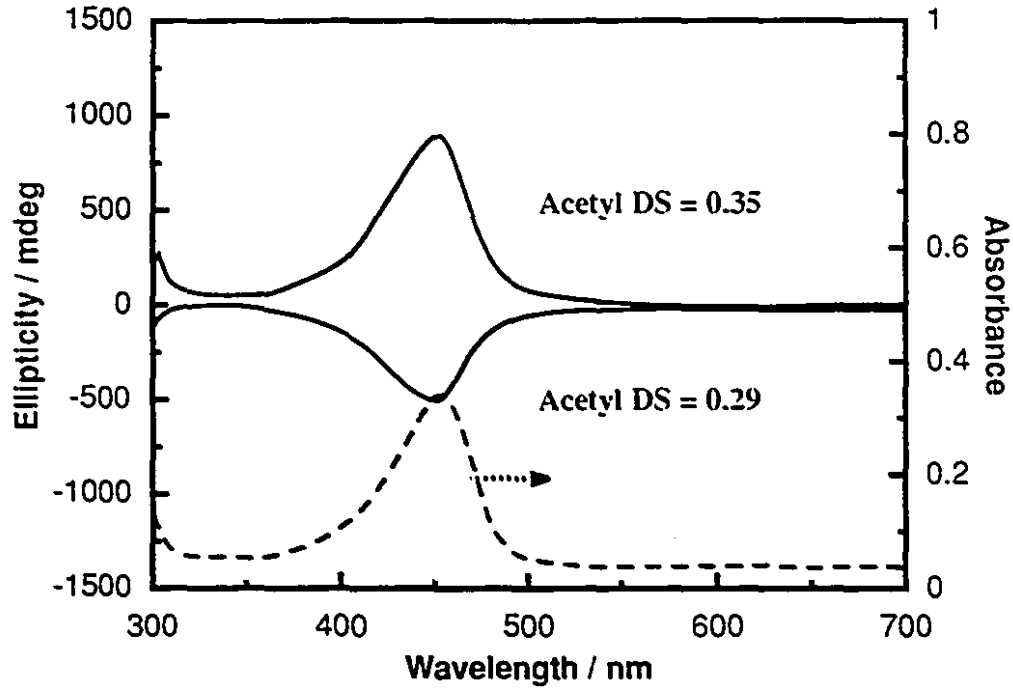


Figure 4.7. Absorption (dashed line) and induced CD (solid lines) spectra for proflavine dissolved in anisotropic AEC/AP solutions (40% wt) at room temperature.

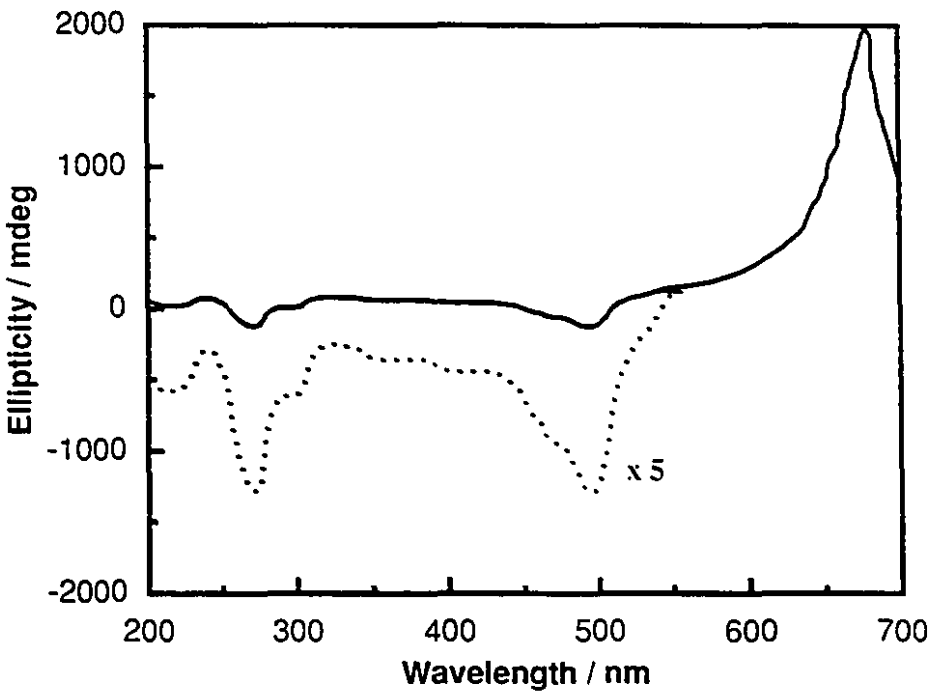


Figure 4.8. Induced CD spectrum for acridine orange dissolved in anisotropic AEC/DCM solutions (~45% wt) at room temperature. The acetyl DS of the sample is 0.16.

the corresponding mesophases are a left- and right-handed liquid crystal, respectively. This assignment is in agreement with the result obtained from ORD measurements, as shown in the previous chapter. Therefore the use of dye as a probe for the handedness inversion of AEC lyotropic solutions with acetyl DS is well demonstrated.

4.3.4. Solvent effects on LCICD

Unlike LCICD in thermotropic liquid crystals, the possible effect of interactions of chromophore molecules with the solvent on LCICD should be considered for LCICD of chromophores in lyotropic solutions. The solvent effect can be neglected for systematic samples of lyotropic AEC mesophases in a given solvent and concentration. However, the solvent does strongly influence the chiroptical properties of AEC liquid crystals, as demonstrated in the previous chapter. If dyes do adopt ordered orientation of their host mesophases as suggested in the above sections, the magnitude and sign of the LCICD peak of the dyes should also depend on the solvent.

Figure 4.9, 4.10, and 4.11 show CD spectra for lyotropic solutions of AEC and AO in m-cresol, DCM and DBM, respectively. Each pair of AEC samples in an individual solvent is representative of a left- and a right-handed liquid crystal, assigned by ORD measurements in Chapter 3. AO dissolved in all left-handed mesophases shows a negative LCICD in the absorption region of the AO. The reverse is observed for AO molecules in all right-handed mesophases. These observations are similar to the result of AEC/AP system in terms of the relation of the sign of LCICD with the handedness of AEC mesophase. Obviously the sign of LCICD of guest molecules is determined by the chiral structure of their host matrix, which in turn depends on solvents. This solvent effect can be further illustrated by an AEC sample with an acetyl DS of 0.24; in m-cresol and DCM the dye shows a negative LCICD and in DBM and AP a positive LCICD. This is a clear indication that the LCICD signals originate from the interaction of guest molecules with the supermolecular structure of host matrix rather than with the individual host molecules. The LCICD behaviour of AO molecules in the AEC lyotropic solutions further demonstrate the importance of polymer-solvent interactions in governing the handedness of chiral mesophases, as concluded in the previous chapter.

4.3.5. ORD evidence of the optical activity for AO induced by AEC mesophases

Since LCICD was first observed by CD spectrometer[3], the same phenomenon has also been observed by ORD in the region of either UV-visible[52] or infrared light[53,54].

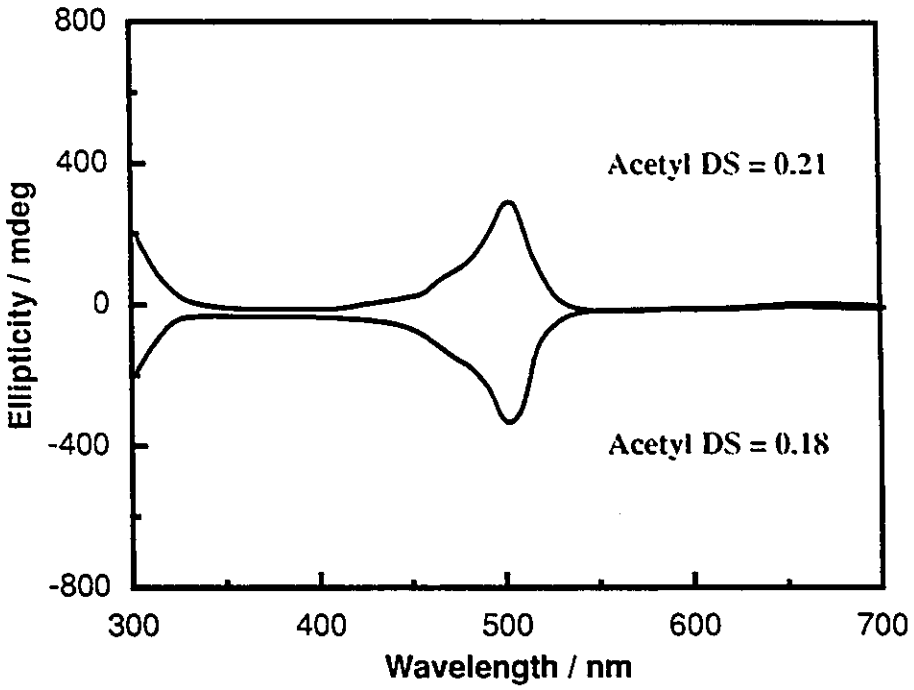


Figure 4.9. Induced CD spectra acridine orange dissolved in anisotropic AEC/m-cresol solutions (42% wt) at room temperature

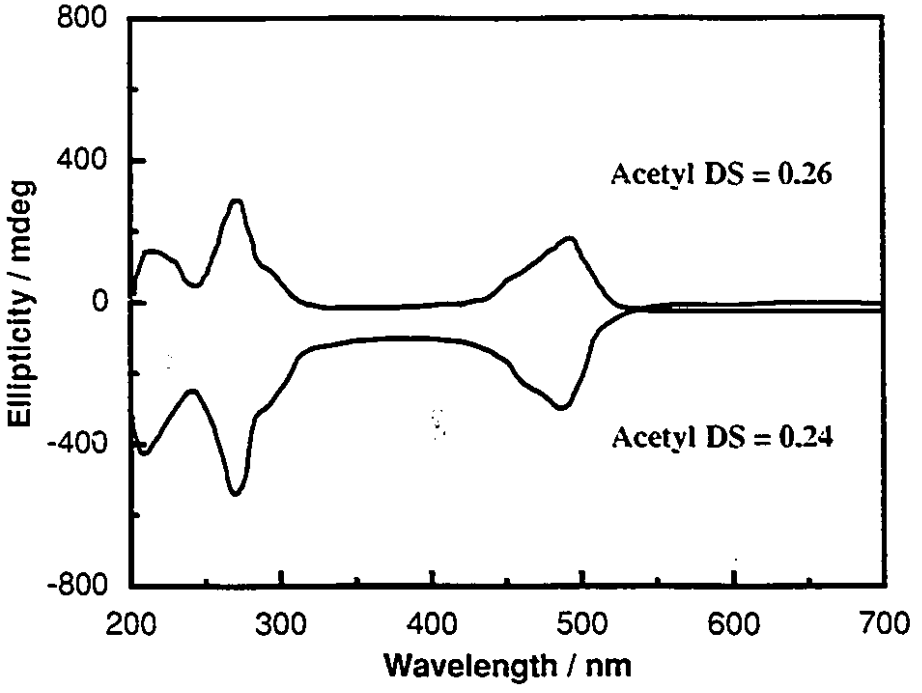


Figure 4.10. Induced CD spectra for acridine orange dissolved in AEC/DCM anisotropic solutions (~45% wt) at room temperature.

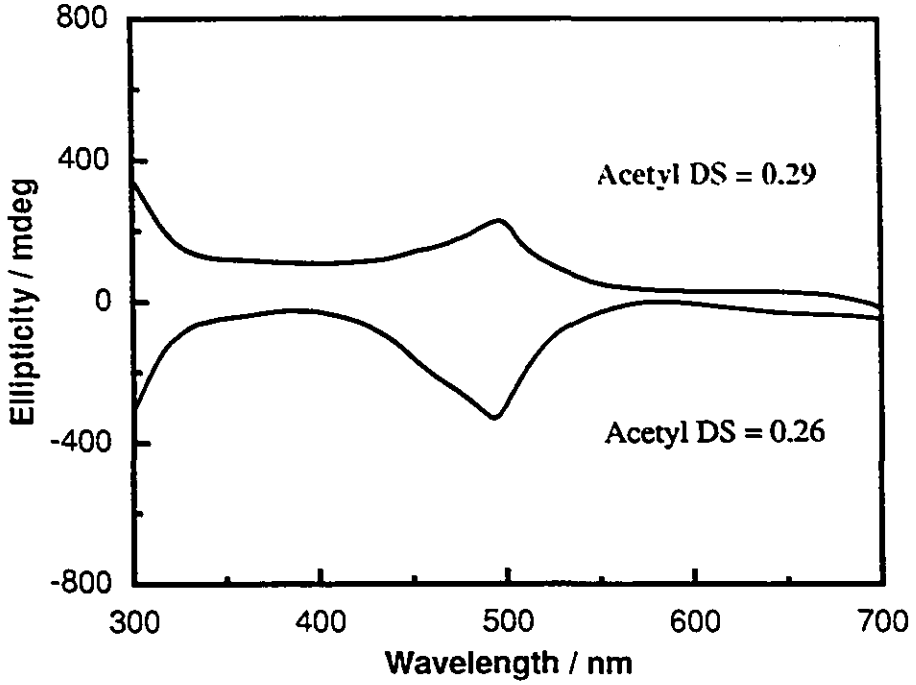


Figure 4.11. Induced CD spectra for acridine orange dissolved in anisotropic AEC/DBM solutions (33% wt) at room temperature.

The theories for LCICD are applicable to induced ORD for the absorbing chiral nematic liquid crystals[30-32]. Provided that the AO molecules in AEC lyotropic solution adopt a helicoidal structure as suggested by LCICD results, an anomalous ORD (Cotton effect) in the region of AO absorption should be observable by ORD measurement. Figure 4.12 shows the ORD spectra of AEC lyotropic solutions in AP with and without AO. The plain positive and negative ORD curves (dashed lines) were observed for the AEC/AP mesophases without AO, as described by the de Vries' theory[55]. In the presence of AO, the Cotton effects in the absorption region of AO are superimposed on the ORD curves. As shown in solid lines in Figure 4.12, negative and positive Cotton effects superimposed on the ORD curves are observed for AO molecules dissolved in lyotropic solutions of AEC polymers with an acetyl DS of 0.26 and 0.44, respectively. The rotation of the samples about the light beam at different angles does not change the ORD curves. Thus the presence of Cotton effect results from the orientation of AO molecules by the AEC mesophase in a helicoidal structure, since no Cotton effect was observed for the same polymers in dilute solution. The negative and positive Cotton effects are therefore attributed to the AO molecules oriented by a left- and right-handed helicoidal structure, respectively. This is consistent with the results of CD measurements for the same specimens as shown in Figure 4.12 (dotted lines). A negative LCICD corresponds to a negative Cotton effect of ORD and a positive LCICD to a positive Cotton effect. These ORD results provide further evidence of a helicoidal arrangement of AO molecules in lyotropic AEC solutions.

4.3.6. Pitch effects on the intensity of the LCICD

The pitch is one of most important structural parameters for chiral nematic liquid crystals. The magnitude of the pitch depends on the chemical structure of the liquid crystalline molecules, the temperature, concentration, external forces, etc. Saeva and Wyscocki were the first to notice that the intensity of LCICD is related to the magnitude of pitch[3]. By applying an electric field to a chiral nematic mesophase containing achiral chromophores, Saeva and his colleagues[6] found that the pitch decreases from 637.8 to 597.9 nm and resultant molecular ellipticity of the LCICD decreases from 2.93 to 2.07 deg cm^2 / dmol.

In the AEC mesophases, the variation of the pitch with acetyl content can be of microns for a given solvent system, concentration and temperature[5], as shown in Chapter 3. Therefore, the series of AEC mesophases should provide good samples to study the effect of pitch on LCICD, without thermal effects and without introducing any

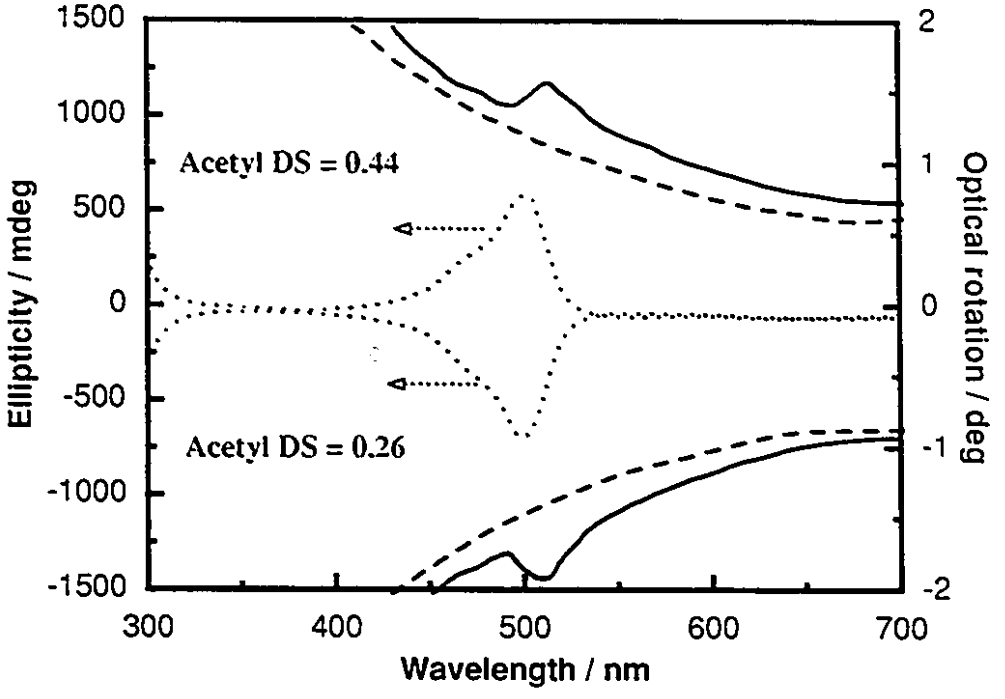


Figure 4.12. ORD (solid) and CD (dashed lines) spectra for acridine orange dissolved in anisotropic AEC/AP solutions (40% wt) at room temperature. The dashed lines are ORD curves for the AEC/AP anisotropic solutions without acridine orange.

external force which might introduce an unwanted macroscopic linear dichroism. Figure 4.13 shows the LCICD spectra for AO molecules dissolved in a series of AEC/AP mesophases, as a function of acetyl DS. The intensity of LCICD increases with acetyl DS for the samples with an acetyl DS below 0.29, and decreases for the samples with an acetyl DS above 0.35. When the intensity of the LCICD is plotted against the magnitude of the pitch (Figure 4.14), it becomes obvious that the intensity is strong by pitch-dependent. The samples have approximately the same thickness and dye content. The change in the sign of LCICD from negative to positive with acetyl DS is attributed to a reversal of the handedness of the host matrix from left to right, as discussed in the above sections. The LCICD intensity thus increases with the magnitude of the pitch for the whole series of AEC lyotropic mesophases, irrespective of their handedness.

Qualitatively, the pitch dependence of LCICD intensity observed here can be described by Chandrasekhar's theory (equation 1-5). Figure 4.15 is a plot of the experimentally-obtained dichroic power (expressed as θ/d, where θ is the observed ellipticity) of the LCICD peak at $\lambda = 498$ nm against inverse pitches for AO dissolved in a series of AEC/AP liquid crystals. As seen in the plot, the dichroic power increases with decreasing inverse pitch and changes the sign on crossing zero inverse pitch, where a handedness inversion takes place. This anomalous LCICD behavior exhibited by AO dissolved in the AEC mesophases is similar to that observed for β-carotene dissolved in a thermotropic liquid crystalline mixture of CC and CM (1.64:1 by weight)[34], whose handedness reverse as an function of temperature.

Changing solvent system for AEC leads to a change in compensated degree of acetylation, as described in Chapter 3. Adding AO molecules to AEC mesophases in m-cresol gave the results shown in Figure 4.16. The only difference between the two sets of spectra in Figure 4.13 and 4.16 is that a change in the dependence of LCICD intensity on acetyl DS (from positive to negative) occurs at an acetyl DS over 0.35 in Figure 4.13 and 0.21 in Figure 4.16. The acetyl content dependence of pitch for the corresponding mesophases also changes form positive to negative at these values. This gives a clear indication that the observed LCICD is a consequence of the orientation of achiral AO molecules by their host chiral nematic structures rather than interaction with individual chiral AEC molecules.

The effect of pitch on the LCICD intensity may be further illustrated by changing the polymer concentration, since the pitch of lyotropic liquid crystals is a function of concentration. For example, when the concentration of an AEC (acetyl DS = 0.29) anisotropic solution in AP increases from 40% to 47% by weight, the pitch of the mesophase decreases from 11.4 to 1.5 μm and the dichroic power for AO dissolved in the

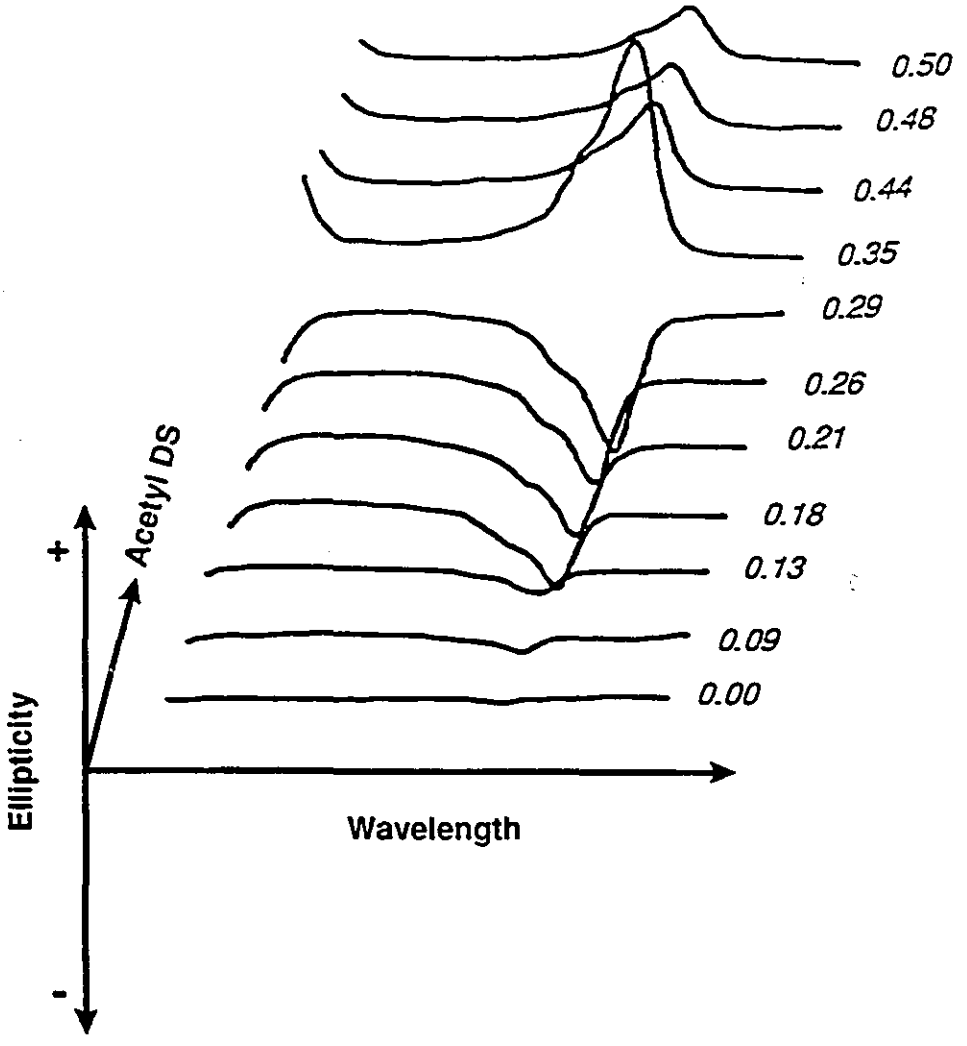


Figure 4.13. Induced CD spectra as a function of acetyl DS for acridine orange dissolved in anisotropic AEC/AP solutions (40% wt) at room temperature. All samples have the same thickness (10 μm).

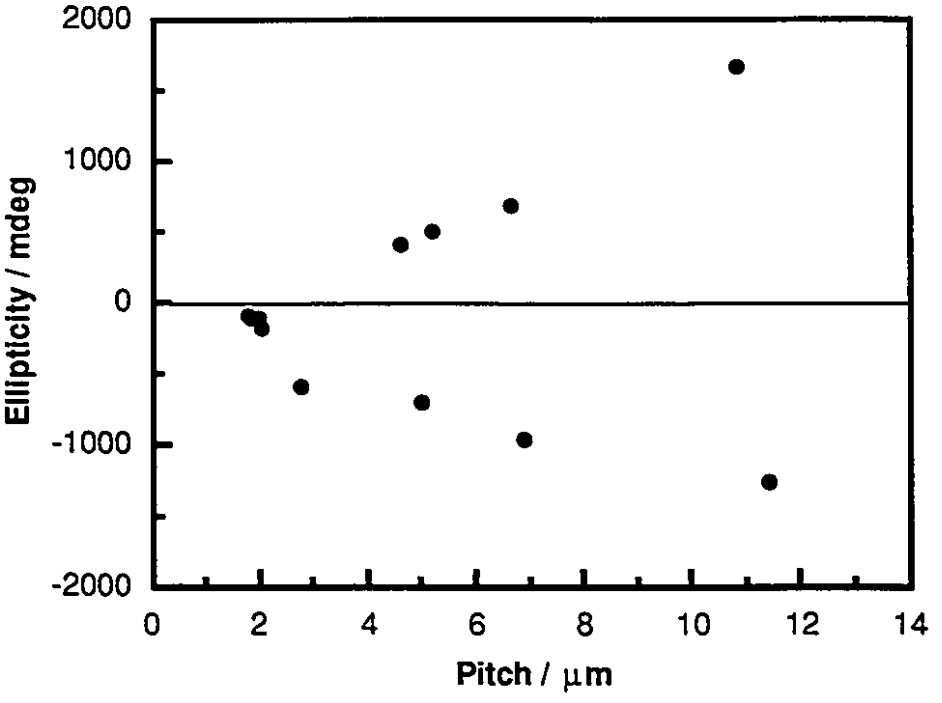


Figure 4.14. Variation of maximum ellipticity (at λ = 498 nm) of LCICD with the magnitude of pitch for the same samples as in Figure 4.13.

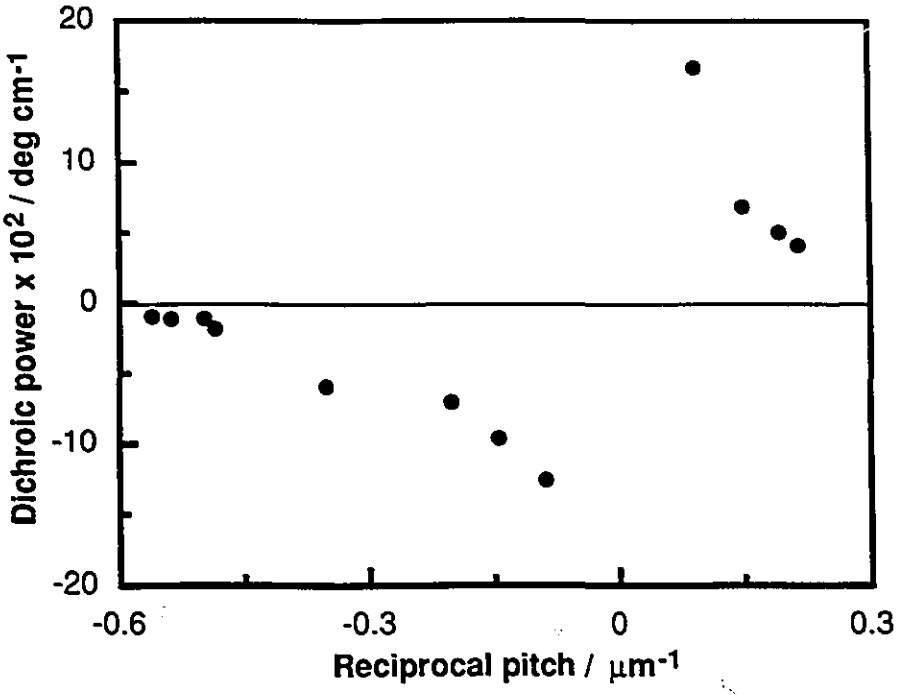


Figure 4.15. Dichroic power at λ = 498 nm as a function of inverse pitch for the same samples in Figure 4.13.

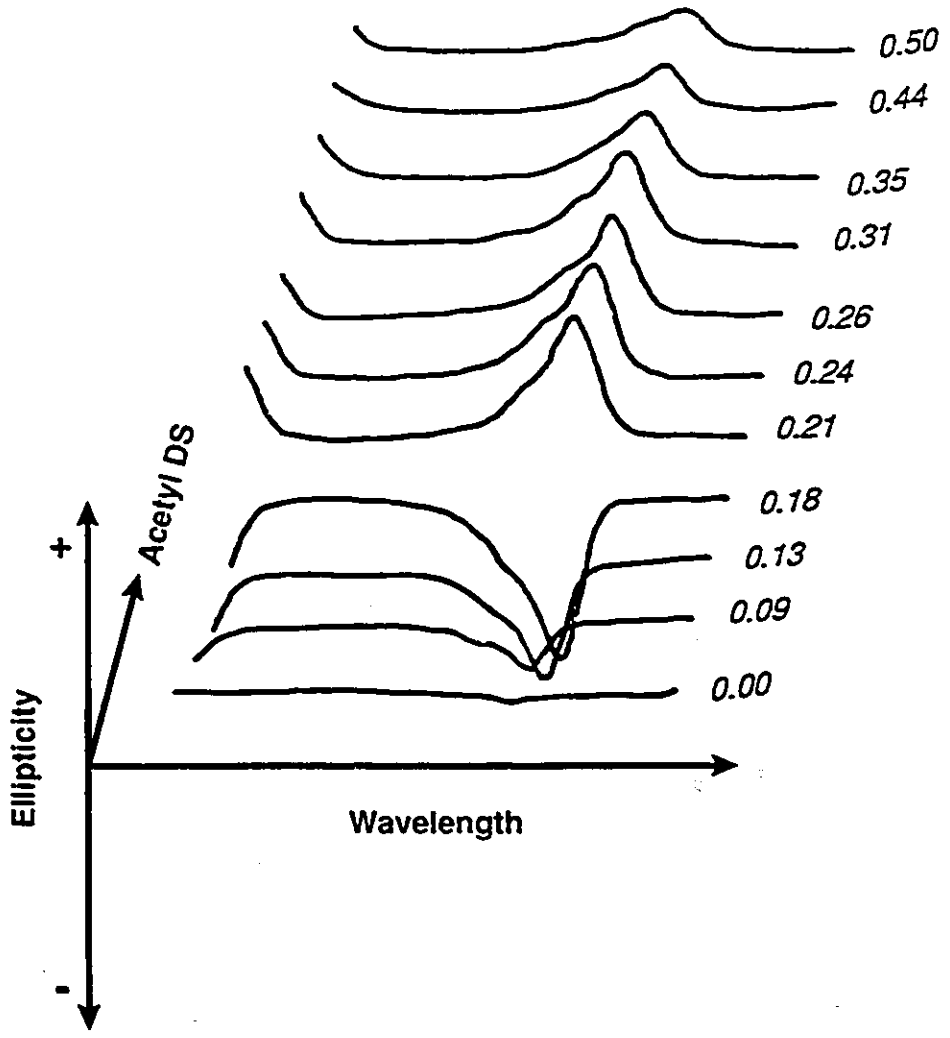


Figure 4.16. Induced CD spectra as a function of acetyl DS for acridine orange dissolved in anisotropic AEC/m-cresol solutions (42% wt) at room temperature. All samples have the same thickness (10 μm).

corresponding mesophases decreases from 80 to 35 deg/cm at the same dye content (6.19 x 10^{-4} mol/L).

4.3.7. Temperature effects

As briefly discussed above, an increase in temperature to the clearing temperature of the ordered phase results in a random orientation of the dye molecules and hence the intensity of LCICD reduces to zero (Figure 4.5). Since the pitch of chiral nematic liquid crystals is also temperature dependent, the effect of the pitch change with temperature will superimpose on the LCICD in addition to any tendency to increased disorder with temperature. As a result, the variation of the intensity of LCICD upon heating must be a combined contribution from these two effects. The change in intensity of LCICD with temperature is expected to show two cases. (i) If the temperature dependence of pitch for the host mesophase is negative, the intensity of LCICD for the ordered guest dye molecules will decrease upon heating. (ii) If the temperature dependence of pitch for the host mesophase is positive, the intensity of LCICD for the ordered guest dye molecules will depend on which contribution is dominant; a decrease for the case where tendency to random orientation predominates over the increase in the pitch upon heating, or an increase for the case that the increase in the pitch predominates over the tendency to disorder.

Figures 17 and 18 show the temperature dependence of pitch and LCICD intensity, respectively, for three AEC/AP lyotropic solutions containing AO. The sample with an acetyl DS of 0.44 shows a slight negative temperature dependence of pitch and samples with an acetyl DS of 0.24 and 0.29 a positive temperature dependence (Figure 4.17); the latter sample (acetyl DS = 0.29) displays a greater sensitivity to temperature than the sample with an acetyl DS of 0.24. The temperature dependence of the LCICD is more complex (Figure 4.18). The sample with an acetyl DS of 0.44 show a monotonic decrease in intensity with temperature. For the sample with an acetyl DS of 0.24, the intensity of LCICD initially increases very slightly with increasing temperature and then decreases at temperatures over 37°C. A rapid increase in the intensity of LCICD is observed for the sample with an acetyl DS of 0.29 with increasing temperature up to 50°C. Further increasing the temperature results in a decrease in the intensity of the LCICD. The temperature dependence of the LCICD in the latter two cases corresponds to the second case above, where the initial increase is postulated as being due to the increase in pitch, but the subsequent decrease is due to the loss of orientational order of the dye

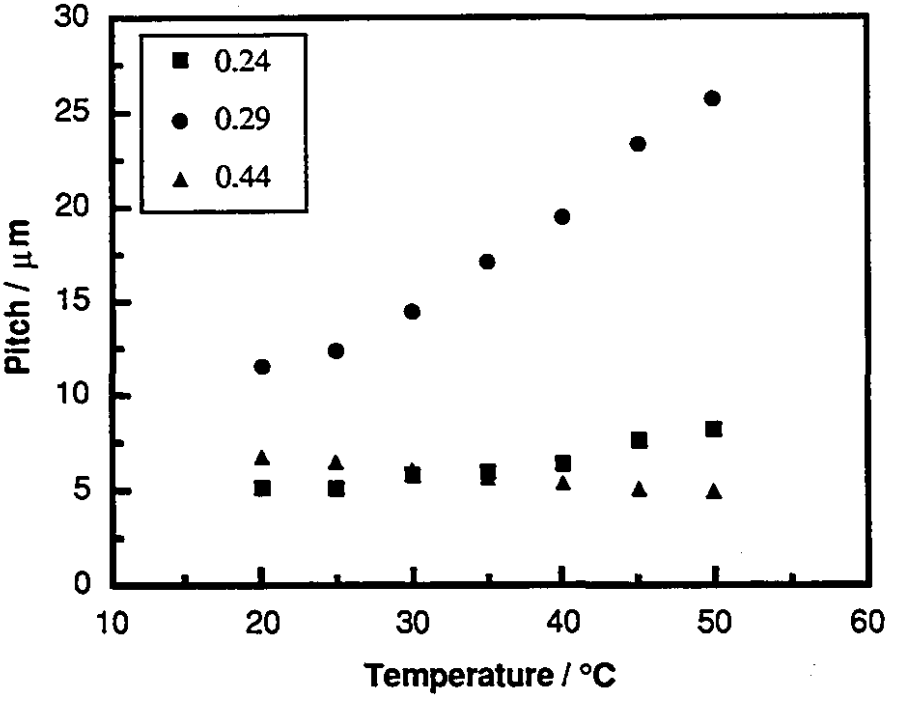


Figure 4.17. Temperature dependence of the magnitude of the pitch for AEC/AP anisotropic solutions (45% wt) containing acridine orange. The acetyl DS' of the AEC samples are as indicated.

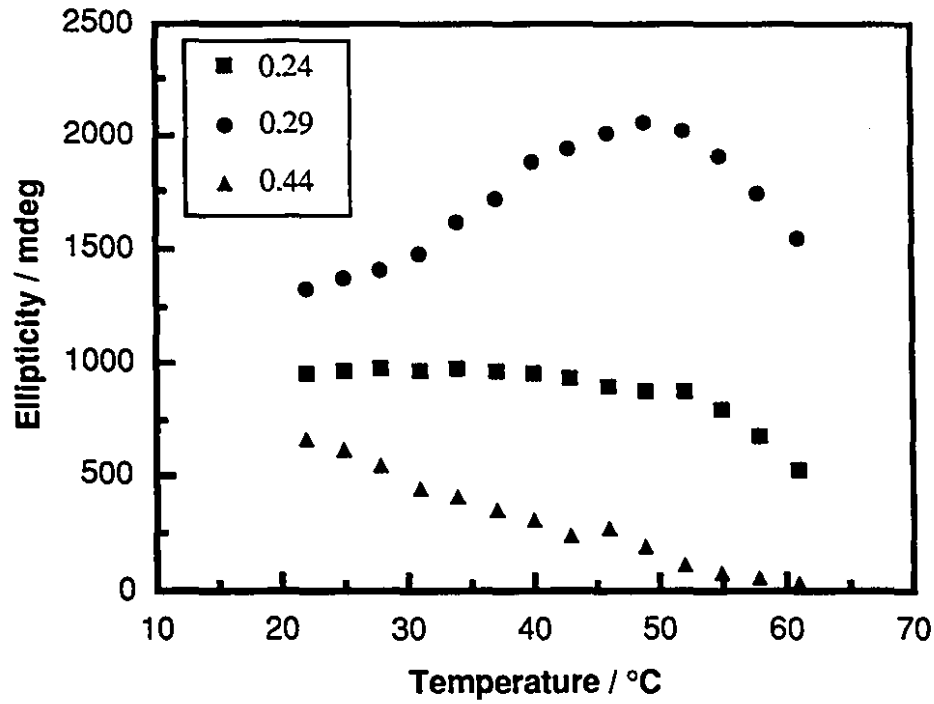


Figure 4.18. Temperature dependence of LCICD intensity for the same samples as in Figure 4.17.

molecules as the temperature is raised, until the order is completely lost, when the phases become isotropic.

If the AO molecules take up a chiral nematic orientation in the liquid crystalline phases, then one may also expect that there is no ICD signal observed for AO dissolved in a compensated AEC mesophase because in this type of mesophase the helicoidal order untwists to give nematic-like order. Figure 4.19 shows the LCICD spectra as a function of temperature for AO dissolved in an AEC/AP liquid crystalline sample with an acetyl DS of 0.31. This sample at room temperature is close to the compensated condition and has an almost infinite pitch as characterized by optical microscope and optical diffraction (see previous chapter). As a result, a strong negative LCICD peak (offscale) is observed for AO dissolved in this sample at room temperature (curve 1 in Figure 4.19) since the intensity of LCICD is proportional to the magnitude of the pitch as discussed above. In Chapter 3, it has also been shown that AEC/AP liquid crystalline samples with an acetyl DS below 0.32 exhibit a positive temperature dependence of the pitch. This implies that the pitch of the sample with an acetyl DS of 0.31 may become infinite upon heating. The change in pitch is not detectable using a microscope or a diffractometer (because the pitch is too large.). As shown in Figure 4.19, the LCICD peak for AO in this mesophase decreases in magnitude with increasing temperature and almost disappears at 40°C, suggesting that at this temperature the mesophase with an acetyl DS of 0.31 and a concentration of 40% (by weight) of AEC in AP looses its twist and forms a nematic structure with an infinite pitch. Further increasing temperature (> 40°C) leads to a change in the sign of the LCICD from negative to positive, an indicative of the appearance of thermally-induced handedness inversion from left to right. This is the first example of a thermally induced handedness inversion observed for cellulosic lyotropic liquid crystals; the thermally-induced handedness inversion of cellulosic liquid crystals has been observed only for thermotropic oligomers of cellulose derivatives[56]. Based on these results, the LCICD seems to be a particularly useful and sensitive indicator for compensated nematic structure and handedness inversion.

4.3.8. Sample thickness effects

Figure 4.20 shows LCICD spectra in the wavelength range 300-700 nm for AO molecules dissolved in a AEC/AP mesophase as a function of sample thickness. As shown in Figure 4.20 (a), the intensity of the LCICD apparently increase with sample thickness for samples with a thickness from 10 to 45 μm. However, when the intensity is expressed as ellipticity per unit sample thickness, the dichroic power (θ/d) decreases with

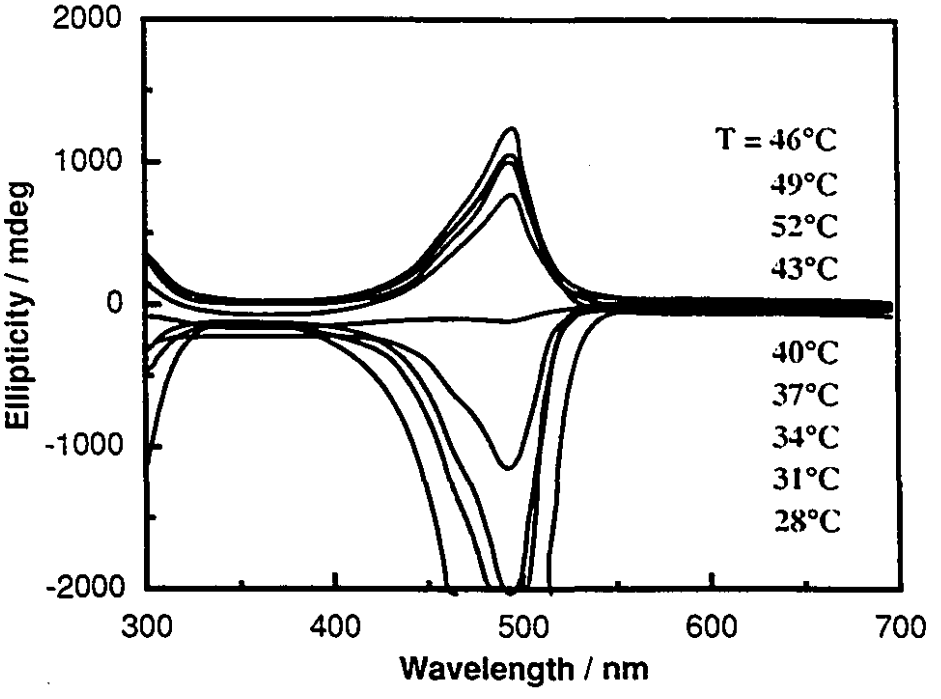


Figure 4.19. Induced CD spectra as a function of temperature for acridine orange dissolved in an AEC/AP anisotropic solution (40% wt). The acetyl DS of the sample is 0.31

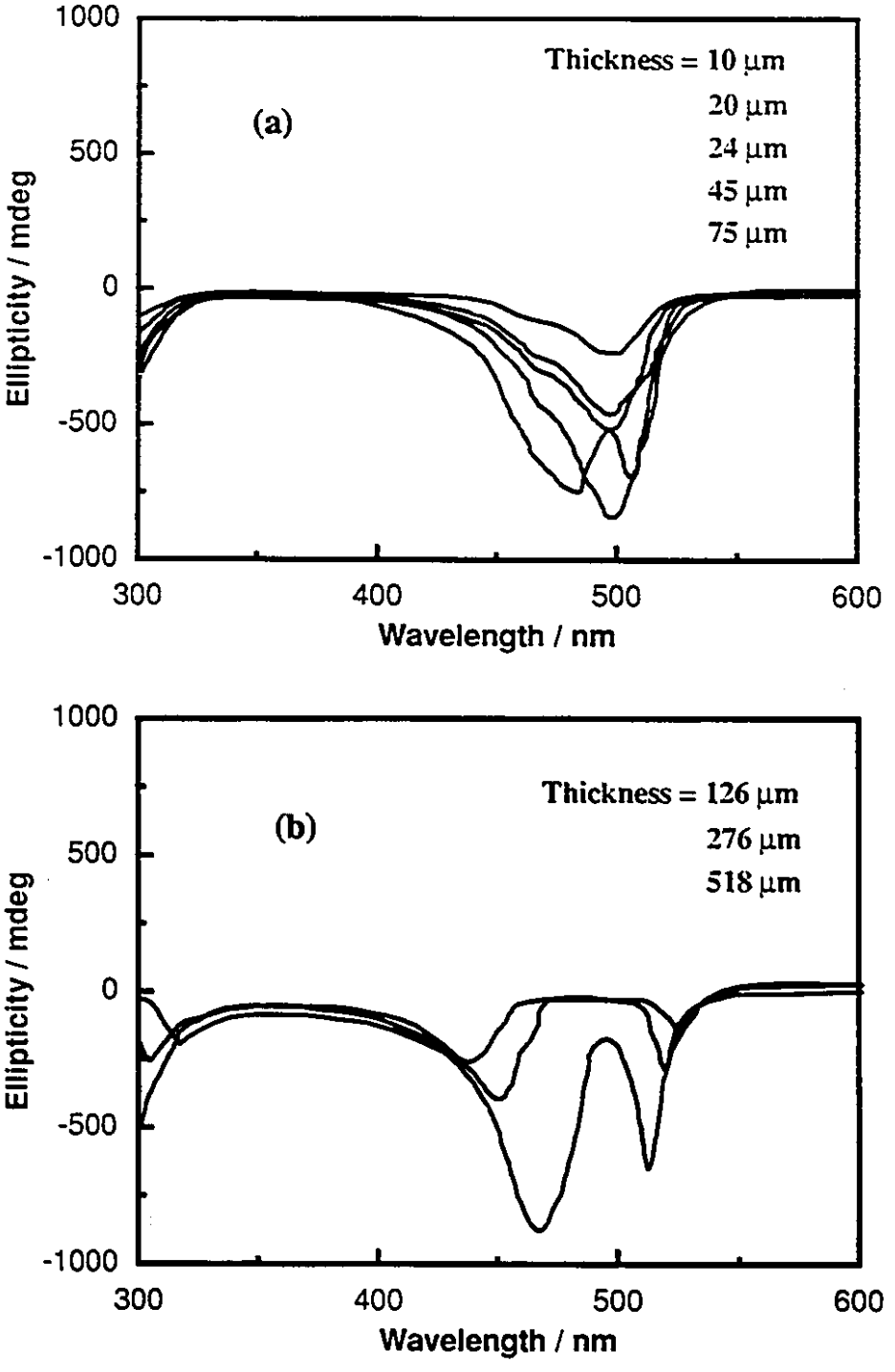


Figure 4.20. Induced CD spectra as a function of sample thickness for acridine orange dissolved in an anisotropic AEC/AP solution (40% wt) at room temperature. The acetyl DS of sample is 0.24. Acridine orange content = 5 x 10^{-3} (Mol/L).

an increase in sample thickness, e.g. the magnitude of the dichroic power for samples with a thickness of 0.10, 0.20, 0.24, 0.45 μm are 235, 227, 205, and 186 deg/cm^{-1}, respectively. A similar sample thickness dependence of LCICD intensity has been observed for β-carotene in liquid crystalline mixtures of CC and CM[34]. Presumably, the decrease in the magnitude of the dichroic power with sample thickness is due to a wall effect. In a thin chiral nematic liquid crystalline films, the molecules close to the surface of substrates such as quartz or glass have a tendency to orient parallel to the surface and thus form a uniform planar texture with optical axes perpendicular to the surface of the substrates[57]. As a consequence of being incorporated in the uniform helicoidal structure, the AO molecules have a higher helicoidal order and thus display a higher intensity of LCICD. With increasing sample thickness, a so-called focal conic texture or a non-uniform polydomain texture is formed, where the chiral nematic axes are tilted to the surface of the glass. Accordingly, the helicoidal order of AO molecules in the thicker mesophase film decreases and the intensity of LCICD becomes reduced with respect to the sample thickness. A decrease in the intensity of LCICD with electric field for pyrene dissolved in a liquid crystalline mixture of CN and CC has also been attributed to a transformation of the texture from planar to focal conic[10]. Theoretical calculation by Chandrasekhar and his colleagues also predicted that the dichroic power D for chromophores ordered in a chiral nematic phase decreases with the sample thickness, in qualitative agreement with the above experimental observations.

As seen in Figure 4.20 (a), the sample with a thickness of 75 μm starts to show a splitting around 498 nm on the LCICD band. The width of the splitting increase with sample thickness as shown in Figure 4.20 (b). The splitting of ICD observed for AO in the AEC mesophases is an artifact due to the high absorption of the thicker samples. Their optical densities are all over 2 in the AO absorption region. As a result, the photomultiplier dinode voltage in the CD measurement exceeds 800V and hence the CD signals become very weak or zero[58]. This explanation is further supported by a CD measurement for AO dissolved in the same AEC mesophase with lower dye content. The result is shown in Figure 4.21. There is no splitting in LCICD spectrum although this sample has a thickness over 100 μm.

4.3.9. Dye content effects

It has been shown in the first section that no induced CD is displayed by AO dissolved in AEC isotropic solutions, irrespective of dye content. For dye molecules dissolved in a thermotropic mesophase, Savea[51] reported that molecular ellipticity did not

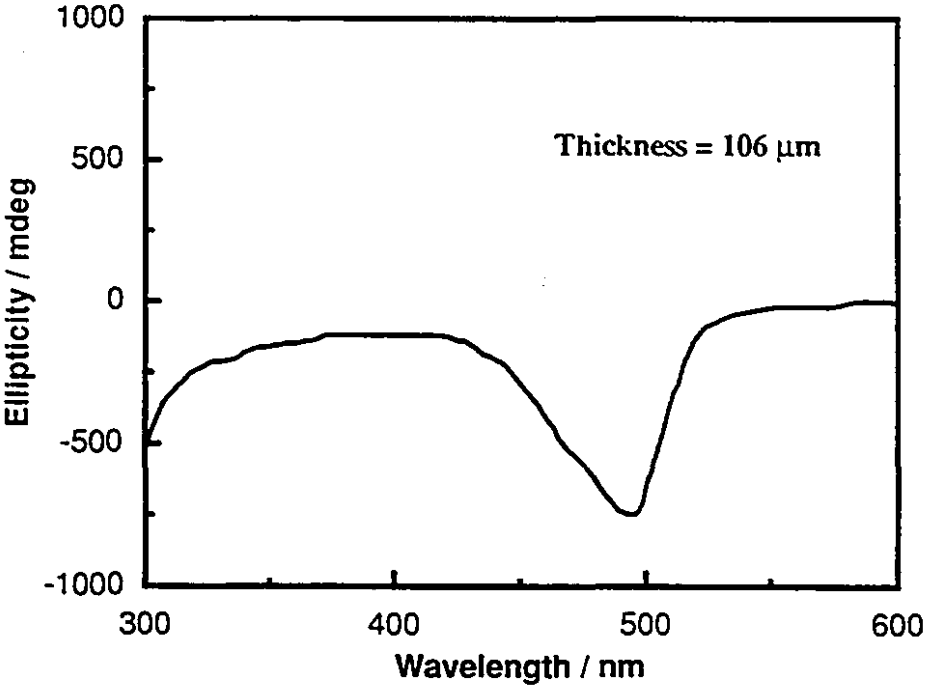


Figure 4.21. Induced CD spectrum for acridine orange dissolved in an anisotropic AEC/AP solution (40% wt) at room temperature. The acetyl DS of sample = 0.24. Acridine orange content = 2×10^{-3} (mol/L).

vary with dye content, but as far as we know, no one has yet investigated the effect of dye concentration in lyotropic systems, where dye/solvent and polymer/solvent interaction may be significant. First, it was found that the pitch of an AEC (acetyl DS = 0.35) lyotropic solution in AP was almost independent of dye concentration in the range from 3.10×10^{-6} to 1.54×10^{-2} mol/L, for a given polymer concentration and temperature. (It was necessary to check this, because effect of LCICD intensity is very sensitive to the pitch, as discussed above).

The variation of molecular ellipticity for AO dissolved in liquid crystalline solutions of AEC in AP is presented as a function of AO concentration in Table 4.1. The molecular ellipticities of these samples are approximately the same within experimental error, although the difference in dye concentration is four order of magnitude. This suggests that dye-dye interactions do not play an important role in the origin of LCICD. This observation is similar to the result for dye molecules in thermotropic liquid crystals[51].

Table 4.1. Variation of molecular ellipticity [θ]* with acridine orange concentration for the LCICD of AO dissolved in AEC/AP anisotropic solutions (40% wt) .

C	3.10×10^{-6}	6.19×10^{-5}	3.10×10^{-4}	6.19×10^{-4}	3.10×10^{-3}	1.54×10^{-2}
[θ]	1.29×10^{-5}	1.48×10^{-5}	1.45×10^{-5}	1.26×10^{-5}	1.53×10^{-5}	1.29×10^{-5}

* $[\theta] = \theta / 10cl$ (deg cm^2 $dmol^{-1}$), where θ is the observed ellipticity (deg), C is mole concentration (mol/L) and l is path length (cm).

4.4. Concluding remarks

Achiral dyes in isotropic AEC solutions display no induced CD signals irrespective of acetyl content and concentration of the AEC polymers and dye content. This observation indicates a random orientation of dye molecules in the isotropic phase. When dissolved in anisotropic AEC solutions, the dye molecules show strong induced CD bands in their absorption region. The induced CD is assumed to be a result of orientation of the dye molecules by the AEC mesophases to give a helicoidal arrangement, since no significant evidence of macroscopic linear dichroism was observed in this study. The LCICD spectra for the dyes in a series of well characterized AEC mesophases, whose handedness depends on solvent, acetyl content and temperature, reveal that the signs of the LCICD signal is determined by the supramolecular structural features of the host matrices. For instance, acridine orange (AO) dissolved in a left-handed liquid crystalline AEC solution displays a negative LCICD whereas a positive LCICD was observed when the AO is dissolved in a right-handed AEC mesophase. Both CD and ORD evidence provide a clear indication that the helicoidal structures of the host liquid crystals are essential for the guest achiral molecules to exhibit the extrinsic optical activity. This is also supported by a strong pitch dependence of the intensity of LCICD for the AO dissolved in the AEC mesophases and an almost independence of the magnitude of the LCICD on the dye content in terms of molecular ellipticity. The use of achiral dyes as a probe for the handedness inversion and compensation induced by changes in acetyl content and temperature for the AEC mesophases are well demonstrated in this study.

Although there may remain a possibility of artifacts, arising from instrumental imperfections coupling with some residual linear dichroism and linear birefringence[59,60], it seems from the high ellipticity compared to the intrinsic optical activity of AEC polymer, the good correlation between the sign of LCICD bands of guest dyes and handedness of their host AEC liquid crystals, and the good agreement between results obtained by LCICD and other methods, that the chiral nematic environment is a dominant source contributing to the induced optical activity in this system. The present study also suggests that the LCICD technique may be generally applicable to characterize the chiroptical properties of chiral nematic liquid crystals provided that suitable chromophores are available. However, in general, great caution must also be exercised because of its sensitivity to orientational order of the liquid crystalline molecules, particularly in solid films cast from chiral nematic phase, and other supporting techniques may be necessary.

4.5. References

1. F.D. Saeva, in Liquid Crystals: The Fourth State of Matter, Ed., F.D. Saeva, Marcel Dekker Inc., New York, 1979, Chapter 6
2. M. Hatano, Adv. Polym. Sci., 77, 1(1986)
3. F.D. Saeva and J.J. Wyscocki, J. Am. Soc. 93, 5928(1971)
4. F.D. Saeva, J. Am. Chem. Soc., 94, 5135(1972)
5. F.D. Saeva and G.R. Olin, J. Am. Chem. Soc, 98, 2709(1976)
6. F.D. Saeva, P.E. Sharpe and G.R. Olin, J. Am, Chem. Soc. 95, 7660(1973)
7. E. Sackmann and J. Voss, Chem. Phys. Lett., 14, 528(1972)
8. H. Falk, O. Hofer and H. Lehner, Monatsh. Chem. 105, 169(1974)
9. F.D. Saeva, Mol. Cryst. Liq. Cryst. 31, 327(1975)
10. F.D. Saeva, in Liquid Crystals and Ordered Fluids, Ed. Vol.2, 581(1973)
11. E. Sackmann and H. Möhwald, J. Chem. Phys. 58, 5407(1973)
12. S.F. Mason and R.D. Peacock, Chem. Phys. Lett. 21, 406(1973)
13. E. Iizuka, Mol. Cryst. Liq. Cryst., 111, 237(1984)
14. Mori Norio, Nippon Kagaku Kaishi, 6, 864(1978), as abstracted in CA, 89(10), 83262Y
15. H. Toriumi and I. Uematsu, Mol. Cryst. Liq. Cryst., 116, 21(1984)
16. F.D. Saeva and G.R. Olin, J. Am. Chem. Soc., 95, 7882(1973)
17. G.P. Spada, G. Gotterelli and B. Samori, Liq. Cryst., 3, 101(1988)
18. N. Tsuchihashi, H. Nomori, M. Hatano and S. Mori, Bull. Chem. Soc. Jpn., 48, 29(1975)
19. E. Iizuka, Polym. J., 15, 525(1983)
20. E.Iizuka and J.T. Yang, Mol. Cryst. Liq. Cryst., 29, 27(1974)
21. H. Nomori, N. Tsuchihashi, S. Takagi and M. Hatano, Bull. Chem. Soc. Jpn. 48, 2522(1975)
22. Y. Uematsu and I. Uematsu, in Mesomorphic Order in Polymer and Polymerization in Liquid Crystalline Media , Ed. A. Blumstein, ACS Synposium Series 74, Washington, DC, 1978; pp.136
23. I. Uematsu and Y. Uematsu, Adv. Polym. Sci., 59, 37(1984)
24. B.R. Harkness and D.G. Gray, Can. J. Chem., 68, 1135(1990)
25. B.R. Harkness and D.G. Gray, Macromolecules, 23, 1452(1990)
26. B.R. Harkness and D.G. Gray, Liq. Cryst., 8, 237(1990)
27. Y. Sato and M. Hatano, Makromol. Chem. 183, 997(1982)

28. Yu.M. Yevdokimov, V.I. Salyanov, A.T. Dembo and H. Berg, Biomed. Biochim. Acta, 42, 855(1983)
29. Yu.M. Yevdokimov, V.I. Salyanov, and M. Palumbo, Mol. Cryst. Liq. Cryst. 131, 285(1985)
30. G. Holzwarth and N.A.W. Holzwarth., J. Optic. Soc. Am., 63, 324(1973)
31. G. Holzwarth, Ilan Chabay and N.A.W. Holzwarth, J. Chem. Phys. 34, 48161973)
32. R.J. Dudley, S.F. Mason and R.D. Peacock, J. Chem. Soc. Farad. Trans. II, 71, 997(1975)
33. G.S. Ranganath, S. Chandrasekhar, U.D. Kini, K.A. Suresh and S. Romasesh, Chem. Phys. Lett., 19, 556(1973)
34. G.S. Ranganath, K.A. Suresh, RS.R. Rajagoplan and U.D. Kini, in Preceeding of the International Liquid Crystals Conference, Bangaore, December, 1973, Pramana Supplement I, P353
35. S. Chandrasekhar, in Liquid Crystals, Cambridge University Press, 1977, chapter 4
36. M. Sisido and R. Kishi, Macromolecules, 24, 4110(1991)
37. F.D. Saeva, Mol. Cryst. Liq. Cryst., 18, 375(1972)
38. Y. Sato and M. Hatano, Makromol. Chem. 183, 971(1982)
39. Y. Sato, A. Tajiri and M. Hatano, Makromol. Chem., 183, 989(1982)
40. J. Lamatro, S. Dayan and P. Sixou, Mol. Cryst. Liq. Cryst. 84, 267(1982)
41. A.M. Ritcey and D.G. Gray, Biopolymers, 27, 1363(1988)
42. M. Hatano, M. Yoneyama and Y. Sato, Biopolymers, 12, 895(1973)
43. D.D. Perrin, W.L.F. Armarego and D.R. Perrin, in Purification of Laboratory Chemicals, 2nd Ed., Pergamon Press, 1980, P. 86
44. R.E. Ballard, A.J. MaCaffery and S.F. Mason, Biopolymers, 4, 97(1966)
45. L. Stryer and E.R. Blout, J. Am. Chem. Soc., 83, 1363(1961)
46. K. Nishida and A. Iwasaki, Kolloid-Z. u Z. Polmere, 251 136(1973)
47. R.L. Disch and D.I. Suerdlik, Anal. Chem. 41(1), 82(1969)
48. H.P. Jensen, J.A. Schellman and T. Troxell, Appl. Spectrosc., 32, 192(1978)
49. Y. Shindo and Y. Ohmi, J. Am. Chem. Soc. 107, 91(1985)
50. M.J.B. Tunis-Schneider and M.F. Maestre, J. Mol. Biol, 52, 521(1970)
51. F.D. Saeva, P.E. Sharpe and G.R. Olin, J. Am. Chem. Soc, 95, 7656(1973)
52. K.J. Mainusch and H. Stegmeyer, Z. Phys. Chem. Neue Folge, 77, 210(1972)
53. I. Chabay. Chem. Phys. Lett. 17, 283(1972)
54. H. Schrader and E. Korte, Angew. Chem. 11, 226(1972)
55. Hl. de Vries, Acta. Cryst., 4, 219(1951)

56. T. Yamagishi, T. Fukuda, T. Miyamoto, T. Ichizhuka and J. Watanabe, Liq. Cryst. 7, 155(1990)
57. G.S. Chilaya and L.N. Lisetski, Mol. Cryst. Liq. Cryst. 140, 243(1986)
58. Intruction manual of Jasco-500C spectropolarimeter
59. Y. Shindo and M. Nishio, Biopolymers, 30, 25(1990)
60. A.M. Ritcey, J.X. Guo and D.G. Gray, To be submitted to Biopolymers

Chapter 5

Some Mechanistic Aspects of the Handedness Inversion for Lyomesophases of (acetyl)(ethyl)cellulose

5.1. Introduction

The handedness inversion phenomena have been long known for lyotropic liquid crystals of synthetic polypeptides[1]. Concentrated solutions of poly(γ-benzyl-L-glutamate) (PBLG) form left-handed liquid crystals in some solvents but right-handed ones in the other solvents even though the PBLG preserves its α-helical conformation in both cases and the solvents are achiral. Moreover, the handedness of these liquid crystals can be reversed by changing temperature or mixing solvents.

The first cellulosic liquid crystal was reported by Werbowyi and Gray[2] in 1976, almost two decades after the first polypeptide liquid crystal was found by Robinson[3]. Since then a large number of cellulose derivatives have been found to form chiral nematic liquid crystals[4-6]. Many recent experimental observations have revealed that the cellulosic liquid crystals are surprisingly similar to polypeptides liquid crystals in many aspects of chiroptical behaviors including solvent dependence of handedness[7-11] and thermally- and solvent-induced handedness inversion[7,12] although the mainchain of the cellulosics is more flexible than that of the polypeptides and there is no direct evidence of a helical conformation for cellulosic chains in solution. In previous chapters, it has been shown that (acetyl)(ethyl)cellulose (AEC) liquid crystals in acetic acid (AA), dichlormethane (DCM), dibromomethane (DBM), aqueous phenol (AP), chloroform, bromoform, and m-cresol all display a reversal of handedness from left to right with an increase in acetyl content on the mainchain. The change in handedness occurs at a compensated degree of acetylation (DA*), where the corresponding mesophases have infinite pitch and behave optically like a nematic. The value of the DA* varies from 0.19 to 0.37 depending on solvent system. Furthermore the occurrence of the handedness inversion in these mesophases accompanies a reversal of temperature dependence of pitch. All these chiroptical observations are summarized in Figure 5.1.

On the other hand, the AEC polymers in dichloroacetic acid (DCA) form a right handed chiral nematic liquid crystal, regardless of acetyl content. These results demonstrate that the optical properties of cellulosic liquid crystals are extremely sensitive to the nature of side chain and solvent. Because of the minor change in number of achiral acetyl groups (e.g. acetyl DS over 0.19 in m-cresol), a question naturally arises of what driving force leads to a dramatic change in chiroptical behaviour. The following four possible mechanisms may be considered.

(i) A specific stereochemical effect of acetate group in determining chiral nematic handedness

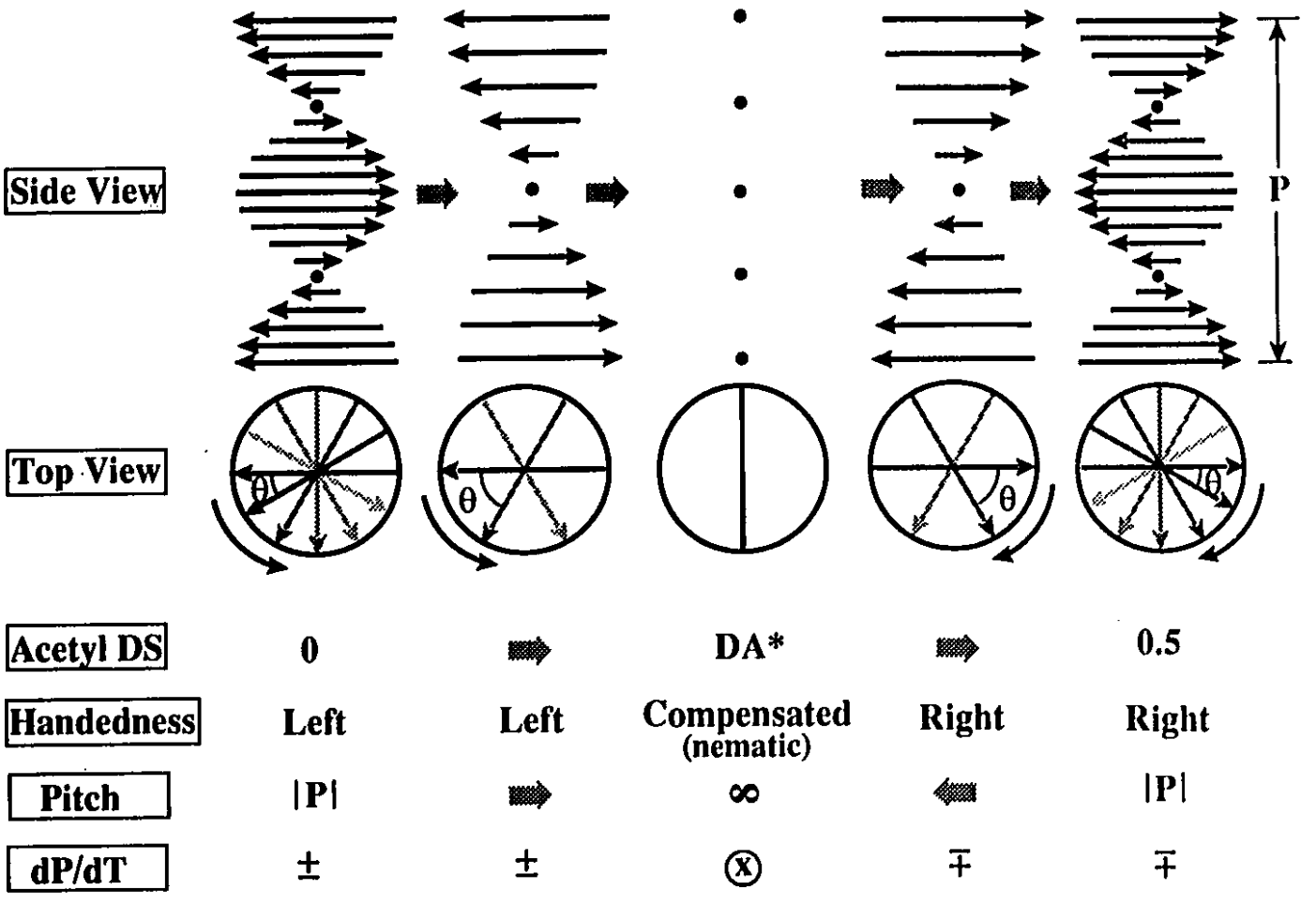


Figure 5.1. Schematic presentation of the handedness inversion for AEC chiral nematic liquid crystals with an increase in acetyl content.

(ii) A change in the conformation of the AEC mainchains in solution

(iii) A decrease in number of intra- or inter-chain hydrogen bonds between AEC chains

(iv) Specific interactions between individual AEC polymers and solvents

In this chapter, experiments concerning the above mechanisms will be described and recently developed theories for chiral nematic liquid crystals will be applied to the AEC liquid crystals. Some aspects of the mechanism for the handedness inversion for the AEC liquid crystals will be discussed on the basis of the present experimental observations together with the theoretical consideration.

5.2. Experimental section

The same series of AEC polymers with an ethyl DS of 2.5 and acetyl DS ranging from 0 to 0.5 and solvents as in Chapters 2-5 are used in this study. Fully substituted (acetyl)(methyl)cellulose (AMC) and (propionyl)(ethyl)cellulose (PEC) were synthesized and characterized as described in detail in Chapter 2.

The polymer dilute solutions (5% by weight) were prepared conventionally and transferred to a 10-mm path length quartz spectrophotometric cell for optical rotatory dispersion (ORD) measurements. The preparation of lyotropic liquid crystalline samples for ORD and circular dichroism (CD) measurements was the same as in previous chapters. The CD and ORD spectra were recorded with a Jasco J-500C and a Jasco ORD/UV Model-5 spectropolarimeters, respectively.

The ethylcellulose (EC) precipitated from EC/DCA solution was characterized with a Mattson Polaris FT-IR spectrophotometer. This EC precipitate was obtained by first dissolving EC in DCA for 5 days and then precipitating it from hexane. The precipitate was redissolved in tetrahydrofuran (THF) and reprecipitated again from hexane. Finally a thin film was cast from a solution in THF (5%) and dried prior to IR measurement. For comparison, a sample of EC was dissolved in THF and precipitated from hexane.

5.3. Results and discussion

5.3.1. Specific acetate group effect

It is natural to assume the acetate group is key factor responsible for the change in the handedness from left to right when the EC is acetylated, since the only change in chemical structure on EC mainchain is the introduction of the acetyl group on the chain. If so, one might expect that the same reversal of handedness should be also observed when a methylcellulose (MC) is acetylated, since MC (DS = 1.6) has been found to form a left-handed liquid crystal in trifluoroacetic acid (TFA) and dichloroacetic acid (DCA)[13]. To check this, a new derivative, (acetyl)(methyl)cellulose (AMC), has been prepared by fully acetylating the MC. Figure 5.2 shows the ORD spectra for anisotropic AMC solutions, which show reflection colour and long-pitch fingerprint texture in TFA and DCA, respectively. The positive pseudo-Cotton effect at the reflection band exhibited by the AMC/TFA sample and the plain negative dispersion in the visible by the AMC/DCA sample in Figure 5.2 indicate a left-handed liquid crystal, similar in handedness to its unacetylated precursor, MC, in the same solvents. Thus, in this case, acetylation does not change the chiral nematic handedness.

That the acetate group is not essential for the reversal of handedness is further shown by the formation of a right-handed liquid crystal for AEC solutions in DCA, irrespective of acetyl DS, as described in Chapter 3. In a particular case, non-acetylated EC in DCA also forms a right-handed chiral nematic structure, different from that of EC in the other solvents studied in this work. Initially it was considered that this might be the result of a dichloroacetylation of the free hydroxyl group on EC chain due to reaction with DCA. The resultant (dichloroacetyl)(ethyl)cellulose in DCA might form a right-handed liquid crystal. Ritcey and Gray[14] reported that fresh cellulose acetate (CA) anisotropic solution in TFA changed handedness from left to right after a few days standing. The reversal of the handedness was attributed to the reaction of TFA with CA. However, FT-IR measurement of the EC precipitated from EC/DCA solution in hexane indicates that dichloroacetylation does not occur in this system. As shown in Figure 5.3, the IR spectrum of this precipitate is almost identical to that of the original EC and no characteristic carbonyl absorption bands appear in the spectrum. One possible explanation for the formation of right-handed liquid crystals by EC in DCA is that the DCA is such a strong acid relative to other the solvents employed in this study that it strongly associates with the free hydroxyl group on the EC or partially acetylated AEC chains through hydrogen bonding as shown below:

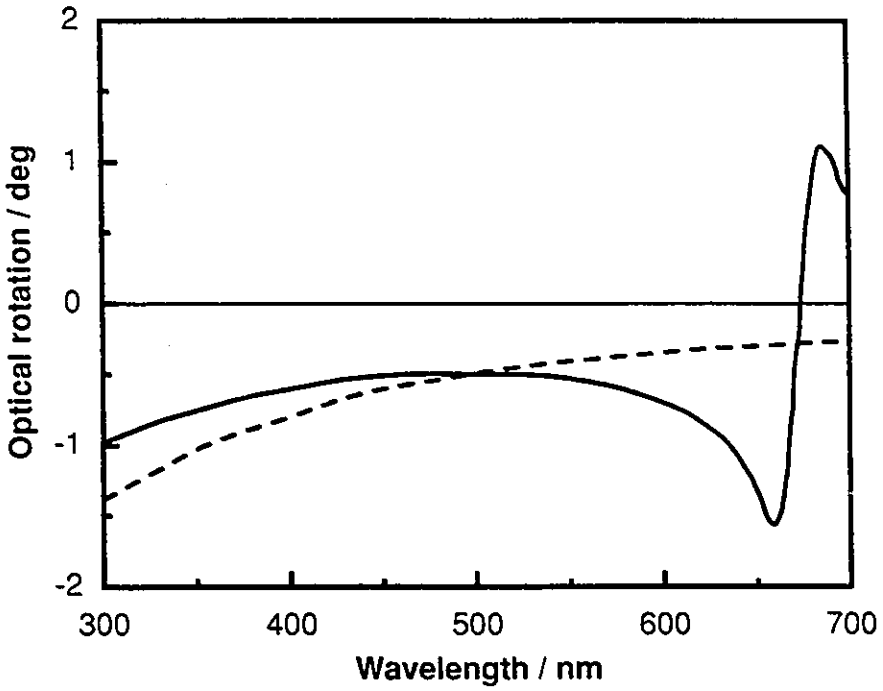


Figure 5.2. ORD curves for fully substituted (acetyl)(methyl)cellulose (AMC) anisotropic solutions in TFA (solid line) and in DCA (dashed line) at room temperature. The concentration of AMC in TFA and DCA is 30% by weight.

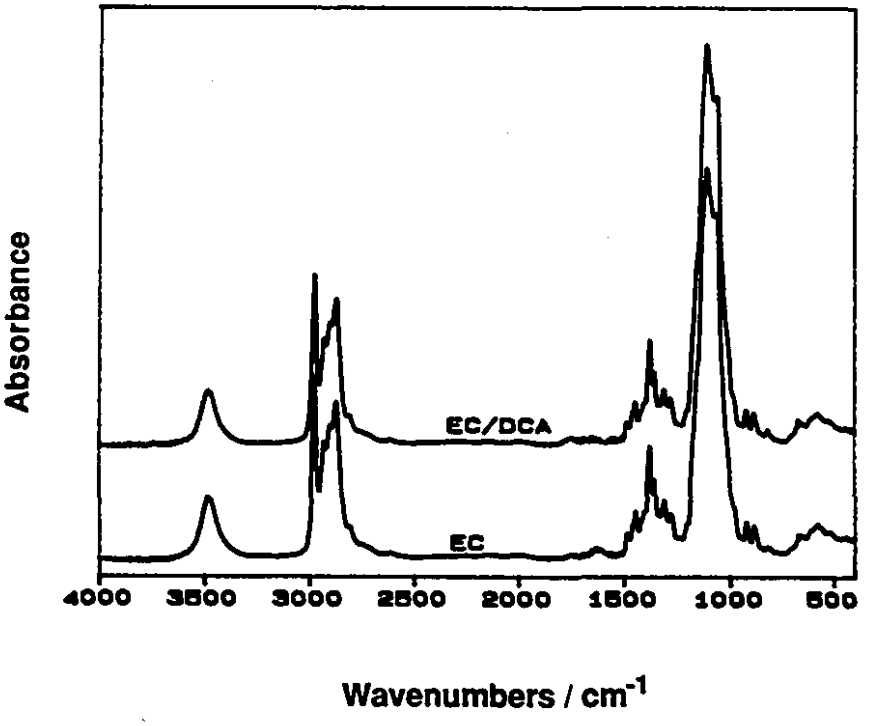
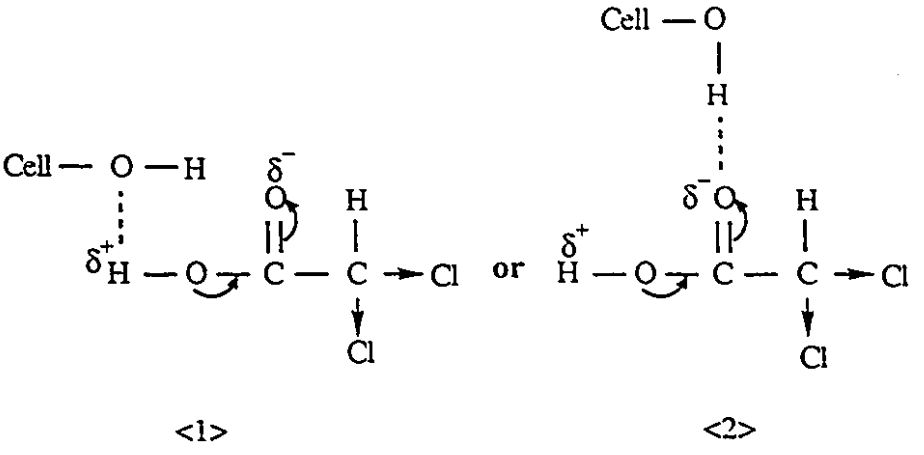


Figure 5.3. FT-IR spectra for a commercial ethylcellulose (EC), and the same EC precipitated after 5 days in DCA solution.



<1> <2>

As the consequence, this association may behave functionally like a substituent such as acetate and thus may prevent hydrogen bonding formation between the cellulosic chains or in some way may change local chirality. Accordingly, the association may energetically favour the formation of right-handed ordering structure. Further evidence of the effect of DCA on chirality of EC in dilute solution will be shown in the next section.

5.3.2. Conformation of AEC polymers in dilute solution

CD and ORD have been widely employed in configurational and conformational studies of chiral biopolymers such as proteins[15]. Because of (i) the limited content of acetate group (acetyl DS = 0~0.5), the only instrumentally-accessible chromophore on the AEC chain, and in addition (ii) the cut-off effect due to high absorption at short wavelength by the solvents employed in this study, a direct CD measurement is unlikely to provide useful information about conformation of the AEC polymers. An attempt to apply induced CD technique to the AEC system has been made in Chapter 4 by adding acridine orange (AO) to AEC dilute solution. The result showed that there is no induced CD signal appearing in the AO absorption region regardless of the acetyl content, indicating that there is no helical complex formation between the AO and AEC molecules with various acetyl content.

Further study of the effect of acetyl content on the conformation of AEC solutions was carried out by a direct ORD measurement. Figure 5.4 is ORD curves for dilute DCM solutions (5%) of AEC with acetyl DS varying from 0 to 0.5. Apparently, all curves exhibit a similar anomalous shape, suggesting that there is no significant change in conformation of AEC in isotropic solution with the introduction of acetate group on the mainchain. In contrast, their anisotropic solutions (45%) display opposite optical rotation

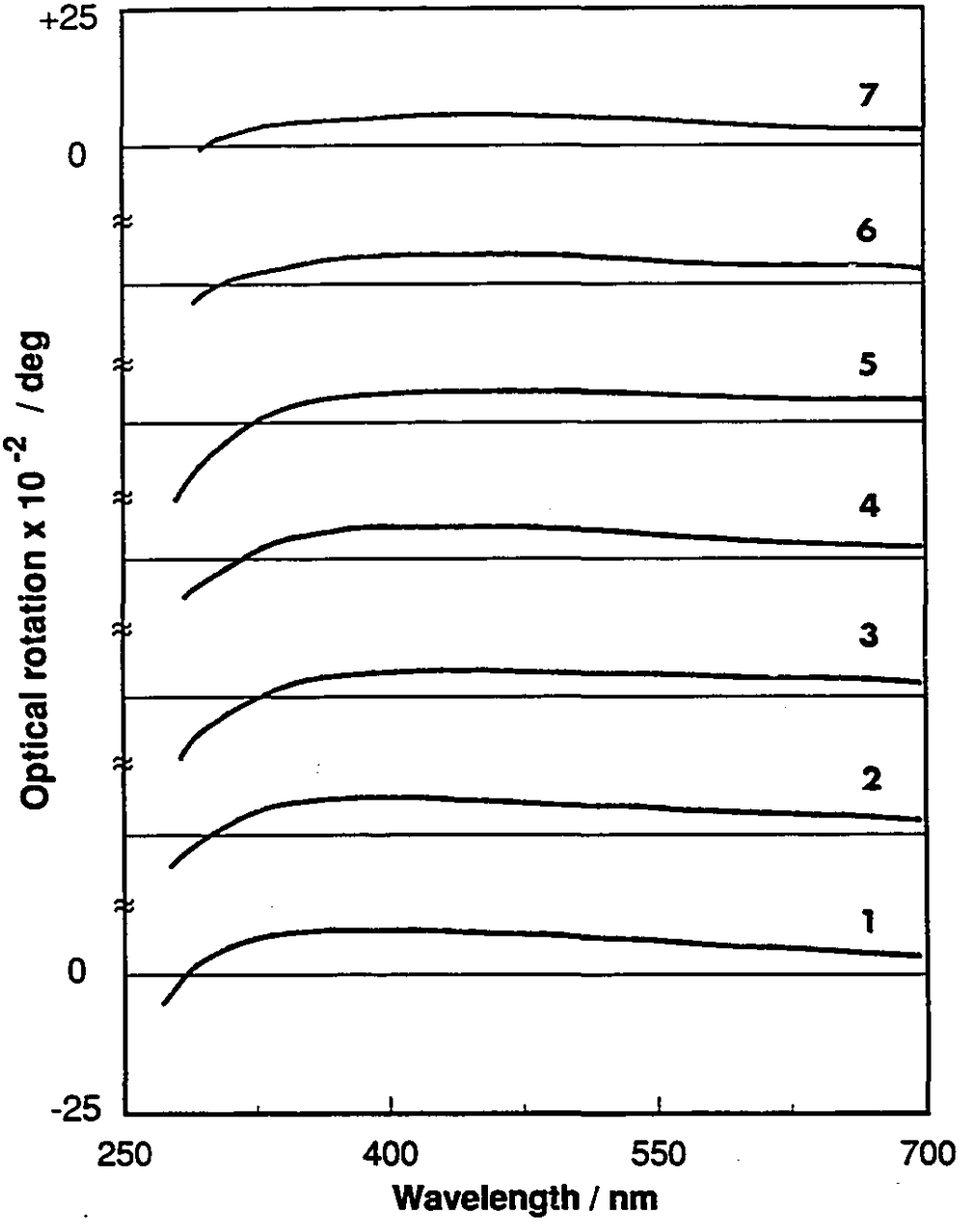


Figure 5.4. ORD curves for EC and AEC dilute solutions (5% by weight) in dichloromethane (DCM) at room temperature. The acetyl DS of samples in curves 1-7 are 0, 0.13, 0.21, 0.26, 0.31, 0,44 and 0.5, respectively.

at acetyl DS over 0.25 (Chapter 3).

A small change in the shape of ORD curves at short wavelength and a little down shift of the ORD curves with an increase in acetyl content (Figure 5.4) are assumed to be a result of a negative contribution to optical activity from the acetate group attached to the chiral cellulosic chain. Mukherjee et al[16] reported that isotropic CA solutions in trifluroethanol (TFE) exhibit an Cotton effect around 210 nm, corresponding to the $n \rightarrow \pi^*$ transition of acetate carbonyl, in both CD and ORD spectra. With increasing the acetyl DS, the Cotton effect becomes more pronounced. As a result, the value of the optical rotation at short wavelengths becomes more negative. Therefore the introduction of the Cotton effect, due to the acetate group, and the simultaneous reduction of the chiral contribution from the hydroxyl group on AEC chains may be responsible for the observed ORD curves in Figure 5.4. A similar result was also observed for AEC solutions in chloroform[10].

Figure 5.5 shows the ORD curves for AEC dilute solutions in DCA. It is surprising that a plain negative dispersion for the EC isotropic solution becomes an anomalous dispersion with increasing the acetyl content on the EC chain (although concentrated solutions all form right-handed liquid crystals, independent of the acetyl content). This is a clear indication that the chiroptical activity of molecules in isotropic solution is not simply related to the macroscopic chirality of anisotropic solutions. Presumably, the dependence of ORD on the acetyl content is due to the strong association between DCA and non- or partially-acetylated EC polymers through hydrogen bonding as suggested in the last section. As a result, EC solution in DCA exhibits a negative dispersion, different in local chirality from that in other solvents such as DCM or chloroform. A similar strong solvent dependence of ORD has been observed for polypeptides[17,18] and cellulose acetate[19]. As the free hydroxyl groups on the EC chain are replaced gradually by acetate group, the H-bonds between DCA and the hydroxyl groups decrease in number, leading to a decrease in negative contribution to total optical activity. Consequently the overall optical activity shifts towards positive values, and displays an anomalous dispersion as a function of wavelength. It has been reported that a random rather than helical conformation for polypeptides in DCA is due to the disruption of the amide hydrogen bonded secondary structure of the polypeptide molecules by the DCA[17]. Although the association of DCA with other atoms such as oxygen on the pyranose ring or at the 1-4 linkage of cellulosics may also contribute to the overall optical activity of the AEC polymers, the association with hydroxyl groups seems to be dominant.

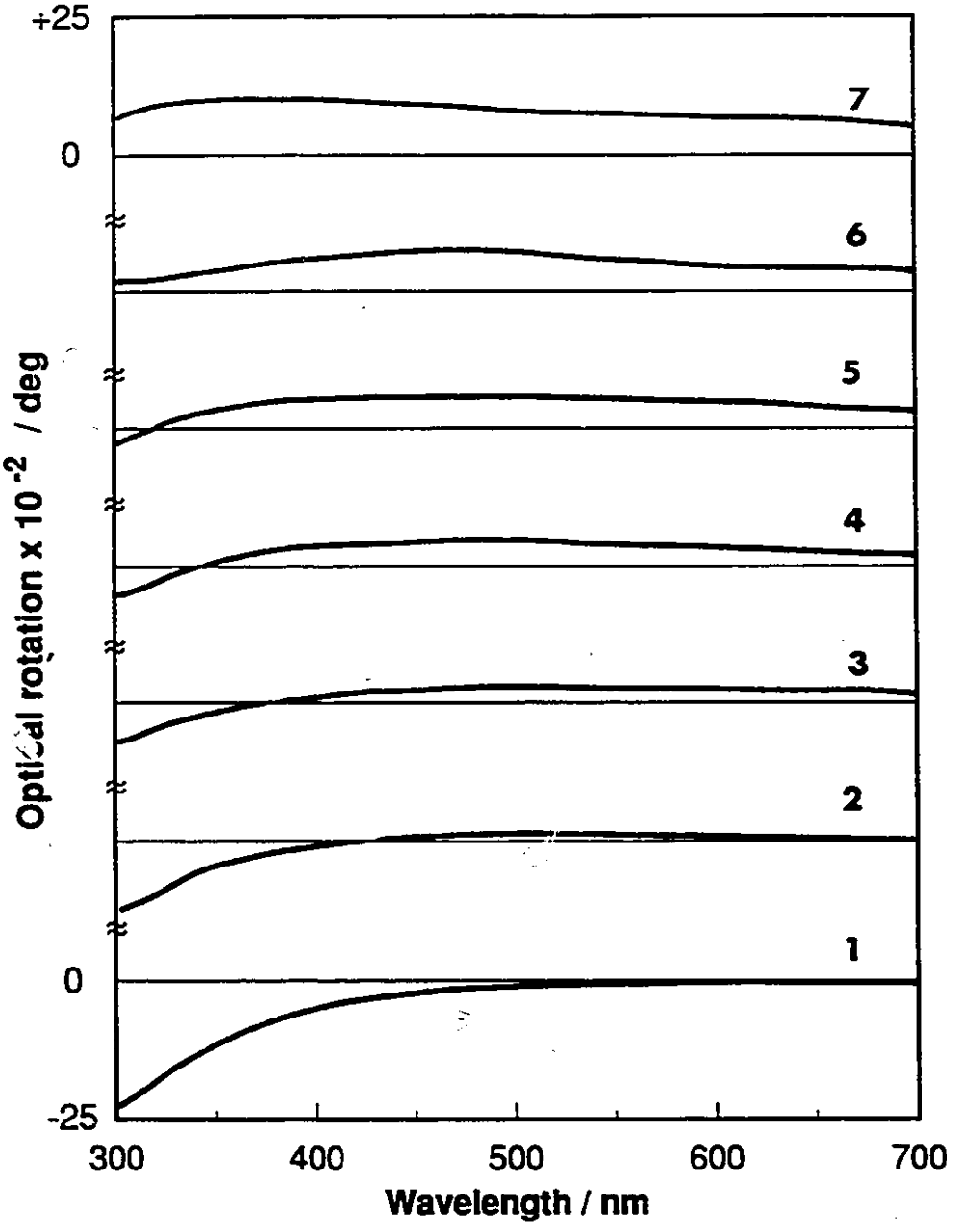


Figure 5.5. ORD curves for EC and AEC dilute solutions (5% by weight) in DCA at room temperature. The acetyl DS of samples in curves 1-7 are 0, 0.13, 0.21, 0.29, 0.35, 0.44 and 0.5, respectively.

Based on the above experimental observations, it appears that the handedness inversion for AEC anisotropic solution with acetyl content does not require a change in their conformations in isotropic solution. Recently, several chromophore-containing cellulose derivatives, 6-O-trityl-2,3-O-alkyl cellulose derivatives, have been prepared in an attempt to correlate the chiroptical activity of the derivatives in dilute solution to the chirality of their lyomesophases by direct CD studies[11,20]. The CD measurements on these polymers in both isotropic and anisotropic solutions failed to provide a direct relation between the conformation of the former and the handedness of the latter. Together with the present observations, this suggests that the chiroptical activity of the cellulosics in dilute solution is necessary for forming chiral nematic liquid crystals in concentrated solution but not sufficient for determining their chiral nematic handedness.

5.3.3. Polymer-polymer and polymer-solvent Interactions

The above ORD studies on AEC dilute solutions have indicated that the hydrogen bonding between solvent and AEC may be involved in their chiroptical behaviour. Is it possible that the hydrogen bonding between AEC polymers also plays an important role in determining the chirality of AEC anisotropic phases? In other words, as the hydroxyl groups on the EC chain are substituted by acetyl groups, does the resultant reduction of hydrogen bonding possibilities lead to the handedness inversion? If so, replacement of acetyl group by other substituents should also result in a change in handedness. To check this, the EC was propionylated instead of acetylated. Figure 5.6 shows the apparent CD spectra of an anisotropic solution of the resultant fully substituted derivative, (propionyl)(ethyl)cellulose (PEC). The exhibition of negative apparent CD bands by the PEC anisotropic solutions in chloroform and DCM indicate a right-handed chiral nematic structure, similar in handedness to the AEC but opposite to the original EC in the same solvents. Recently, Budgell[8] also demonstrated that triethylcellulose (TEC) form a right-handed liquid crystal in chloroform while ethylcellulose with an ethyl DS of 2.3 form a left-handed one in the same solvent. Therefore, the substitution of the free hydroxyl group on the EC chain by either ester (propionyl) or ether (ethyl) groups gives the same change in handedness as that caused by acetylation. This tendency to form right-handed system when hydroxyl groups are blocked is also shown by right-handed mesophases formed in the strongly acidic DCA, as mentioned in 5.3.1 above.

However, the solvent dependence of the value of DA* for handedness inversion of AEC liquid crystals, discussed in the previous chapters, can not be explained by the same hydrogen bonding effect. Given a certain acetyl DS, the AEC polymer in

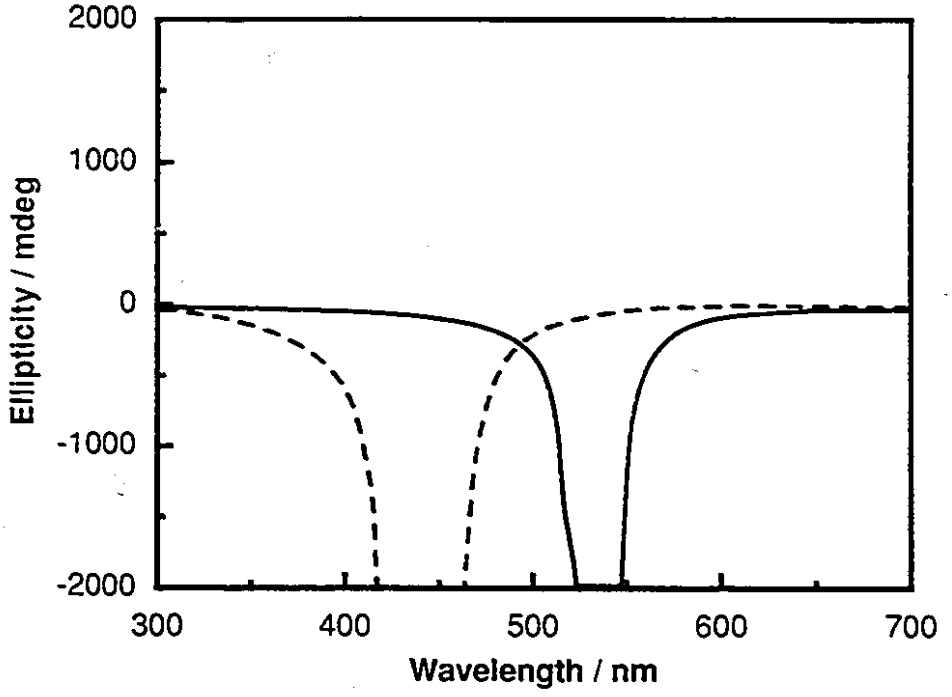


Figure 5.6. Apparent CD spectra of (propionyl)(ethyl)cellulose (PEC) anisotropic solutions in chloroform (solid line) and DCM (dashed line) at room temperature. The concentrations of PEC in chloroform and DCM are 35% and 55% by weight, respectively.

mesophase should have an unique handedness in all solvents (except for DCA). Similarly, a solvent dependence of handedness should not be observed in lyomesophases of other fully substituted cellulose derivatives. In fact, the formation of both right- and left-handed liquid crystals in different solvents has been recently reported for fully substituted cellulose tricarbanilate (CTC)[9] or 6-O-trityl-2,3-O-hexylcellulose (TrHC)[11], suggesting that other interactions between polymers through the solvent, in addition to hydrogen bonding, also contribute to their chiral arrangement. In conclusion, the handedness inversion for lyotropic AEC liquid crystals with varying acetyl content, in general, may result from solvent-mediated intermolecular interactions between chiral AEC molecules, with hydrogen bonding playing an important role.

5.3.4. Theoretical consideration

As discussed in Chapter 1, many theories have been developed to describe the chiroptical phenomena observed for chiral nematic liquid crystals[21-26]. Basically, these theories are developed on the basis of the energy minimization of intermolecular interactions between rod-like chiral molecules. Polypeptide molecules have been frequently cited. Many chiroptical properties of polypeptide liquid crystals have been well explained by the theories of Samulski[24], Kimura[25] and Osipov[26]. However, a comprehensive chiral nematic theory explaining all experimental observations has not yet emerged.

Cellulosic liquid crystals, resulting from the chiral and semirigid nature of the cellulose chain, have been widely explored experimentally in the last decade[4-6]. The similarities and differences in chiroptical behaviors between these two classes of liquid crystals have led to the development of molecular theories extending to the cellulosic liquid crystals by Osipov[27,28] and Varichon[29,30]. In the following discussion, these two theories, particularly that of Osipov, will be applied to AEC liquid crystals.

Osipov's approach is based on his molecular statistical theory[26] for rigid chiral macromolecules, where an express for the energy of chiral interaction between chiral molecules in a dielectric medium was obtained as a function of temperature and dielectric parameters of the system. By assuming that the semirigid cellulose chain adopts a "twisted belt" conformation rather than a helix (Figure 1.7.) and that the persistence length, l, of the cellulose chains is much smaller than that of a rigid chain, he arrived at the following expression for twisting power,

$$2\pi / P = -\rho^2 (\chi - \lambda kT) / 2 K_{22} \qquad [1]$$

where χ is related to the attraction interaction, P is the pitch, k is constant, K_{22} is the twist elastic constant, ρ is the number density of rigid segments, $\rho = cL/l_o$, where c is the number density of the macromolecule chains, l_o is the length of the segments, L is total length of the chain ($L > l > l_o$), and the pseudoscalar parameter λ is determined by the steric repulsion between chains. In the case of perfect orientational order of the molecules ($S \rightarrow 1$), the λ can be expressed as equation 2

$$\lambda = -(\kappa T/2) \rho^2 q_m h^2 (d + 5h/3\pi) l_o^2 \qquad [2]$$

where d and h are the thickness and breadth of the belt, respectively, and q_m is equal to $2\pi/P_m$, where P_m is the period of the twist. The equation 11 is valid when $q_m/(d+h) \gg 1$.

The theory predicts that the handedness of cellulosic liquid crystalline solutions (the handedness here is defined by the sign of the pitch) depends not only on temperature and on the steric repulsion of the chains, λ, which is related to the nature and position of the substituents on the cellulose mainchains, but also on an attractive interaction parameter, χ, which involves a contribution from the nature of the solvent surrounding the cellulosic chain. The importance of the solvent-cellulosic interactions has been described in previous chapters. The theory predicts that the criteria for compensation is $(\chi - \lambda kT) = 0$. Under this condition, the pitch of the cellulosic mesophase should become infinite, and the mesophase resembles a normal nematic phase. Qualitatively, this can explain the handedness inversion occurring in AEC anisotropic solutions. Assuming that the term $(\chi - \lambda kT)$ is a function of acetyl DS, temperature, concentration, dielectric constant of solvent, etc. in AEC lyomesophase systems, i.e. F (acetyl DS, T, C, ε, ...) = $(\chi - \lambda kT)$, variation of one of these factors while the other factors are held constant would result in occurrence of compensation at a specific value. A handedness inversion has been observed for lyotropic AEC mesophases (i) at a specific acetyl DS, DA*, and (ii) at a specific temperature, T*, as shown in the previous chapters, and for lyotropic EC (acetyl DS = 0) mesophases (iii) for a specific mixture of two solvents with different ε, as shown by Sieker and Zugenmaier[9].

A fully quantitative interpretation of the relation between pitch and the other parameters in Osipov's theory remains difficult and even impossible at present, because the parameters in the "twisted belt" model for the AEC with various acetyl DS', are not available, in part because the distribution of substituents along the cellulosic chain and among the C(2), C(3) and C(6) positions in the glucopyranose residues is not known. In

this sense, specific cellulose derivatives with known position and distribution of substituents are required to evaluate quantitatively the theory to the cellulosic liquid crystalline behaviour. In addition, it is difficult to specify what kind of interaction between given solvent and given AEC polymer contributes to χ. In Chapter 3 it has been shown that no simple correlation between solvent dielectric constant and handedness was found for the AEC lyotropic liquid crystals. Other physical properties of the solvent in addition to ε may also be involved in the contributions to the chiral interactions. Furthermore, many of the items in equation 1 and 2 are not independent. For example, the persistence length, l, for cellulose derivatives is strongly dependent on temperature[31], and so presumably are K_{22} and q_m. In spite of these difficulties and limitations, Osipov's theory at least shows a qualitative agreement with the results for AEC mesophases. This agreement demonstrates the importance of chiral polymer-solvent interaction in the role of organizing chiral nematic structure.

More recently, Varichon et al.[29,30] extended the Lin-Liu's molecular statistical theory[23] by explicitly considering the orientational entropy terms. After minimization of the total free energy of a chiral nematic liquid crystal with respect to the orientational distribution, they obtained an express for chiral nematic pitch,

$$\frac{2\pi d}{P} = \frac{n_0 + \frac{\hat{x}n_1 + \hat{x}^2 n_2}{n}}{\frac{\lambda_2}{\gamma_2} + \frac{\hat{x}d_1 + \hat{x}^2 d_2}{n}} \qquad [3]$$

where the terms in the equation are defined in reference 29 and are related to the ratio of the second and fourth order parameters S(T), the chiral interaction parameter μ_m, and the nematic interaction parameter γ_2. The magnitude and sign of the pitch are correlated to temperature, concentration, and degree of polymerization (DP) by these parameters. The resulting theory is in qualitative agreement with some experimental results, in that the pitch and handedness of cellulosic liquid crystals depend on temperature[12] and concentration[32], and they are in semiquatitative agreement with experimental data for the pitch dependence on molecular weight for acetoxypropylcellulose (APC) liquid crystals[33]. Based on the experimental data of our preliminary work on AEC liquid crystals in chloroform[10], they also predicted that theoretical values of DA* for handedness inversion for AEC liquid crystal are around 0.16 to 0.21[30], which is close to the result for AEC in chloroform but lower than that observed for other solvent systems in this study. The difference may be due to the fact that the solvent was considered to act

only as a diluent for the anisotropic solution, and the chiral contribution from the nature of the solvent was not taken into account in their theory. However, the significance of the theory is obvious and the semiquantitative fitting is still satisfactory in light of the complexity of the mixed ester/ether structure of AEC. In their conclusion, they speculated that the left-handed cellulosic liquid crystals might be due to the presence of hydrogen bond related interactions whereas the right-handed ones might involve induced quadrupole interactions. At the moment, neither Osipov's nor Varichon's theory is able to quantify the specific interaction responsible for the handedness inversion. In reality, a combination of multiple interactions may be responsible.

5.4. Concluding remarks

Optical rotational dispersion studies of AEC polymers have shown that no significant change in conformation occurs for acetyl DS ranging from 0 to 0.5 in dilute solution. Thus chain conformation change with acetyl content are unlikely to be responsible for the handedness inversion observed for their anisotropic solutions. Observation of left-handed liquid crystals formed in both methylcellulose (DS=1.6) and fully acetylated MC polymers in dichloroacetic acid and trifluoroacetic acid also suggests that the chiral nematic handedness is not determined purely by some specific chemical structure of the acetyl groups. Replacement of the free hydroxyls on commercial ethylcellulose by either ester (acetyl or propionyl) or ether (ethyl) groups (ref. 8) leads to the same handedness inversion for their liquid crystalline solutions, implying that hydrogen bonding between free hydroxyl groups on cellulosic chains may play a role in arranging molecules in the mesophase. These observations provide a possible explanation for the formation of right-handed liquid crystals by EC and AEC polymers in DCA regardless of acetyl DS; DCA is such a strong acid relative to the other solvents employed in this study that it may strongly associate with the free hydroxyl groups on the EC or partially acetylated EC chains through hydrogen bonding, and as a result, functions like substituents such as acetyl, propionyl or ethyl group. However, the observed solvent dependence of DA* for lyotropic AEC mesophases also suggests that interactions other than hydrogen bonding between AEC polymers and solvent contribute to their chiral arrangements. In conclusion, the handedness inversion for lyotropic AEC liquid crystals with variation in acetyl content, seems to involve intermolecular interactions between chiral AEC molecules through the solvent medium, with hydrogen bonding playing an important role. Application of Osipov's theory for chiral nematic liquid crystals, in which polymer-polymer and polymer-solvent interactions are taken into account, to the

lyotropic AEC systems reveals that the handedness inversion induced by varying the acetyl DS, temperature and solvent can be qualitatively described by the theory. However full interpretation of chiral nematic behaviour, especially handedness inversion or compensation, still needs a great deal of experimental and theoretical effort.

5.5. References

1. I. Uematsu and Y. Uematsu, Adv. Polym. Sci. 59, 37(1984), and reference cited therein.
2. R.S. Werbowyi and D.G. Gray, Mol. Cryst. Liq. Cryst. (letters), 34, 97(1976)
3. C. Robinson, Trans. Farad. Soc. 52, 571(1956)
4. R.D. Gilbert and P.A. Patton, Prog. in Polym. Sci., 9, 115(1983)
5. D.G. Gray, J. Polym. Sci., Appl. Polym. Symp., 37, 179(1983)
6. B.R. Harkness and G.G. Gray, in Liquid Crystal and Mesomorphic Polymers, Ed., V. Shibaev and L. Lam, Springer, New York, 1991 in press.
7. P. Zugenmaier and Petra Haurand, Carbohydr. Res., 160, 369(1987)
8. D.R. Budgell, Ph.D. Thesis, McGill University, Montreal, 1989
9. M. Siekmeyer and P. Zugenmaier, Makromol. Chem., Rapid., Commun.,8, 511(1987)
10. J.X. Guo and D.G. Gray, Macromolecules, 22, 2086(1989)
11. B.R. Harkness and D.G. Gray, Can. J. Chem., 68, 1135(1990)
12. T. Yamagishi, T. Fukuda, T. Miyamoto, T. Ichizhuka and J. Watanabe, Liq. Cryst. 7, 155(1990)
13. J.X. Guo and D.G. Gray, unpublished results
14. A.M. Ritcey, K.R. Holme and D.G. Gray, Macromolecules, 21, 2914(1988)
15. E. Carney, in The molecular basis of optical activity, R.E. Krieger Publishing Campany, Malabar, Florida, 1985, Chapter 5
16. S. Mukherjee, R.H. Marchessault and A . Sarko, Biopolymers 11, 291(1972)
17. J.T. Yang and P. Doty, J. Am. Chem. Soc., 79, 761(1957)
18. K.K.Yamaoka, Biopolymers, 2, 219(1964)
19. A.S. Buntjakov and V.M. Averyanova, J. Polym. Sci.: Part C, 38, 109(1972)
20. B.R. Harkness and D.G Gray, Liq. Crys. 8, 237(1990)
21. P.N. Keating, Mol. Cryst. Liq. Cryst., 8, 315(1969)
22. W.J.A. Goosens, Mol. Cryst. Liq. Cryst., 12, 237(1971)
23. Y.R. Lin-Liu, Yu Ming Shih and Chia-Wei Woo, Phys. Rev. A, 15, 2550(1977)
24. T.V. Samulski and E.T. Samulski, J. Chem. Phys. 67, 824(1977)

25. H. Kimura, M. Hoshino and H. Nakana, J. Phys. Soc. (Japan), 51, 1584(1982)
26. M.A. Osipov, Chem. Phys. 96, 259(1985)
27. M.A. Osipov, Nuovo Cimento Soc., Ital. Fis, 10D, 1249(1988)
28. M.A. Osipov, in Liquid Crystal and Mesomorphic Polymers Eds., V. Shibaev and L. Lam, Springer, New York, in press
29. L. Varichon, A.Ten Bosch and P. Sixou, liq. Cryst. ,9, 701(1991)
30. L. Varichon and A.Ten Bosch, Macromolecules, , 22, 3812(1992)
31. G.V. Laivins and D.G. Gray, Macromolecules, 18, 1746(1985)
32. U. Vogt and P. Zugenmaier, Ber. Bunsenges. Phys, Chem., 89, 1217(1985)
33. G.V. Laivins. P. Sixou, D.G. Gray, J. Polym. Sci. Polym. Phys. 24, 2779(1986)

Chapter 6

Conclusions

6.1. General conclusions

The research project undertaken in this thesis was originally motivated by a curiosity about the unusual chiral nematic behaviour exhibited by commercial ethylcellulose, when compared to the majority of cellulosic liquid crystals. The work was initiated by acetylation of the commercial ethylcellulose and with an investigation of chiroptical properties of the resultant mesomorphic polymers in an attempt to better understand the chiral nematic ethylcellulose mesophase and perhaps other cellulosic mesophases. It was thought that achiral chemical modification of the ethylcellulose might be a relatively straightforward approach to achieve the above objective since the chemical modifications seemed minor, and any change in chiral nematic properties (although unknown at the beginning of this project) must be a result of the chemical structure of the newly-introduced substituents or/and the subsequent change in conformation. In the course of this study, several unexpected phenomena revealed that the situation was far more complex than the original approach suggested, but they did also provide insights into the factors which determine chiroptical properties of cellulosic liquid crystals.

(Acetyl)(ethyl)celiulose polymers with an ethyl DS of 2.5 and acetyl DS ranging from 0 to 0.5, fully substituted (propionyl)(ethyl)cellulose and fully substituted (acetyl)(methyl)cellulose prepared from commercial ethylcellulose and methylcellulose retain good solubility in a wide range of organic solvents and are capable of forming chiral nematic mesophases in concentrated solution. This feature made this project feasible. The critical concentration for liquid crystal formation was found to depend on the acetyl DS and solvent.

The most unforeseen finding of this research was that the handedness and pitch of lyotropic AEC liquid crystals were extremely sensitive to the acetyl content of AEC even though the acetyl group is achiral and the same chiral cellulose backbone is shared by all polymers. This was illustrated by the variation in pitch from a few nm to infinity and by a reversal of handedness of the supermolecular helicoidal structures from left to right for anisotropic AEC solutions in dichloromethane, dibromomethane, chloroform, bromoform, m-cresol, acetic acid and aqueous phenol, as the acetyl DS increased from 0 to 0.5. The handedness inversion for AEC liquid crystals in a given solvent system occurred at a specific acetyl DS, called the "compensated degree of acetylation", DA*, where a compensated mesophase characterized by an infinite pitch and a nematic-like optical behaviour was formed. The ORD studies of these AEC polymers in dilute solution revealed that there is no significant change in ORD curves while the corresponding AEC polymers in concentrated solution display a handedness inversion, suggesting that the

handedness of the chiral nematic structures is not determined directly by the conformation of the AEC chains in dilute solution. The temperature dependence of the pitch for AEC mesophases was also found to be strongly acetyl DS dependent. For example, the temperature dependence of pitch for an AEC mesophase with an acetyl DS below DA* was the reverse of that for an AEC mesophase with an acetyl DS greater than DA*.

Another unexpected observation was that achiral solvents strongly influence the handedness, the value of DA* and the temperature dependence of pitch. The lyotropic solutions of AEC polymers with low acetyl content showed a left- or right-handed chiral nematic structure, depending on solvent, while AEC polymers with high acetyl content only formed right-handed mesophases in all the solvents examined in this study. However, the temperature dependence of pitch for AEC mesophases was solvent dependent, regardless of the acetyl content. The value of DA* for handedness inversion or compensation for lyotropic AEC mesophases, made from a given AEC with different solvents, varied from 0.19 to 0.37. No simple correlation between the values of DA* and the dielectric constants of the corresponding solvents has been found. Dichloroacetic acid is the only solvent in which the AEC mesophases showed a right-handed helicoidal structure and a positive temperature dependence of pitch, regardless of acetyl DS. All these observations indicated that strong specific solvent-AEC interactions play an important role, in addition to substituent effects, in determining the chiroptical activity of AEC mesophases.

Induced CD studies of achiral dye molecules dissolved in the above series of lyotropic AEC mesophases revealed that the orientational behaviour of the guest dyes were determined by the chiral nematic structures of the host matrices. Achiral dyes in isotropic AEC solutions displayed no induced CD signals regardless of acetyl content, concentration of the AEC polymers and dye content, indicating a random orientation of the dye molecules. When dissolved in anisotropic AEC solutions, the dye molecules showed strong induced CD bands in their absorption region. The induced CD is assumed to be a result of orientation of the dye molecules by the AEC mesophases to adopt a helicoidal arrangement, since there is no significant evidence of macroscopic linear dichroism observed in this study. Acridine orange dissolved in a left-handed liquid crystalline AEC solution displays a negative LCICD whereas a positive LCICD was observed when the AO was dissolved in a right-handed AEC mesophase. A change in handedness due to a variation of acetyl DS or temperature, or a change of solvent system was indicated by a reversal of sign of LCICD for the oriented dye molecules. Thus the use of achiral dyes as a probe for the handedness inversion for AEC mesophases is well

demonstrated in this study. The other observations, of a strong pitch and temperature dependence on the intensity of LCICD for the AO dissolved in the AEC mesophases, and almost no dependence of the molecular ellipticity of the LCICD on the dye content, also strongly suggested that the helicoidal structures of the host liquid crystals were essential for the guest achiral molecules to exhibit the extrinsic optical activity. The present study also suggested that the LCICD technique may be generally applicable to polymeric chiral nematic liquid crystals provided that suitable chromophores are available and macroscopic linear birefringence and linear dichroism are negligible.

Although handedness inversion phenomena have been observed for several cellulosic liquid crystals, to date no comprehensive explanation has been proposed for this behaviour. An attempt to address this question for AEC mesophases was made in this work. Observation of left-handed liquid crystals formed by both methylcellulose (DS=1.6) and fully acetylated MC polymers in dichloroacetic acid and trifluoroacetic acid eliminates the possibility that reversal of handedness is specifically associated with the chemical structure of the acetyl group. ORD studies of AEC polymers in dilute solution have shown that no significant change in conformation occurred at the DA* corresponding to the handedness inversion. Replacement of the free hydroxyls on commercial ethylcellulose by either ester (acetyl or propionyl) or ether (ethyl) groups (Chapter 5, ref. 8) leads to the same handedness inversion from left to right for their liquid crystalline solutions, implying that hydrogen bonding between free hydroxyl groups on cellulosic chains may play a role in arranging molecules in the mesophase. The involvement of hydrogen bonding in chiroptical behaviour of lyotropic AEC mesophases seems also evident by fact that EC and AEC polymers in DCA all form right-handed liquid crystals, regardless of acetyl DS. In this case, a strong association, through hydrogen bonding, of the free hydroxyl groups on the EC or partially acetylated EC chains with relatively strong acid, DCA, may function like substituents such as acetyl, propoinyl or ethyl group. However, solvent dependence of DA* observed for the handedness inversion for lyotropic AEC mesophases suggests that interactions other than hydrogen bonding between AEC polymers and solvent also contribute to their chiral arrangements. It is thus concluded that the handedness inversion for lyotropic AEC liquid crystals with variation in acetyl content seems involve intermolecular interactions between chiral AEC molecules through the solvent medium, with hydrogen bonding playing a significant role. Qualitatively, the handedness inversion induced by varying the acetyl DS, temperature and solvent, observed for lyotropic AEC liquid crystals in this research, can be described by Osipov's theory for chiral nematic liquid crystals, in which polymer-polymer and polymer-solvent interactions are taken into account. However full

interpretation of chiral nematic behaviour, especially handedness inversion or compensation, still needs a great deal of experimental and theoretical effort.

6.2. Contributions to original research

The research described in this thesis represents the first detailed report on the influence of achiral substituents and solvents, and degree of substitution on the chiroptical properties of cellulosic liquid crystals. Specific contributions of this work to original research are outlined below.

1. Methods of preparation for (acetyl)(ethyl)cellulose polymers with an ethyl DS of 2.5 and acetyl DS ranging from 0 to 0.5, and fully substituted (propionyl)(ethyl)cellulose (PEC) and (acetyl)(methyl)cellulose (AMC) have been developed. These new cellulose derivatives were characterized by FT-IR, ^{13}C NMR and GPC.

2. Chiral nematic liquid crystalline solution of a series of AEC polymers were prepared in a variety of organic solvents. The critical concentration for the mesophase formation was found to depend on the acetyl DS and the solvent.

3. Lyotropic solutions of the AEC polymers show a reversal of handedness and a reversal of temperature dependence of pitch as the acetyl DS is varied. The specific acetyl DS, at which the handedness inversion occurred, DA*, was determined in several solvents. For the first time, the work in this thesis allowed a quantitative relationship between DS and the handedness of a cellulosic mesophase to be established.

4. Liquid crystalline AEC at DA* displayed properties of a nematic (not chiral nematic) phase. This is the first observation that the compensation for cellulosic liquid crystals can be induced by systematic chemical modification rather than by changing temperature, solvent or optically active composition.

5. The achiral solvents were found to strongly influence the handedness, the magnitude of pitch, the temperature dependence of pitch and the DA* for lyotropic AEC liquid crystals.

6. The first detailed application of liquid crystal induced circular dichroism to cellulosic liquid crystals was made. A correlation between the induced CD signals of

guest achiral dyes and the host chiral nematic structures of lyotropic AEC liquid crystals was established. This has not been reported for any other cellulosic polymers, as far as is known.

7. The use of achiral dyes as a probe for the handedness inversion induced by changing acetyl DS, temperature and solvent for lyotropic AEC liquid crystals was well demonstrated. This work provides some phenomenal and technical aspects for the potential application of LCICD to polymeric chiral nematic liquid crystals.

8. The molecular theory developed by Osipov for chiral nematic liquid crystals was qualitatively tested for the first time on a chiral nematic cellulosic system.

6.3. Suggestions for future research

The results presented in this thesis have demonstrated that the chiroptical properties of cellulosic liquid crystals depend to large extent on the nature of substituents, degree of substitution and solvent. On the other hand, they also exposed the disadvantages of using commercial cellulosic products as starting materials, whose structural features, such as distribution of substituents along the cellulose chain and among the three hydroxyls in each anhydroglucose unit, are unknown. Without this information, it is unlikely that one can establish a clear relationship between molecular structure and chiroptical properties, or that molecular theories for chiral nematic liquid crystals can be tested quantitatively. Therefore, future studies in any continuation of this project should involve synthesis of specific cellulose derivatives with the following features; (1) a wide range of DS, (2) a homogeneous distribution of substituents, (3) specific substitution with respect to the C(2), C(3) and C(6) positions in an anhydroglucose unit , and (4) capability of forming mesophases in a wide range of solvents. In addition, chromophoric substituents with absorption regions accessible by CD spectroscopy would be desirable since the CD spectrometer has proved to be a powerful tool for characterizing the chiroptical activities of chiral polymers in isotropic and anisotropic phases. Direct CD measurements of these kinds of cellulose derivatives in isotropic and anisotropic phases may permit their conformations to be correlated to their liquid crystalline chirality, if this relation exists. Other topics involving AEC polymers studied in this thesis may also yield some informative results if more work were undertaken and these areas might include the following:

1. An investigation of the interaction parameters between each solvent and the AEC polymers may provide some insights on the solvent dependence of handedness of DA*.

2. It may be of interest to investigate the chiroptical behaviour of liquid crystalline mixtures of EC (left-handed) and fully acetylated EC (right-handed) in the same solvent at different ratios and to compare these results with those observed in this work. The result may provide information on the miscibility of opposite handed liquid crystals and on the differences in chiral nematic behaviour exhibited by moderately acetylated EC and by mixtures of EC and highly acetylated EC. The total acetyl content could be kept constant in each individual sample.

3. It has been shown that the magnitude of the pitch for anisotropic AEC solutions in chloroform, bromoform, dichloromethane and dibromomethane varies from a few nanometer to infinity and the handedness is either left or right, depending on the acetyl DS. It may be of interest to study the orientational behaviour of the above solvents (deuterated or non-deuterated) in the mesophases by means of NMR spectroscopy since LCICD results in this thesis have shown that small dye molecules can adopt the helicoidal structures of their matrices. By analogy, these solvents may have the same orientation as AEC molecules in the mesophase, and the orientational order may be inferred from NMR results.

4. Preliminary results from flow time measurements for AEC mesophases with various pitch have shown that there exists a strong dependence of viscosity on chiral nematic pitch. It would be interesting to follow this remarkable rheological behaviour in a rheometer under different shear rates. Very few studies on the rheological behaviour of chiral nematic liquid crystals, especially pitch effects, have appeared to date. The AEC mesophase seems to be a good system to conduct this study since the pitch changes over a wide range with a minor change in the acetyl DS, while the polymer concentration, degree of polymerization and temperature can be held constant.

5. Evaluation of the rigidity of AEC polymers in dilute solution as the acetyl DS increases may be constructive in terms of verifying the relationship between rigidity of chiral polymers and the chiroptical properties of their mesophases, as proposed in Osipov's theory.