Defence Science Journal, Vol. 58, No. 5, September 2008, pp. 626-635

REVIEW PAPER

Chiral Nanoscience and Nanotechnology

Dibyendu S. Bag, T.C. Shami, and K.U. Bhasker Rao

Defence Materials and Stores Research and Development Establishment, Kanpur-208 013

ABSTRACT

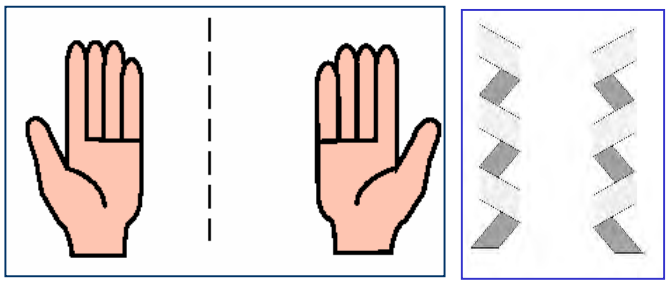
The paper reviews nanoscale science and technology of chiral molecules/macromolecules-under two subtopics-chiral nanotechnology and nano-chiral technology. Chiral nanotechnology discusses the nanotechnology, where molecular chirality plays a role in the properties of materials, including molecular switches, molecular motors, and other molecular devices; chiral supramolecules and self-assembled nanotubes and their functions are also highlighted. Nano-chiral technology describes the nanoscale approaches to chiral technology such as asymmetric synthesis and catalysis, chiral separation and detection, and enantiomeric analysis. Chiral sensors have also been included. The state-of-the-art chiral research at DMSRDE,Kanpur is also presented.

Keywords: Chiral nanotechnology, nano-chiral technology, molecular devices; chiral supramolecules and chiral nanotubes; chiral sensors

1. INTRODUCTION

Chiral nanoscience and nanotechnology, as the name indicates, include nanoscience and nanotechnology in which chirality plays a useful role. A chiral object is not superimposable on its mirror image. Examples include hands, screws, propellers, keys, etc. A person's right and left hands are almost identical, only reversed (Fig. 1). They are mirror images, but not superimposable on each other. Nonsuperimposability of left and right hands can be easily understood because gloves of left hand cannot be used for right hand. Throughout the biological world, in all living things, there are molecules which have such types of left- and right-hands forms and are chiral. The two forms of a chiral molecule are known as enantiomers (Fig. 2). The essential criterion of a molecule to be chiral is either the molecule has an asymmetric carbon centre (Fig.2) or the polymer molecule forming chain helicity [Fig. 1(b)]. Chiral molecules exhibit chiroptical properties and can rotate the plane-polarised light. Most naturally occurring bio-molecules/macromolecules, such as nucleic acids, proteins, and polysaccharides are chiral. About 97 per cent of the drugs derived from natural sources are optically active (only 2 per cent are racemates and only 1per cent are achiral). Chirality is essential for these molecules/macromolecules to exert their sophisticated functions in living systems to maintain life.

The word nano comes from the Greek word nanos which means dwarf. The nanometer is a factor of 10^{-9}, i.e., one-billionth of a meter; the size of a molecule. It is 10-times bigger than a hydrogen atom (dia 0.1 nm). On the other hand, width of a DNA molecule is 2.5 nm. Usually, nanoscience and nanotechnology work on the nanometer scale viz.1 nm to several hundred nanometers (usually 1-100 nm). Thus, nanoscience and nanotechnology have been defined as the ability to control or manipulate at the atomic, molecular or supra-molecular levels to create and use structures, devices, and systems with fundamentally new properties and functions resulting from their small structures. Two distinct strategies have been used to explore the nanometer domain: top-down and bottom-up approaches. Top-down approach manipulates progressively smaller



(a) (b)

Figure 1. Non-superimposable mirror images of: (a) person's left and right hands (b) left and right-handed helix.

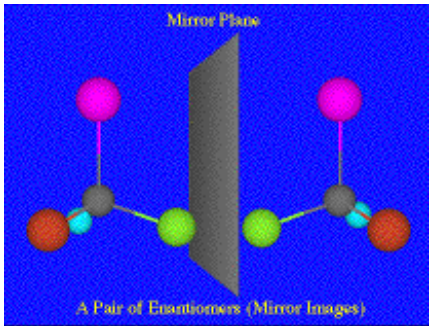


Figure 2. Two enantiomers of a molecule.

Received 01 May 2007, revised 29 October 2007

pieces of matter by lithography, embossing, and contact printing, while the bottom-up approach builds up nanoscale materials from smaller atoms or molecules.

The subject of chiral nanoscience and nanotechnology can be divided into two categories: (i) nanotechnology that benefits from molecular chirality which may be called chiral nanotechnology and (ii) nanoscale approaches to chiral technology, which can be called nano-chiral technology[1] It should be pointed out here that DNA is chiral by virtue of both the asymmetric centre in the ribose units and as a result of the twist of the helix. Many interesting features of DNA structures are observed on the nanometer scale such as DNA nanowires, nanodevices, molecular computing systems, etc. Recently, more interest has been shown to its application in nanotechnology. However, the DNA nanotechnology associated with the bionanotechnology and biomedicine is itself a vast subject and is beyond the scope of this review.

2. CHIRAL NANOTECHNOLOGY

Chiral nanotechnology means nanotechnology dependent upon molecular chirality. Exciting advances in research are going on towards the development of materials and devices that benefit explicitly from molecular chirality. Here, a few of such examples are given.

2.1 Chiroptical Molecular Switches

A molecular switch is a molecule that can be reversibly interconverted between two stable states upon external stimulus. Such switches may be photochemically triggered switches, chiroptical switches, redox switches, conformational switches etc. Chiroptical molecular switches are switches in which chiroptical properties are reversibly changed due to external stimuli such as temperature, light, chemical environment, etc[2]. A number of examples of such switches based on polymer solution and thin film have been reported. Two such chiroptical switches are based on chiral thermoresponsive molecules and chiral photoresponsive molecules (Fig. 3).

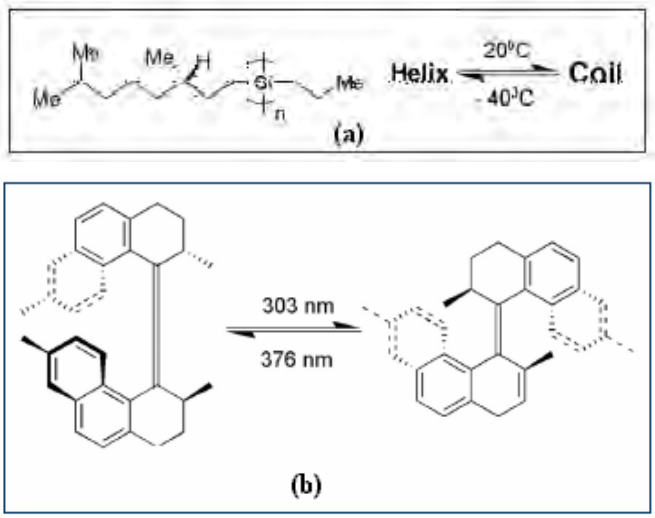


Figure 3. Chemical structures for chiroptical molecular switches: (a) thermo-driven switch of polysilane film[3] and (b) photodriven switch[4].

In principle, it may be possible to trigger the handedness between +1 and –1 states (helix-helix transition) or between +1 and 0 states (helix-coil transition). Chiral polysilane can function +1 and 0 states switching upon thermal stimulus. It shows predominately one helicity at low temperature (–40 °C) which was verified by circular dichroism and other techniques. When the temperature is changed to 20 °C, the helicity is diminished and transformed into coil. For the photoreversible molecule as shown in [Fig. 3 (b)], two distinct chiral states were achieved by light stimulus.

The photoreversible system is based on the interconversion of two chiral forms of helically shaped molecules which are denoted by P and M for right-and left-handed helical structures. The P and M helices in the chiral optical switch represent two distinct states in a binary logic element. Nondestructive read-out in an optical recording system containing these organic materials is feasible by monitoring the change in optical rotation at wavelengths remote from the wavelengths used for switching.

$$P \underset{h\nu_2}{\overset{h\nu_1}{\rightleftharpoons}} M$$

Now, the principle of an information storage system based on a chiroptical molecular switch, using stereo-isomers P and M of opposite helicity, is schematically shown in Fig. 4. Writing occurs with unpolarised light (UPL) at λ_1 (P → M) which is detected with linear polarized light (LPL), and finally erasing (M → P) takes place with UPL at λ_2.

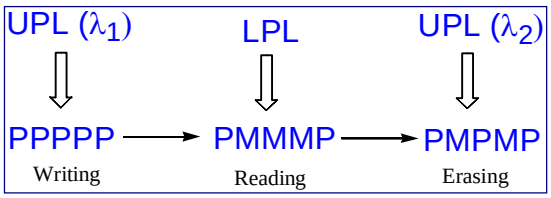


Figure 4. Schematic diagram of a chiral information storage device based on chiroptical switching.

Precise control of chirality at the molecular and macroscopic levels, i.e., the unique combination of molecular architechtures and optical properties of chiral photoresponsive molecules offer the development of multicomponent molecular switches[5] (Fig.5).

2.2 Chiroptical Molecular Motors

A molecular motor is a molecule that can undergo continuous, unidirectional motion in response to external stimuli to perform mechanical work[6]. The basic requirements

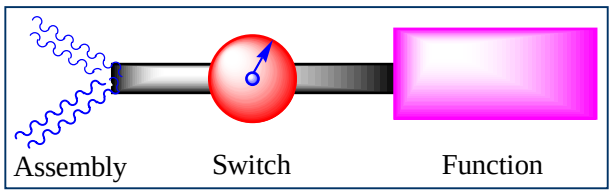


Figure 5. Multi-component chiroptical molecular switch.

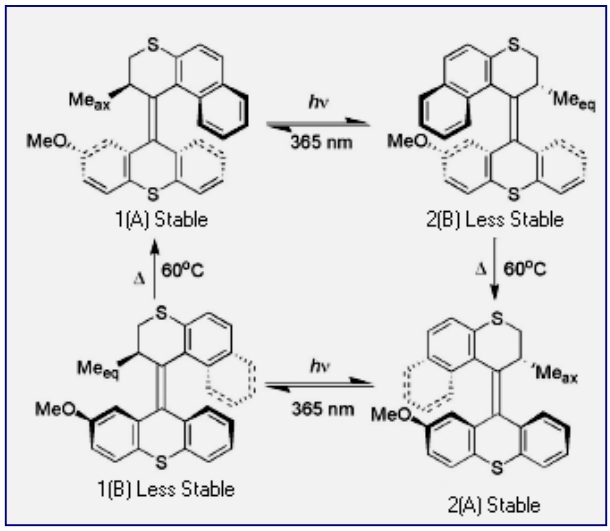


Figure 6. Different molecular structures and their interconversion for a photo-driven molecular motor system[7].

for a molecular motor are: (i) repetitive rotary motion, (ii) energy consumption, and (iii) unidirectional rotation. Chirality is critical for molecular motor design, providing an element of asymmetry that is required to produce useful work. An interesting light-driven molecular switch was elaborated to create a molecular motor. The helicity of the molecule changes from M to P upon irradiation. Using another wavelength of light converts the molecule's helicity back to the original state. A full 360° rotation cycle is achieved by two photochemical steps along with two alternate thermal steps (Fig. 6).

The rotation rate of this molecular motor is sensitive to stereochemistry of the molecule, substituents, steric hindrance, bridging atom, and ring structures. For example, changing sulphur into oxygen reduces the energy barrier for helix inversion by 5.1 kcal. Similarly, changing six-membered rings to five-member rings decrease the thermal barrier for helix inversion.

2.3 Other Molecular Devices

Chiral architectures from macromolecular building blocks have been reviewed recently[8]. Chiral polymers and liquid crystalline polymers with photochromic side chains and/or dichoric azo dye units represent novel promising materials for various photo-optical, opto-electronic and optical storage applications[9-10]. Optical properties of such polymer films that can be modified selectively and reversibly by light, have good potential for use in photonics.

2.4 Self-assembled Chiral Nanotubes and Supramolecules

Self-assembly is the autonomous organisation of components into patterns or structures without human intervention[11]. It is the most efficient strategy for the bottom-up approach in nanotechnology. Spatial disposition may be transferred from one or more chiral centers to macromolecular aggregates or supramolecules and then to the nanoscopic dimension[11-12].

Chiral, self-assembled nanotubes are particularly interesting and their references are found in several recent reports. A system is reported in which molecular chirality is expressed at the macromolecular level via two hierarchical processes[13]. A synthetic building block assembled into a racemic mixture of right (P)- and left (M)-handed helical rosette nanotubes. The system, i.e., the helical rosette nanotubes has tunable chiroptical properties depending on whether the crown ethers in the nanotube were fully or partially occupied with a promoter. The synthesized compound exists mainly in the non-assembled state. The promoter triggers a sequence of supramolecular reactions leading to the chiro-genesis of helical rosette nanotubes with predefined helicities (Fig.7).

A new class of nanotubes based on cyclic peptide molecules that consist of an even number of alternating D- and L-amino acids has been reported[14]. Through H-bonding interactions, these molecules self-assemble into nanotubes and arrange into ordered parallel arrays. The diameter and functions of the nanotubes depend on the amino acid residues and their composition in the ring. Self-assembled nanotubes from cyclic D, L-α-peptides and cyclic ß-peptides have also been reported[15-16]. Another example of self- assembled peptides is the assembly of anionic p-octiphenyls with homologous molecules containing guanidinium and ammonium cations into supramolecular oligomers and polymers in the presence of spherical lipid bilayers[17]. The

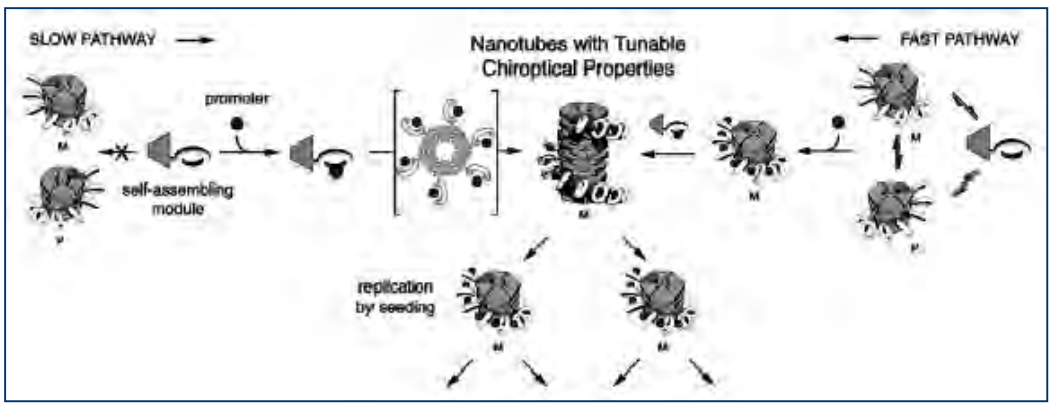


Figure 7. Supramolecular pathways of the formation of helical rosette nanotubes[13].

cylindrical assembly of oligomers like barrel pores could be programmed by electrostatic interactions between carboxylate anions and ammonium or guanidinium cations. Temperature-dependent circular dichroism (CD) experiments showed qualitative inversion of supramolecular chirality at intermediate and high temperatures. Chirality inversion was also triggered by solvent polarity.

Synthetic peptides with a large number of residues (32 or 33), based on the coiled-coil structural motif, are formed by two or more α-helical peptides that wrap around each other with a slight left-handed superhelical twist[18]. Mitchell et al. presented template-synthesised nanotubes with hydrophilic groups on the nanotube surface and lipophilic ones on the inner surface[19].

Self-assembly systems can form helical pores also. Amphiphilic dendritic dipeptides are reported to self-assemble into helical pores in solution and in the bulk through a complex recognition process[20]. A molecular model of a dendritic derivative of the dipeptide L-Tyr-L-Ala with a pore size of about 1.3 nm is shown in Fig. 8. The capability to modify

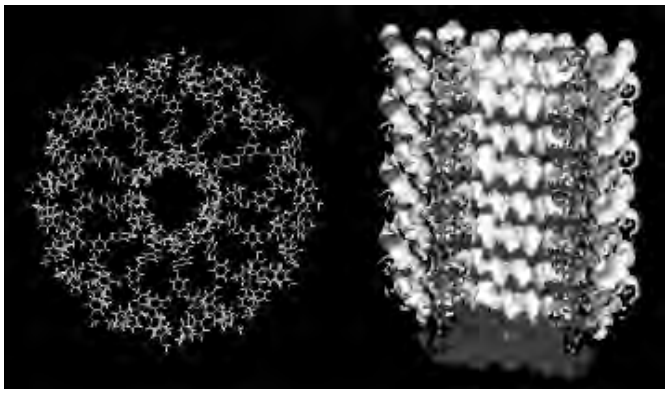


Figure 8. Self-assembled helical pore formation through a complex recognition process[20].

the pores suggests the application of this self-assembly strategy to a variety of biologically inspired systems with functional properties resulting from their porous structure.

Supramolecular engineering of polymers is an interesting and active area with strong conceptual overlap with chiral nanotechnology. For example, stereoselective interactions between mirror-image polymers have been reported. Stereoselective complexes of non-identical pairs of polymers with opposite chirality; namely, poly(L-peptides) and poly(D-lactic acid) provide a new approach to control delivery of peptides and proteins that depends on the stereo-interactions between the peptide and poly(D-lactic acid) at a molecular level[21]. Reinhoudt built an enantiomerically pure H-bonding assembly using the non-covalent chiral memory concept [21]. Three portions of achiral calix[4]arene dimelamines were assembled with six portions of chiral barbiturates through H-bonding. The handedness of the macromolecule was defined by the chirality of the barbiturates. If the barbiturates were replaced by achiral cyanurates, handedness persisted. The reason for the chiral memory effect is the stronger association of the latter.

C_3-Symmetrical molecules were also demonstrated to associate into supramolecular stacks (Fig. 9). Aromatic molecules with amide and urea substituents facilitated aggregation by π-π stacking and H-bond interactions to form nanostructured fibres and organic gels. The chirality of the side chain caused stacked columns to form helical configurations, which was verified by circular dichroism (CD) spectroscopy[23].

The applications of chiral nanotubes and supramolecular materials are reported mainly in the field of biotechnology and biomedicine e.g. preparation of novel antibacterial, cytotoxic and drug-delivery agents to catalysis and other applications in materials science such as smart nanotubes for bioseparation and biocatalysis.

3. NANO-CHIRAL TECHNOLOGY

Nano-chiral technology means nanoscale approaches to the important areas of chiral technology such as asymmetric synthesis and catalysis, chiral separation process, analytical technology for assay of enantiopure substances, etc. A variety of interesting and exciting approaches to nano-engineering of chiral synthesis, separation, and detection have been reported.

3.1 Nanomaterials for Asymmetric Synthesis

In the process of synthesising molecules by normal chemical reactions, both the right-and left-hand forms of the molecules tend to be produced. But just as human beings have a right- or left-handed preference, one form of the molecule tends to be very active and the other tends to be at best not very active, may be worst. For example, drug thalidomide originally used as a sedative which was prescribed to pregnant women to aid morning sickness. However, while one hand of the molecule relieved the

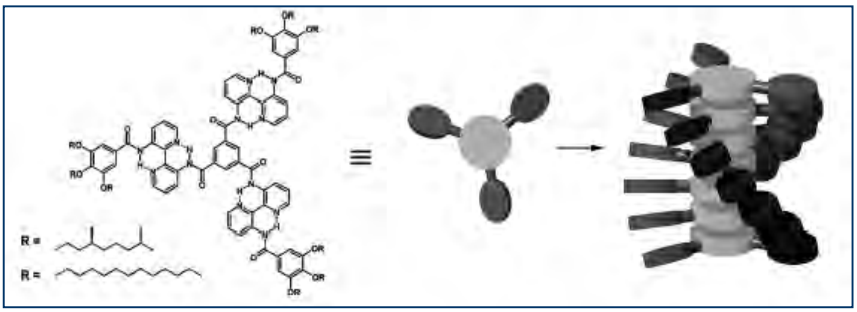


Figure 9. Self-assembled helical column aggregated by π-π stacking and H-bond interactions[23].

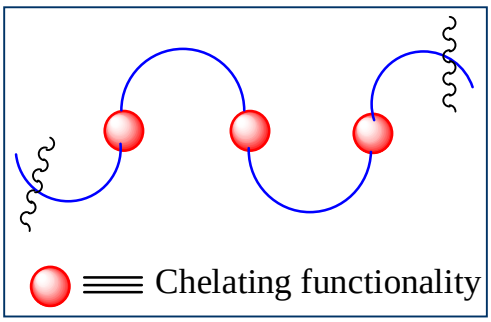


Figure 10. Schematic representation of a general chiral polymeric ligand.

woman's nausea, the other hand was toxic, and caused birth defects. Another common pharmaceutical example of chirality is the drug ibuprofen, commonly found in over-the-counter pain relievers. In its case, the molecule's left hand is 100-time more powerful than the right. Hence, the discovery of novel methods to produce enantiomerically pure compound (either left hand or the right hand) is very critical for the drug, pharmaceuticals, and agrochemicals industries.

Several classes of chiral polymers are found to provide unique chiral environment for many asymmetric synthesis[24-26]. In many cases, high levels of stereoselectivity are obtained under optimised conditions. General structure of a chiral polymeric ligand may be represented as shown in Fig. 10. The polymeric ligands offer many advantages:

- Ease of their separation: (a) many polymers function as insoluble ligands that can be removed from the reaction by simply filtration, (b) soluble ligands can be precipitated out from the solution when the reaction is complete.
- Possibility for many reactions to occur simultaneously on a single polymer.
- Each polymeric ligand may contain several sites for chelation and thus could dramatically increase the turnover number in comparison to comparable monomeric ligands.

Several issues related to nanotechnology may be of potential benefit to strategies in asymmetric synthesis and catalysis. Some such strategies are new, but some are related to long-established principles. For example, nanoporous zirconium phosphonates containing chiral dihydroxy functionalities were shown to catalyse heterogeneously the addition of diethylzinc to a wide range of aromatic aldehydes[27]. The chiral secondary alcohols produced possessed enantiopurity of up to 72 per cent (Fig. 11). This type of chiral porous hybrid solid can also catalyze the asymmetric hydrogenation of aromatic ketones and ß-keto esters[28]. Similarly, stereocontrol photooxidation of enecarbamates within confined spaces of zeolite has been reported[29]. Asymmetrically modified zeolites have also been employed to achieve high stereoselectivity in photo-oxygenation. This preference for Z or E alkenes was dictated by external interactions with the enecarbamate, such as cationic interactions of the carbonyl and phenyl groups with the zeolites. When oxazolidinone-substituted chiral enecarbamates were photo-oxidized inside chiral zeolite Y supercages, the Z and E diastereomers produced different enantiomers of the ketones by controlling the facially selective addition of oxygen to the double bond. The enantiopurity of the products was moderate, with an ee of about 50 per cent

3.2 Nanomaterials for Chiral Separation

Chiral separation is another area where nanoscale materials play significant role. Typically chiral separation is performed by column chromatography, preferential crystallisation, or stereoselective transformation. Ultrafiltration using chiral porous membranes has the advantage that it saves energy and can be scaled up easily. Antibody-based bio-nanotube membranes for enantiomeric drug separation was reported[30]. Nanoporous alumina films with pore diameters of 20 nm or 35 nm were used for enantiomeric drug separations[31].

General method for chiral imprinting of sol-gel thin films has been reported exhibiting enantioselectivity32. An example is based on the design of chiral cavity in a sol-gel matrix which can discriminate enantiomers. A template molecule such as propranolol, 2,2,2-trifluoro-1-(9-anthryl) ethanol, DOPA, or tyrosine was used to imprint a sol-gel matrix. After polymerisation and then removal of template obtained a well-defined cavity inside the sol-gel films. In the propranolol example, the (S) imprinted film recognized (S)-propranolol better, and the (R)-imprinted film recognised (R)-propranolol. Similarly, TiO_2 thin films imprinted by chiral carboxylic acids were also reported, which exhibited enantioselectivity[33]. A variety of other imprinting approaches are reported including polymers and dendrimers for chiral discrimination and separation[34].

3.3 Nanomaterials for Enantiomeric Analysis

Recently, novel enantiomeric- recognition strategies have been developed to obtain direct information on configuration and enantiopurity of substrates. Enantiomeric recognition of biological substrates can lead to better understanding of the mechanism of molecular recognition in biological systems. Helical polymer was reviewed recently for its application as chiral detection and amplification of chirality[35].

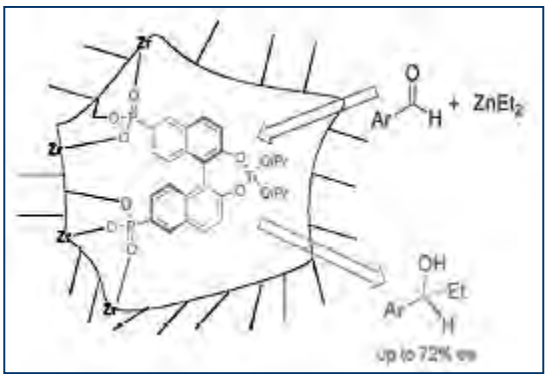


Figure 11. Nanoporous zirconium phosphonates containing chiral dihydroxy functionalities used for asymmetric catalysis.

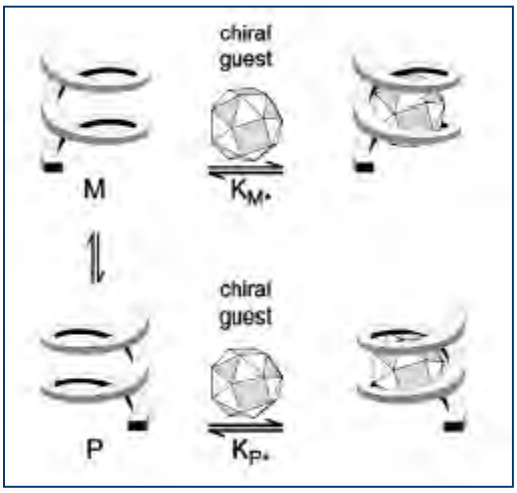


Figure 12. Schematic representation of nanoscale systems used for enantiomeric recognition: Foldamer system adopts helicity induced by complexation of small guests such as a-pinene[36].

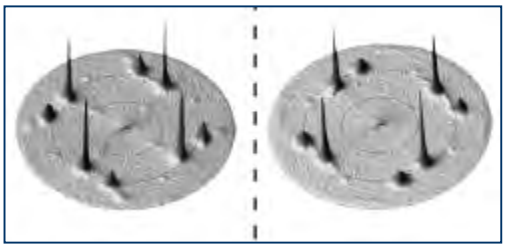


Figure 13. Chiral electrodeposited *CuO* film in the presence of (a) L-tartaric acid (left), and (b) D-tartaric acid (right): either a left-handed or right-handed orientation[37].

Polymers and oligimers, which fold into a compact helical conformation, are called foldamers. The absolute configuration of several small chiral guests was differentiated successfully using foldamers. An m-phenylene ethynylene oligomer folds into a compact helical conformation by π-π stacking interaction of the aromatic groups. The ordered conformation creates a high-affinity binding site for small molecules, and this cavity was used for enantiomeric recognition[36]. Small chiral guests, such as (-)-α-pinene and (+)-α-pinene, were detected successfully using this foldamer (Fig. 12). The M and P enantiomers of the foldamer have different binding abilities wrt a chiral guest; if KM* is larger than KP*, then the M conformation will dominate over the P conformation. This preference can easily be observed by circular dichroism spectroscopy.

4. CHIRAL SENSORS

Electrodeposited *CuO* onto achiral *Au*-substrates using solution templating chiral agents such as tartaric acid and amino acids produces chiral surfaces[37] (Fig. 13). Such chiral surfaces offer the possibility of developing heterogeneous enantioselective catalysts that can more readily be separated from the products and reused as compared to be the presently used homogeneous catalysts. In addition, the chiral *CuO* was also shown to function as a chiral electrochemical sensor. Such electrochemical sensor surfaces can serve for sensing chiral biomolecules and pharmaceuticals[38]. The implantable chiral sensors could be used to monitor drug levels in the body. It would allow diabetics to monitor blood sugar levels. Chiral electrochemical sensors may be developed to detect chemical warfare agents.

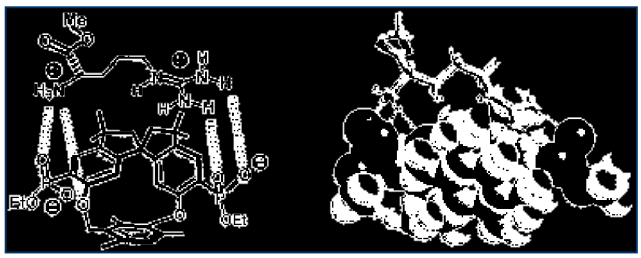


Figure 14. Schematic representation of molecular interaction of analytes in chiral sensor[39].

Means of distinguishing between enantiomers of a chiral molecule are of critical importance in many areas of analytical chemistry and biotechnology, particularly in drug design and synthesis. In particular, sensor systems capable of distinguishing between the left- and right-handed forms of chiral drugs would be of tremendous pharmaceutical value. Hence the design of such molecular sensors is one of the most pressing challenges. A chiral sensor for arginine and lysine has been reported[39] which is based on a spirobisindane skeleton (Fig. 14). Of all the amino acid methyl esters, only those of lysine and arginine with the correct distance between their cationic groups have been recognised.

The chiral discrimination of D- and L -monosaccharides using a designed receptor molecule that acts as a sensor by virtue of its fluorescent response to binding of the guest species has been reported[40]. The receptor contains boronic acid groups that bind saccharides by covalent interactions and has an advantage over others based on H-bonding interactions for which polar protic solvents such as water can compete with guest binding. This water-soluble molecular sensor might form the basis of a quantitative and selective analytical methods for saccharides.

Based on the stereoselectivity of immunoglobulins, a chiral sensor for the detection of low-molecular-weight analytes has been reported[41]. Such immuno-sensors can readily detect traces of enantiomeric impurities and are attractive for a range of applications in science and industry. Underivatised α-amino acids can be monitored in a competitive assay by their interaction with antibodies specific for the chiral centre of this class of substances.

Enantioselective sensors and biosensors in the analysis of chiral drugs have been reviewed[42]. Enantioselective sensors based on antibody-mediated nanomechanics have been reported[43]. An antibody was covalently immobilised, forming a receptor layer on the nanostructured side of microfabricated cantilevers (MC) and thereby providing a bioaffinity sensor (Fig. 15). The antibodies bind selectively to a wide variety of D- or L- α-amino acids. Stereoselective interaction of the receptor (antibody) with analytes (amino acids)

Figure 15. Microfabricated cantilevers with surface-immobilised antibodies (gray and yellow symbols) bind only with enantiomers of the correct configuration (red and cyan symbols), detected by the deflection of a laser beam[43].

induced nanoscale mechanical bending of the cantilever, which was detected by the deflection of a laser beam.

Chiral selectors such as crown ethers, cyclodextrins, and enzymes were used for both chromatographic enantioseparation methods and enantioselective electrochemical sensors and biosensors. The enantioselective sensors and biosensors have the advantages over separation techniques. However, detail discussion is beyond the scope of the review.

5. CHIRAL RESEARCH AT DMSRDE

The research activity of the development of novel chiral polymers, particularly for application in EM- absorbing coating, was commenced in 2003 at DMSRDE[44-45]. For the perspective of technology development in large- scale synthesis of any developed material, initial thought was put to synthesise chiral polymers by simple free-radical polymerisation process. In order to achieve it, we have to have vinyl monomers with chiral moieties i.e., chiral vinyl monomers. However, chiral vinyl monomers are not commercially available. Therefore, initially we designed chiral vinyl monomers based on a chiral D(+) aromatic amine compound. The polymerisation of such monomer produces chiral polymer. To achieve chain helicity, the chiral vinyl monomer was copolymerised with other vinyl monomers of different functionalities such as methacrylates, acrylamides and methacrylamides. Thus, a series of copolymers and terpolymers were synthesised. The chain helicity was achieved to be 69 per cent due to H-bonding and secondary interactions in a copolymer, [2-alkyl-N-(1-aryl alkyl) acrylamide-Co-acrylates]. The polymer helix chain was converted to random coil by thermal energy i.e., helix-coil transition which was observed by DSC analysis. Similarly, chiral polymers were synthesised using the counterpart, i.e., L(-) aromatic amine compound. The chiroptical properties of such chiral polymers and copolymers have been extensively studied[46-49].

In another approach, chiral amino acids such as L-leucine, L-valine containing vinyl monomers have been synthesised followed by polymerisation and copolymerisation to obtain chiral polymers and copolymers[50]. A L-leucine containing chiral polymer exhibited chiral amplification as high as 233 per cent in ethanol solvent. The predominant secondary structure is due to H-bonding which is observed by circular dichroism. They exhibit reversible swelling-deswelling behavior by change of *pH* and solvent.

The chiral polymers are prepared in the form of powder, beads, spheres, fibre and film forms. SEM micrographs of some samples are given in Figs 16-18. These have also been prepared in the form of cross-linked chiral spheres. Apart from the use of chiral polymers for EM application, these may also be explored for other novel applications. The behaviour of helix-coil transition of chiral polymers may be explored for further development of chiroptical molecular switches and devices. The reversible responses to external environment such as change of *pH* and solvent make this class of amino acid containing chiral polymer as potential candidate for mechanical responder and drug delivery application. A chiral film was observed to absorb chiral amine compound which is measured by CD spectroscopy. This type of film may be used for chiral sensor. Chiral cross-linked spheres may be used for chiral separation

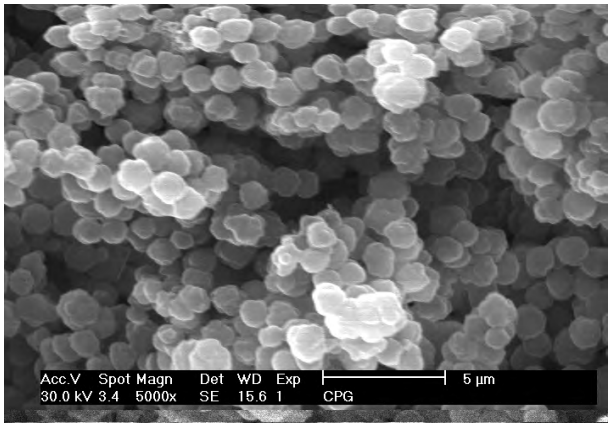


Figure 16. SEM micrograph of chiral beads.

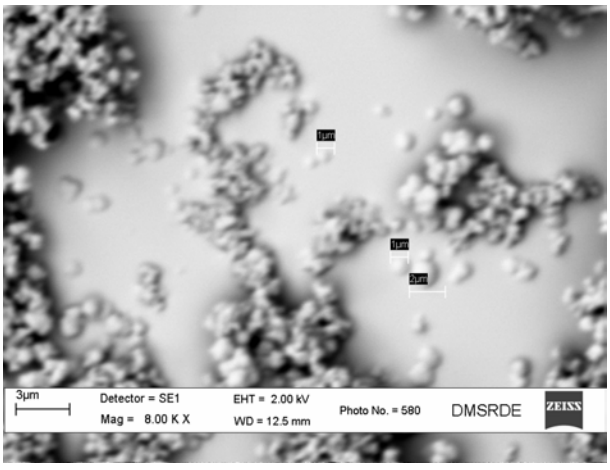


Figure 17. SEM micrograph of cross-linked chiral spheres.

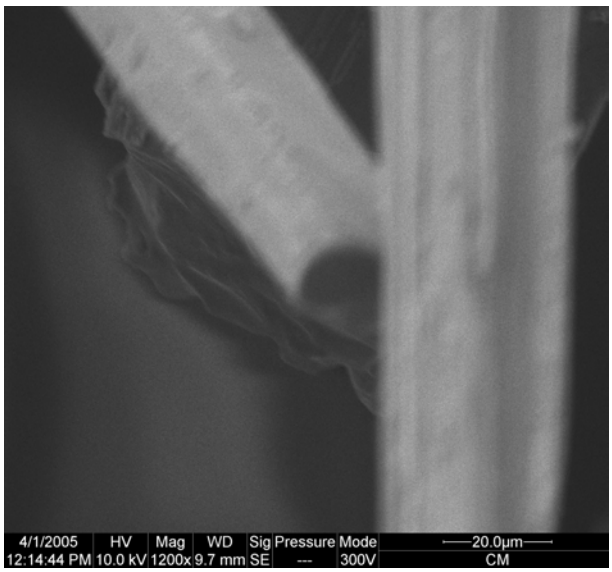


Figure 18. SEM micrograph of hollow chiral fibre.

process. There is a possibility of making chiroptical devices based on the high chiral amplification behaviour. The chiral materials may also be used for nonlinear optical application. Synthesis procedures for synthesising various novel chiral polymers have been established. Characterisation facilities, particularly measurement of chiroptical properties have been created. Different possible applications of novel chiral polymers in defence system have been initiated particularly with electrooptical and NLO applications.

6. CHIRAL RESEARCH IN INDIA

The research in the field of chiral nanoscience and nanotechnology in India is scanty. All aspects of chiral research including small organic molecules would become a huge subject to cover, and hence, the discussion is limited to chiral polymers only. Based on the information available in the open literature, the state-of-the art of chiral research in India is summarised below:

1. In Chirality-2007: 19th International Symposium on Chirality (ISCD-19) held at San Deigo, USA during July 8-11, 2007, two papers were represented on behalf of India: one from our group, DMSRDE, Kanpur which is related to chiral polymers and another from Birla Institute of Technology and Science (BITS), Pilani which is related to peptide synthesis.
2. A research project on "side chain chiral liquid crystal polymers", has been sanctioned to Thapar University, Patiala by DST, Govt. of India.
3. The research on chiral liquid crystal polymers for nonlinear optics is being carried out at Cochin University of Science and Technology.
4. Polymer anchored chiral catalyst is being utilised for asymmetric Michael addition reactions at the Indian Institute of Technology, Madras, Chennai.
5. Hierarchical structures of chiral coordination polymers are being explored for optical second harmonic generation (SHG) capability at the University of Hyderabad.
6. Research on chiral polymers as well as its optical applications is being carried out at the National Chemical Laboratory (NCL), Pune.

In the opinion of the authors, the chiral research in India is scattered and not focused as chiral research only. At this juncture, only the commercial aspect of chiral technology is mentioned here. The worldwide sale of chiral technology-enabling products (products for chiral manufacturing and chiral analysis) was 1910 million$ in1999 and 3,007 million$ in 2004. Thus, an average annual growth rate is 9.5 per cent.

7. CONCLUSIONS

Chiral phenomena have been a part of the excitement as nanoscience and nanotechnology have evolved. The goal is to use nanotechnology for new approaches to solving problems in chiral technology or to use molecular chirality to engineer useful properties in nanoscale materials. A number of nano-innovations have appeared in the realm of chiral technology. All aspects of chiral technology, including synthesis, separation, and analysis have already seen nanoscale revolutionary approaches. New developments are worth watching.

Many nanotech innovations benefit greatly from molecular chirality. The development of molecular devices such as chiroptical molecular switches, molecular motor, etc appears very intriguing where chirality can play the determinative role for providing useful work in many applications.

Supramolecules and self-assembled structures on nanometer scale, e.g., nanotubes, nanopores of different functionalities are other interesting areas which are being explored for a number of applications such as preparation of antibacterial agents, drug-delivery agents, catalysts and bio-recognition and bio-separation processes. Chiral sensor is another broad area of extreme excitement. Chiral sensor may be implanted into body and used to monitor drug levels in the body. It could be extended for sensing chemical war-fare agents. It is hoped that chiral sensors based on molecular-recognition principle would become a future strategy for detecting chemical and biological warfare agents for defence applications. Chiral membrane or film may also act as molecular absorber for such agents. The areas of chiral nanoscience and nanotechnology represent an approach with exceptionally strong promise for further developments.

ACKNOLEDGEMENT

One of the authors, Mr D.S. Bag gratefully acknowledges Prof G.N. Mathur, Former Director of this Establishment for his active interest and encouragement to initiate research activity on this novel field of chiral polymers.

REFERENCES

1. Zhang, J.; Albelda, M. T.; Liu, Y. & Canary, J.W. Chiral nanotechnology. *Chirality*, 2005, **17**, 404-20.
2. Feringa, B.L; van Delden, R.A.; Koumura, N. & Geertsema, E. Chiroptical molecular switches. *Chem. Rev.*, 2000, **100**, 1789-816.

3. Kim, S.Y.; Fujiki, M.; Ohira, A.; Kwak, G. & Kawakami, Y. Thermodriven chiroptical switching of a polysilane thin film. *Macromolecules*, 2004, **37**, 4321-324.
4. van Delden, R.A.; ter Wiel, M. K. J. & Feringa, B.L. A chiroptical molecular switch with perfect stereocontrol. *Chem. Commun*., 2004, 200-201.
5. Feringa, B.L; Huck, N.P.M. & Schoevaars, A.M. Chiroptical molecular switches. *Adv. Mater*., 1996, **8** (8), 681-84.
6. Davis, A. P. Synthetic molecular motors. *Nature*, 1999, **401**, 120-21.
7. Koumura, N.; Geertsema, E. M.; van Gelder, M. B.; Meetsma, A. & Feringa, B. L. Second generation light-driven molecular motors. Unidirectional rotation controlled by a single stereogenic center with near-perfect photoequilibria and acceleration of the speed of rotation by structural modification. *J. Am. Chem. Soc.*, 2002, **124**, 5037-051.
8. Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R.J.M. & Sommerdijk, N. A. J. M. Chiral architectures from molecular building blocks. *Chem. Rev.*, 2001, **101**, 4039-470.
9. Kozlovsky, M. V. Chiral polymers with photoaffected phase behavior for photo-optical and optoelectronic applications. *Synth. Met*., 2002, **127**, 67-70.
10. Liu, J. H. & Yang, P. C. Preparation and optical performance of chiral polymers having azobenzene segments. *J. Appl. Polym. Sci*., 2004, **91**, 3693-704.
11. Whitesides, G. M. & Grzybowski, B.Self-assembly at all scales. *Science*, 2002, **295**, 2418-421.
12. Mateos-Timoneda, M. A.; Crego-Calama, M. & Reinhoudt, D.N. Supramolecular chirality of self-assembled systems in solution. *Chem. Soc. Rev.*, 2004, **33**, 363-72.
13. Fenniri, H.; Deng, B.L. & Ribbe, A. E. Helical rosette nanotubes with tunable chiroptical properties. *J. Am. Chem. Soc*., 2002, **124**, 11064-1072.
14. Ghadiri, M. R.; Granja, J. R. & Buehler, L.K. Artificial trans-membrane ion channels from self-assembling peptide nanotubes. *Nature*, 1994, **369**, 301-04
15. Hartgerink, J. D.; Clark, T. D. & Ghadiri, M.R. Peptides nanotubes and beyond. *Chem. Euro J*., 1998, **4**, 1367-372
16. Bong, D.T.; Clark, T. D.; Granja, J. R. & Ghadiri, M. R. Self-assembling organic nanotubes. *Angew. Chem. Int. Ed.*, 2001, **40**, 988-1011.
17. Sakai, N. & Matile, S. Programmed assembly of rigid-rod ß-barrel pores: thermal inversion of chirality. *Chirality*, 2004, **16**, S28-S35.
18. Severin, K.; Lee, D.H.; Kennan, A. J. & Ghadiri, M. R. A synthetic peptide ligase. *Nature*, 1997, **389**, 706-709.
19. Mitchell, D. T.; Lee, S. B. & Trofin, L.; Li, N.; Nevanen, T. K.; So¨derlund, H & Martin, C. R. Smart nanotubes for bioseparations and biocatalysis. *J. Am. Chem. Soc*., 2002, **124**, 11864-1865.
20. Percec, V.; Dulcey, A. E.; Balagurusamy, V. S. K.; Miura, Y.; Smidrkal, J.; Peterca, M.; Nummelin, S.; Edlund, U.; Hudson, S. D.; Heiney, P. A.; Duan, H.; Magonov, S. N. & Vinogradov, S. A. Self-assembly of amphiphilic dendritic dipeptides into helical pores. *Nature*, 2004, **430**, 764-68.
21. Slager, J.; Cohen, Y.; Khalfin, R.; Talmon Y. & Domb, A. J. Peptides form stereoselective complexes with chiral polymers. *Macromolecules*, 2003, **36**, 2999-3000.
22. Prins, L.J.; de Jong, F.; Timmerman, P. & Reinhoudt, D. N. An enantiomerically pure hydrogen-bonded assembly. *Nature*, 2000, **408**, 181-184.
23. van Gorp, J. J.; Vekemans, J. A. J. M.& Meijer, E. W. C_3-Symmetrical supramolecular architectures:fibres and organic gels from discotic trisamides and trisureas. *J. Am. Chem. Soc.*, 2002, **124**, 14759-4769.
24. Pu, L. Recent developments in asymmetric catalysis using synthetic polymers with main chain chirality. *Tet. Assymm.*, 1998, **9**, 1457.
25. Jayaprakash, D.; Kobayashi, Y.; Arai, T.; Hu, Q.; Zheng, X.; Pu, L. & Sasai, H. Catalytic Epoxidation of a, ß-unsaturated ketones using polymeric BINOL. *J. Mol. Cat. A: Chem*., 2003, **196**, 145.
26. Reggelin, M.; Doerr, S.; Klussmann, M.; Schultz, M. & Holbach, M.Helical chiral polymers: A class of ligands for asymmetric catalysis. *Proc. Natl. Acad. Sci.*, 2004, 101, 5461-465.
27. Ngo, H. L; Hu, A. & Lin, W. Molecular building block approaches to chiral porous zirconium phosphates for asymmetric catalysts. *J. Mol .Catal. A: Chem*., 2004, **215**,177-86.
28. Hu, A.; Ngo, H.L. & Lin, W. Chiral porous, hybrid solids for highly enantioselective heterogeneous asymmetric hydrogenation of ß-keto esters. *Angew. Chem. Int. Ed*. 2003, **42**, 6000-003.
29. Sivaguru, J.; Poon, T.; Franz, R.; Jockusch, S.; Adam W. & Turro, N. J. Stereocontrol within confined spaces:enantioselective photooxidation of enecarbamates inside zeolite supercages., *J. Am. Chem. Soc*.2004, **126** ,10816-0817.
30. Higuchi, A.; Higuchi, Y.; Furuta, K.; Yoon, B.O.; Hara, M.; Maniwa, S.; Saitoh, M. & Sanui, K. Chiral separation of phenylalanine by ultrafiltration through immobilized DNA membranes. *J. Mater. Sci.*, 2003, **221**, 207-08.
31. Lee, S.B.; Mitchell, D. T.; Trofin, L.; Nevanen, T.K.; Soderlind H. & Martin, C.R. Antibody-based bio-nanotube membranes for enantiomeric drug separations. *Science*, 2002, **296**, 2198-200.
32. Fireman-Shoresh, S.; Avnir, D. & Marx, S. General method for chiral imprinting of sol-gel thin films exhibiting enantioselectivity. *Chem. Mater*. 2003, **15**, 3607-613.
33. Lahav, M.; Kharitonov, A.B. & Willner, I. Imprinting of chiral molecular recognition sites in thin TiO2 films associated with field-effect transistors: novel functionalized devices for chirospecific analysis. *Chem. Eur. J*. 2001, **7**, 3992-997.
34. Palmer, C.P.& McCarney, J.P. Development in the use of soluble ionic polymers as pseudo-stationary phases for electrochromatography. J. Chromatogr. A, 2004, **1044**, 159-76

35. Yashima, E.; Maeda, K. & Nishimura, T. Detection and amplification of chirality by helical polymers. *Chem. Eur. J.*, 2004, **10**, 42-51.
36. Prince, R.B.; Barnes, S.A. & Moore, J.S. Foldamer-based molecular recognition. *J. Am. Chem. Soc.*, 2000, **122**, 2758-762.
37. Switzer, J. A.; Kothari, H.M.; Poizot, P.; Nakanishi S. & Bohannan, E.W. Enantiospecific electrodeposition of a chiral catalyst. *Nature*, 2003, **425**, 490-493.
38. Kothari, H.M.; Kulp, E.A.; Boonsalee, S; Nikiforov, M.P.; Bohannan, E.W.; Poizot, P.; Nakanishi, S. & Switzer, J. A. Enantiospecific eletrodeposition of chiral CuO film from aqueous Cu (II) complexes of tartaric and amino acids on single-crystal Au (001). *Chem. Mater*. 2004, **16**, 4232-244
39. Wehner, M.; Schrader, T.; Finocchiaro, P.; Failla, S. & Consiglio, G. A chiral sensor for Arginine and Lysine. *Org. Lett.*, 2000, **2**, 605-08.
40. James, T. D.; Samankumara, K. R. A. & Shinkai, S. Chiral discrimination of monosaccharides using a fluorescent molecular sensor. *Nature*, 2002, **374**, 345-47.
41. Hofstetter, O.; Hofstetter, H.; Wilchek, M.; Schurig, V. & Green, B. S. Chiral discrimination using an immunosensor. *Nature Biotechnology*, 1999, **17**, 371-74.
42. Stefan, R.I.; van Staden, J.F. & Aboul-Enein, H. Y. Analysis of chiral drugs with enantioselective biosensor: An overview. *Electroanalysis*, 1999, **11**, 1233-235.
43. Dutta, P.; Tipple, C. A.; Lavrik, N.V.; Datskos, P.G.; Hofstetter, H.; Hofstetter, O. & Sepaniak, M. J. Enantioselective sensors based on antibody-mediated nanomechanics. *Anal. Chem.* 2003, **75**, 2342-348.
44. Bag, D.S.; Lal D. & Mathur, G.N. A chiral polymer material for EM wave attenuation and the process thereof. *Indian Pat.*, Appl. No. 1265/DEL/2005
45. Bag, D.S.; Lal D. & Mathur, G.N. A process for the preparation of chiral fiber material for EM wave attenuation, *Ind. Pat.* Appl. No. 1260/DEL/2005
46. Bag, D.S.; Lal D. & Mathur, G.N. Study of a chiral polymer using circular dichroism (CD) spectroscopy. *In* Proceedings of Int. Symp. Adv. Mater. and Processing (ISMAP), edited by B. Adhikari, *et.al*, IIT Kharagpur, 2004, pp. 528-33
47. Bag, D.S.; Lal, D. & Bhasker Rao, K.U. Characterisation of chiroptical properties of chiral copolymers. *In* Proceedings of National Seminar on Polym. Maters.: Present Status and Future Prospects, ATIRA, Ahmedabad, December 2005, 10-11.
48. Bag, D.S.; Shami, T.C. & Bhasker Rao, K.U. Chiroptical properties of chiral polymers. *In* Proceedings of Polys. for Adv. Techn., (Macro-2006: 9th National Conference of SPS, India), NCL Pune, Dec., 2006, 17-20.
49. Bag, D.S.; Shami, T.C. & Bhasker Rao, K.U. Synthesis and characterisation of a chiral polymer, poly [D-(+) a-methyl benzyl methacryloylamine]. *J. Polym. Mater.* (Accepted for Publication)
50. Bag, D.S.; Dutta; Shami T.C. & Bhasker Rao, K.U. Study of chiroptical properties of L-leucine containing chiral monomer and its polymer. Chirality 2007: *19th Int. Symp. on Chirality (ISCD 19)*, San Diego, CA, USA, July 2007 8-11.