

# Chirality and polymers

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Optical activity, since its discovery, has been a fascinating field, from the seemingly simple issues related to transfer of (chiral) information to its cosmic connections and the origin of life itself. There has been much progress made on both fronts which include the discovery of strong infrared circular polarization from dust scattering to the more down to earth knowledge of how chiral information is transferred to solutes by chiral additives, piezoelectricity and opalescent elastic networks. The progress made in the past few years and their implications for various aspects of chirality are discussed.

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### Introduction

Optical activity, since the time it was discovered by Biot in the early 1800s, has captured the imagination of scientists, and seemingly knows no disciplinary boundaries [1-3]. Optical activity, as generally defined, implies that the plane of polarization of a linearly polarized light beam is rotated as it traverses through an optically active medium. While optical activity due to anisotropic crystals exists (as was discovered by Biot and Arago), it will, however, not be the focus of this article. Optical activity due to organic molecules that lack reflectional symmetry will form the topic.

Chiral molecules are those molecules whose mirror images are non-superimposable (lack of mirror or reflection symmetry) and hence chirality is a geometrical attribute. The fact that chirality is a property of the whole molecule and not just the chiral centers present in a molecule, allows one to manipulate the chirality of the whole molecule using synthetic means. One sees the manifestation of chirality in a variety of instances ranging from the climbing habits of plants [4], switching of liquid crystals with circularly polarized light [5-8], induction of a helical conformation in an otherwise planar molecule [9], to the attainment of a large enantiomeric excess in a reaction catalyzed by a very small enantiomeric excess [10,11]. All of these rely in some form or another on the transfer of information about the chirality so that one can observe the manifestation of such information transfer.

It will become obvious that personal taste plays a key role in both topical coverage and referencing. For instance, this review will primarily focus on molecules that form ordered phases thus leaving out a host of other elegant materials relating to chirality [12-15]. Also, in keeping with the length of this article many an issue worthy of elaborate discussion will receive an overly simplified mention. For all these sins I can do little more than apologize at the beginning.

There have been a range of questions in the past that have attracted attention from the scientific community regarding optically active materials and in particular about polymeric materials. It is well known that the addition of a small amount of an optically active molecule to a nematic phase (a phase that has long range orientational order of molecules) transforms that phase to a chiral nematic phase (or cholesteric phase). *The question of how this chiral information is transferred to the bulk fluid has been of interest for some time* [16,17]. The molecular origins of this chiral information transfer to the solute is still unclear. This is particularly true in the case of lyotropic nematic fluids where the nematic phase is formed by dissolution of the solute in a solvent. There have been elegant experiments in the recent past that shed light on this question [18,19]. Probing the question of chiral information transfer has also led to an interesting way of characterizing preferential solvation [20].

Chiral recognition is of particular importance in living systems. In the case of biopolymers, like proteins, the structural organization is in most instances mediated carefully by molecular chaperones [21,22]. It has been a challenge to make synthetic polymeric materials where their conformational characteristics are so mediated. *How does one go about accomplishing conformational changes mediated by chiral molecules as an example?* Imagine a molecule that is a dynamic helix, which can be thought of as a single macromolecular chain possessing regions of left-handed and right-handed screw sense separated by helix reversals (e.g. polyisocyanates), which when brought in contact with a chiral molecule assumes a helical conformation with a single screw sense. Such a change in conformation would be the first step towards conformational changes of a macromolecule mediated by a chiral chaperon. This review will discuss the issue of such conformational changes brought about by synthetic means [23].

Almost twenty years ago, in what is now a classic text in polymer science, de Gennes [24], thought (and wrote) about the very interesting possibility of a polymer acquiring a helical screw sense when the polymer is

synthesized in a chiral medium. The helical sense would be that of the chiral medium in contact with the achiral polymer. *Can such a structure be formed? And what might such structures be good for?* Just such a structure has recently been reported [9<sup>\*</sup>] in the case of a polyacetylene, where the polymerization was carried out in a chiral environment. As de Gennes envisioned, such network formation in the presence of ordered media has attracted much attention due to the possibility of using such materials in display devices [25]. Formation of such networks and their application in storing information [26<sup>\*</sup>], as colorless pigments with color [27], as white reflectors [28], and in the study of piezoelectric effects [29–32] will be described as well. This brief review will describe the progress that has been made to answer the questions posed above.

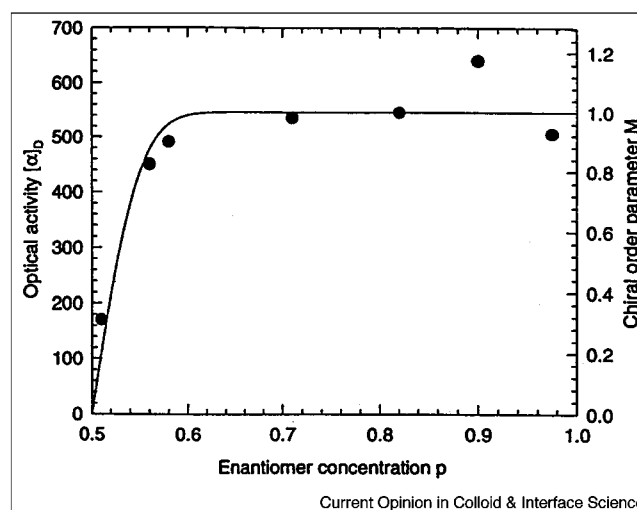
## Chiral information transfer

### Dilute solutions

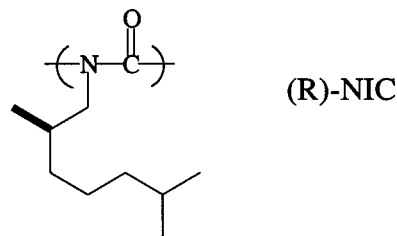
The simplest way to form a chiral nematic (cholesteric) phase is by the addition of a small amount of a chiral molecule (guest) to a nematic phase (host). Among the many polymers that have been studied in the past which form ordered phases, the polyisocyanates are a special class of materials, in that the nitrogen–carbon backbone with pendant sidegroups are forced to take on a helical conformation but with roughly equal numbers of right-handed and left-handed helices [33,34]. Thus the molecule is dynamically racemic, and when dissolved in appropriate solvents, forms a nematic phase and not a chiral nematic phase. However, in recent years much has been learnt about how to manipulate the helical sense of this particular macromolecule. Beautiful experiments carried out by Green *et al.* have established the general principles of how one can manipulate the overall helical sense of this macromolecule, with implications to perhaps one more mechanism for the origin of homochirality [35], as will be discussed at the end of this review.

When the pendant group is achiral, as in polyhexylisocyanate (PHIC), the molecular conformation in dilute solution is a dynamic racemic mixture. However, a polyisocyanate made from 2,6-dimethylheptyl isocyanate [(R)-NIC] with a low enantiomeric excess (the structure is shown below for the sake of clarity) exhibited optical activity that was virtually indistinguishable from that of a nearly enantiomerically pure sample [33]. This observation is quite remarkable considering the minute excess necessary to drive the helix reversals out of the polymeric system. Over the past decade, Green *et al.* have demonstrated that a very slight excess of one enantiomer in a copolymer will eliminate all the helix reversals in a dynamically racemic polyisocyanate, the required excess being as small as 1%.

Figure 1



Optical activity  $[\alpha]_D$  of a random copolyisocyanate as a function of enantiomer composition  $p$ .  $p$  is defined as the concentration of the right-handed enantiomeric pendant group. The solid line is given by the equation  $M \sim \text{erf}[(2L)^{1/2}(p-1/2)]$  where  $L$  is the domain size and  $M$  the chiral order parameter (Equation 4 in Ref. [36]). After 36.



The helical order of the polyisocyanates has been studied theoretically using both the *uniform* one-dimensional Ising model (in the case of homopolymers) and *random-field* Ising models (in the case of copolymers) in analogy with *magnetic* systems. In keeping the analogy with magnetic systems, the polymers are characterized by the chiral order parameter  $M$ , which is defined as the difference in the fractions of the two helical senses. Experimentally this order parameter is directly related to the optical activity normalized by the optical activity of a chain with one-handedness. The theory predicts  $M$  in terms of the chiral composition of polymer and the two key energetic parameters: the energy for a helix reversal  $\Delta G_r$ , and the chiral bias  $\Delta G_h$ , which is the energetic preference for the right- or left-handed helix. The model is in excellent agreement with the experiments [36<sup>\*</sup>] as is shown in Figure 1.

### Ordered phases

So far we have considered information transfer by a chiral element that is in the backbone of the polymer, while the starting point for this discussion was about information transfer from chiral dopant to the molecules comprising a nematic phase. In particular we are inter-

ested in information transfer in a lyotropic mesophase from a chiral additive or dopant as it is generally referred to. In comparison to thermotropic systems, the lyotropic phases have not received much attention. It was first demonstrated by Radley and Saupe [37] that amphiphilic systems can be transformed from their nematic phases to a chiral nematic (cholesteric) phase by the addition of optically active compounds. There have been some studies devoted to understanding how chirality in a macroscopic sense is transferred by a chiral additive [16,18<sup>••</sup>,19<sup>•</sup>].

Here again, Green *et al.* [18<sup>••</sup>] among others, have carried out beautiful experiments with the polyisocyanates. In general one can express the helical twisting power (HTP) of a chiral additive as  $\beta_m = (\rho cr)^{-1}$  where  $\rho$  is the pitch of the cholesteric helix ( $\mu\text{m}^{-1}$ ),  $c$  is the concentration (mol of solute/mol of solution), and  $r$  is the enantiomeric purity of the chiral additive. Both lyotropic and thermotropic liquid crystals have been studied, with far fewer studies on lyotropic fluids. In order to study the mechanism of twist induction, several chiral compounds having twisted biphenyl structures were studied primarily due to the fact that the molecules of the liquid crystal have biphenyl structures as well. It has been found that the helicity of the optically active bridged biphenyl molecules is the main factor determining their high helical twisting power [17,18<sup>••</sup>,38]. So, in essence, the transfer of chirality is thought to arise from the interaction between the chiral dopant and the molecules making up the liquid crystalline phase. In order to probe if the chiral additive is acting directly on say the polymer, in this instance PHIC, one can study the optical activity of the additive in dilute solutions of PHIC, since such a study is not feasible in the cholesteric state due to its large optical activity. It was found that the additive favored an excess of the helical senses of this dynamically racemic polymer even in dilute solution. It was also found that the HTP values of the dilute isotropic phase correlated well with those in the cholesteric phase, thus providing further evidence that a chiral additive in fact acts directly on the polymer chain, at least in this example, thus transferring the chiral information to the bulk of the fluid. Based on this observation Green *et al.* have used chiral additives as a probe of preferential solvation of helical polymers in mixed solvents [20]. Such studies will shed light on the mechanism of induction of the cholesteric phase.

Yarovoy and Labes studied the effects of a helical polymer dissolved in a micellar lyotropic mesophase [19<sup>•</sup>]. The helical polymer, hydroxypropylcellulose (HPC), in this case is the chiral additive. Based on the observations they came to the conclusion that HPC transfers the chiral information through a distortion of the shape of the micellar aggregates forming the nematic phase.

In a completely different system, Gray *et al.* have

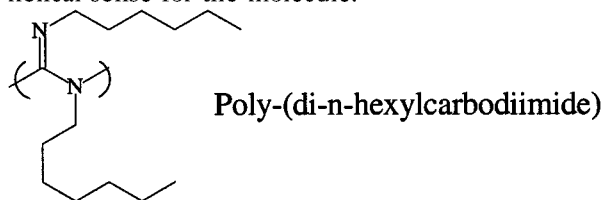
isolated crystallites of cellulose and chitin, which when suspended in water at the appropriate concentration and pH, will form a chiral nematic phase [39<sup>•</sup>,40<sup>•</sup>,41]. The cellulose or chitin crystallites can be considered as rodlike particles and the formation of an ordered phase is not surprising [39–41]. What is surprising, however, is the fact that they form a chiral nematic phase. The question then is what is responsible for the formation of this macroscopic chiral phase? The answer is not very clear, however, it is a very interesting phenomenon that deserves attention. One hypothesis is that the crystallites themselves have a geometric attribute that provides a chiral bias for the macroscopic phase. One might wonder if the chitin or cellulose crystallites might induce a chiral nematic phase in micellar mesophases.

### Chiral chaperon

In many systems of biological interest, the organization of macromolecular structure is mediated by molecules often referred to as molecular chaperones. However, it has been difficult to mimic such systems using synthetic polymers [42<sup>••</sup>]. There have been a few elegant examples of such behavior through the use of complexation. It has been noted that ‘L-proteins interact more avidly (than D-proteins) with D-nucleic acids’ (R.A. Hegstrom and D.K. Kondepudi, *Sci Am*, 1990, 253:98–105). Minsky *et al.* [21,22] show that plasmid DNA in bacteria interact rather preferentially with peptides exhibiting greater affinity toward L-peptides. However, this occurs only in the presence of DNA in the form of an ordered chiral nematic or cholesteric phase, thus leading to the suggestion that prominent chiral discrimination exists and it does so only in the presence of amplification of the inherent chirality, as is the case when a chiral nematic phase exists. It is intriguing that they report a change in the helical sense of the cholesteric phase (although not confirmed using microscopy) as indicated by the circular dichroism signals which are sensitive to a change in pH. They also reported that the chiral discrimination took place as long as the peptide had a slight excess of one enantiomer over the other, a remarkably similar result to those reported by Green *et al.* for PHICs.

A different kind of chiral amplification has been studied by Schlitzer and Novak [23]. They started with a chiral homopolymer made from *N*-(R)-2,6-(dimethylhexyl)-*N'*-hexylcarbodiimide and found that the polymer had trapped kinetic states because the optical rotation took sometime before reaching its equilibrium value. This led them to conclude that the molecule must be a dynamic helix. They then proceeded to remove the chiral center from the starting monomer so that one can in principle have a dynamic helix (the structure of the polymer is shown below) which, when protonated with (S)-camphorsulfonic acid, gave rise to

large optical rotation signalling the formation of a single helical sense for the molecule.



Control of chirality or the helical sense through protonation and complexation is likely to be very important in biological systems. For example, in the case of scarab beetles the exocuticle is made of chitin and is a multi-layer superstructure with alternating cholesteric and oriented layers of chitin [43]. The question then is how does the beetle grow structures like that? It is known that the oriented layer of chitin has in it uric acid; so perhaps the exocuticle structure may be due to ion pairing which leads to an unwinding of the cholesteric helix. This is only a hypothesis which may turn out to be completely incorrect. However, it is worthwhile to think about this mechanism as a possible way of producing such multilayered structures.

### Chiral reaction media and networks

As de Gennes envisioned some twenty years ago, network formation or the formation of polymeric materials in liquid crystalline phases has received considerable attention in the past few years due to the fact such networks are being considered as materials for better display devices. A beautiful illustration of polymerization in a chiral nematic medium [9], where the polymer formed is achiral, was recently reported recently. However, due to the fact that the polymerization was carried out in a chiral nematic medium, the polymer chains formed inherited the 'twist' of the reaction medium. In this case, the polyacetylene  $[-CH=CH-]_n$  was formed in a chiral nematic medium. One wonders how the chiral information of the reaction medium was transferred to the polymer chains during the polymerization? The mechanism for the transfer of this chiral information to the polymer chain was not discussed.

It is well known that chiral liquid crystals like cholesterics and chiral smectics are piezoelectric. Such materials are characterized by the appearance of electric polarization when a mechanical stress is applied. Since low molecular weight liquid crystals do not support a static shear stress, and behave like liquids, it was suggested by Brand [44] that ordered chiral networks might be good candidates for the study of piezoelectric properties. Chang, Chien and Meyer, in a very nice experiment [30], using a cholesteric network, found that a polarization in a direction normal to the helix and the shear stress can be induced on the application of a static shear stress in a direction perpendicular to the helix. The experiments were found to be in good agreement with the theory of Pelcovits and Meyer [45]. Terentjev

and Warner [31] proposed a molecular theory based on freely jointed chains of chiral monomers in a polymer network leading to predictions of three phenomenological piezoelectric coefficients. The molecular model at first glance seems to agree with the experiments of Meyer *et al.*

As is obvious I have left out many other areas of chirality that are worth discussing. I have left out work on chiral surfaces [46,47], chiral switching with polarized light [48], and reflectivity enhancements due to chiral surfaces [49,50]. I also have left out work that uses a chiral template during cyclopolymerization to transfer its chirality to a polymeric chain [51•]. Very recently, Zentel *et al.* [52••] reported on work done using polyisocyanates with a chiral azo chromophore, which when irradiated with light converted the dynamic helix to a single screw sense. It is conceivable that such systems will serve as a model system for creating structures that are akin to the exocuticles of the scarab beetles. I have tried to point out the importance of understanding chiral information transfer from a chiral molecule to the surrounding media, be it a polymer chain that is a dynamic helix or polymerization reaction in a chiral medium or generation of polarization in a chiral network. The mechanism discussed here for chiral amplification has been proposed as one more possible mechanism for amplification of chirality to account for the occurrence of homochirality [35]. There are still several issues related to chiral information transfer that are worth further study. How does the information about chirality get transferred in the case of cellulose and chitin crystallites? Can one form images purely based on chirality? Can such an image be used for work related to sequencing? Can there be phase separation at some small enough length scale in racemic mixtures of optically active polymers? Answers to many such questions will hopefully be found in the coming years.

### Noted added in proof

The author is thankful to Prof. ET Samulski for pointing out the following.

Czarniecak and Samulski [53] showed that the chiral nature of polypeptides (Poly- $\gamma$ -benzyl-L-glutamate, PBLG) in an oriented (compensated cholesteric) lyotropic LC is acquired by achiral probe molecules: the deuterium NMR spectra of achiral benzyl alcohol in PBLG LCs show an "induced" inequivalence of its benzyl protons which was attributed to conferred chirality via H-bonding of the alcohol to the chiral polypeptide. This conferred inequivalence was lost—"averaged away"—when the LC was composed of an equimolar mixture of right- and left-handed helices, a racemic mixture of PBLG and PBDG. The authors attributed this conferred probe chirality to biased collision complexes with a chiral macromolecular surface—a chiral

“grooved” surface on the exterior of the  $\alpha$ -helical polypeptide core. Such grooves were implicated in an early model of how chiral interactions might be transmitted from molecule-to-molecule to generate the helical (cholesteric) supramolecular structure evident in lyotropic polypeptide LCs. [54].

The polypeptides LC exhibits a curious anomaly: the sense of the cholesteric twist changes sign on changing one achiral solvent for another, e.g., methylene chloride versus dioxane. Moreover, in a mixed solvent, the cholesteric pitch can be compensated, a nematic LC forms! This observation in the context of the mechanical model alluded to above requires that the polypeptide sidechain secondary—the surface chirality—changes on changing the solvent. (PBLG is a right-handed  $\alpha$ -helix in both solvents.) Another explanation of this anomalous observation has to do with a potential more of transmitting chiral “forces” from molecular to molecule: Samulski and Samulski [55] showed that the sign of the asymmetry in Van der Waals-Lifshitz forces between two polarizable helices was a function of the dielectric permittivity of the medium in which the helices were embedded.

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