Chirality, Amplification, and Molecular Switching in the Helical Polyguanidines

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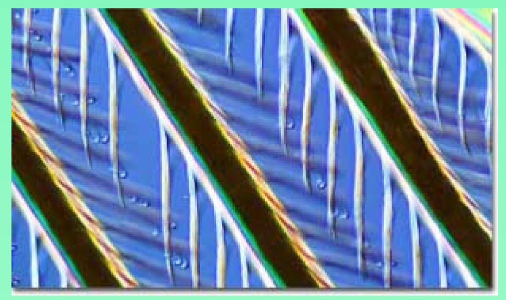
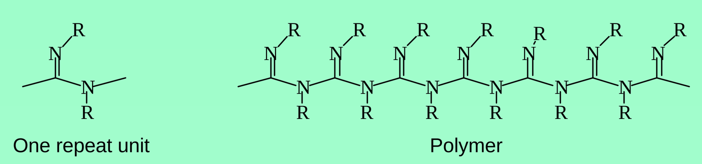
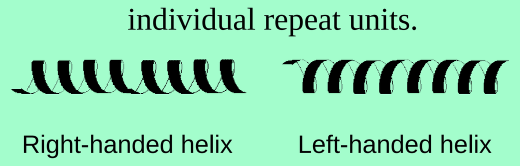


The most brilliant colors of nature like those of butterfly wings or bird feathers are created not by dyes but from the selective diffraction of light. Using liquid crystals and nanotechnology we create mimics of these natural gratings and impart unusual properties into synthetic materials.

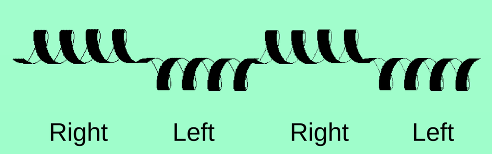
We have been interested in polymers that adopt extended chain, helical conformations. These helical polymers have a variety of uses such as reversible optical storage, chiral separations, and as chiral catalyst supports. Many of these polymers are made up of individual chains that have regions of right- and left-handed helices. Enantiomerically pure chiral groups added to helical polymers bias the polymer toward either the right- or left-handed sense. For many applications, the reversible switching of the helical sense would have utility. Controlling the switching process is possible if; 1) the kinetic barrier of helix inversion is sufficiently low, and 2) in addition to chiral groups, the polymer's side chains contain switching elements. One potential switch is an azobenzene moiety, which can undergo *trans* to *cis* photochemical isomerization. To this end, we are currently investigating helical polyguanidines with side chains containing chiral azobenzene units and the effect of the reversible photochemical isomerization of those azo chromophores.



Polymers are large molecules made up of thousands of individual repeat units.



Many natural polymers have a helical shape, or **conformation**.



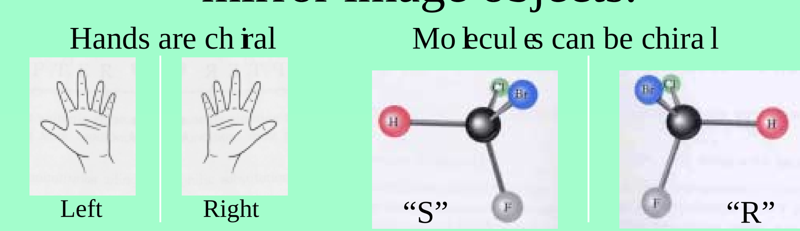
Some synthetic polymers such as **polyguanidines** also have this helical conformation; however, it is usually a mixture of left- and right- handed helical segments.

A polymers **conformation** can strongly influence it's **properties**.

CONFORMATION	Purely Right handed helix	Mixture of right and left handed helices
Solution Properties	rod-like Polymer	worm-like Polymer
Solid State Properties	HIGHER thermal stability	LOWER thermal stability
Liquid Crystal Properties	Cholesteric	Nematic

If we can influence the conformation of the polymer we can influence the properties of the material.

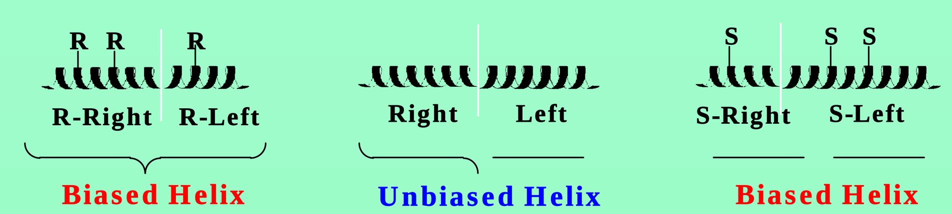
Chirality: A property of non-superimposable mirror image objects.



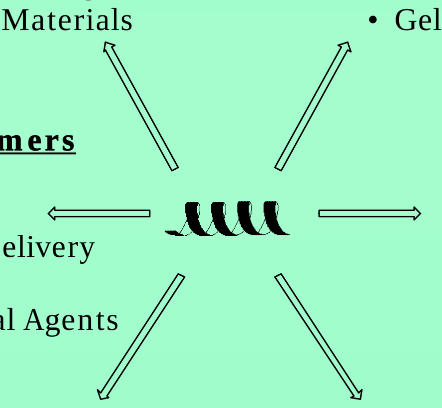
Left-handed and right-handed helices are chiral

Right Left

Adding chiral molecules to helical polymers biases the helical sense.



Applications of Helical Polymers



Optical Device Applications
- Reversible Optical Storage
- Nonlinear Optical Materials

Chiral Separations
- Chiral HPLC Columns
- Gel Technologies

Biomimetic Polymers
- Artificial Proteins
- Ion Channels
- Controlled Drug Delivery Systems
- Antibacterial/Viral Agents

Asymmetric Catalysis
- Chiral Catalyst Supports
- Chiral, Polymeric Acid/Base Catalysts

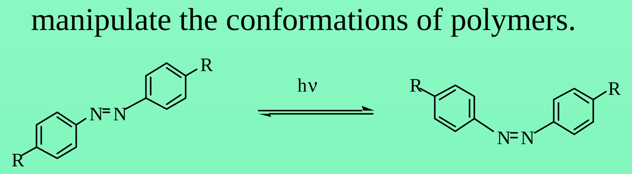
Recyclable/Degradable Polymers
- New Degradation Strategies
- Activation by Chiral-Achiral Switching

High Strength Materials
- Liquid Crystalline Polymers
- Thermoplastic Elastomers
- Organic-Inorganic Composites
- High Strength Fibers

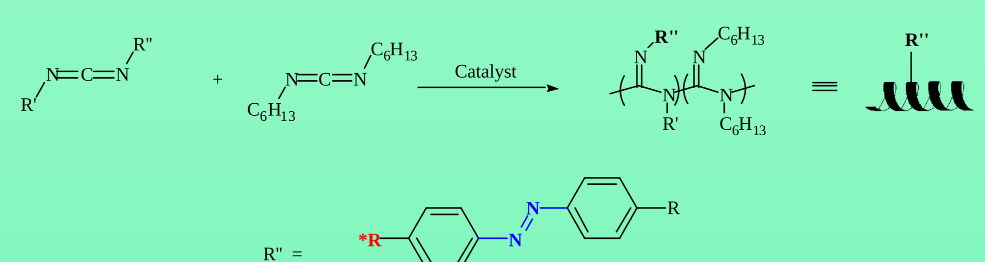
We manipulate the conformation of helical polyguanidines using chiral side groups and switching elements.

Some molecules change their conformation in response to outside influence, e.g. ultraviolet light.

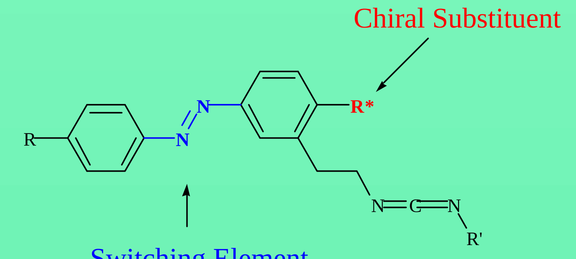
We want to take advantage of this "switching" to reversibly manipulate the conformations of polymers.



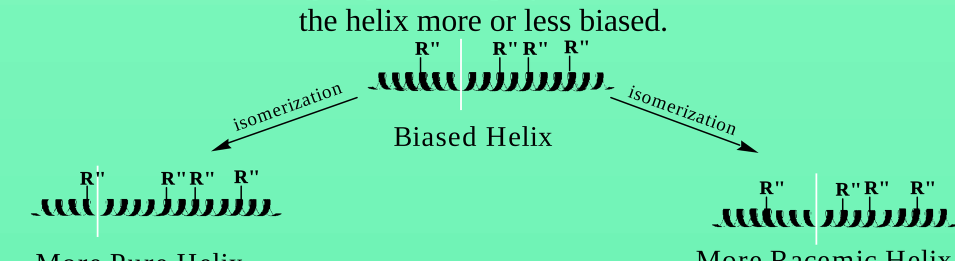
Isomerization of azobenzene



Our carbodiimide monomers contain both chiral substituents and azobenzene switching elements.

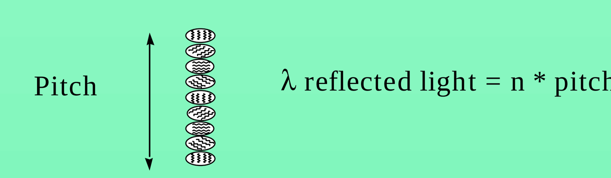


Isomerization of the azobenzene unit changes interactions between the chiral group and the polymer backbone which makes the helix more or less biased.

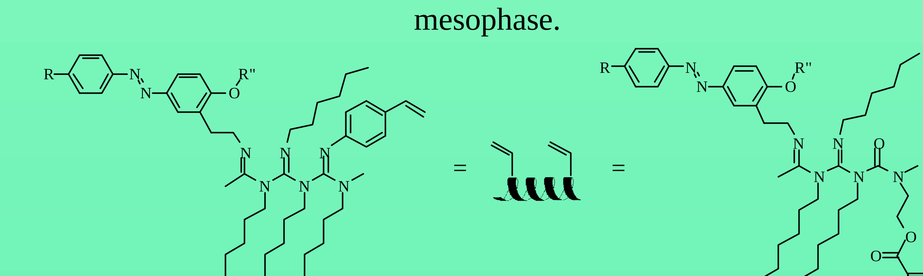


We use liquid crystalline properties of helical poymers for selective diffraction of light.

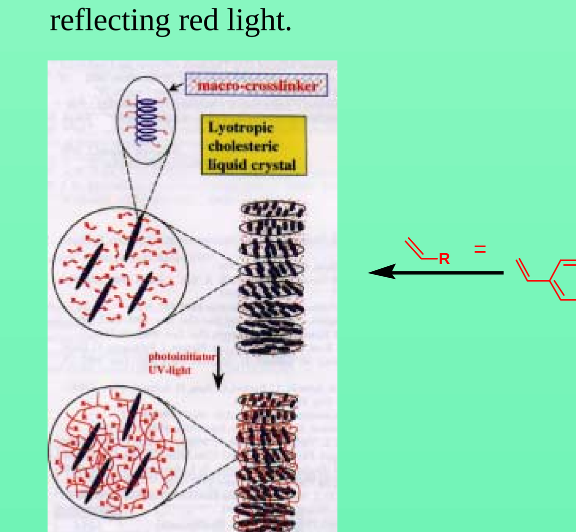
Biased helical polymers will align into a cholesteric mesophase which selectively reflects visible light.



Terpolymer of chiral azo, spacer, and crosslinker forms a cholesteric mesophase.



Using a template we can selectively photopolymerize a cholesteric network locking in the pitch that reflects green light. Upon removal of the template the sample is heated expanding the pitch until red light is reflected. Photopolymerization then locks in the pitch reflecting red light.



Network with "locked-in" cholesteric structure