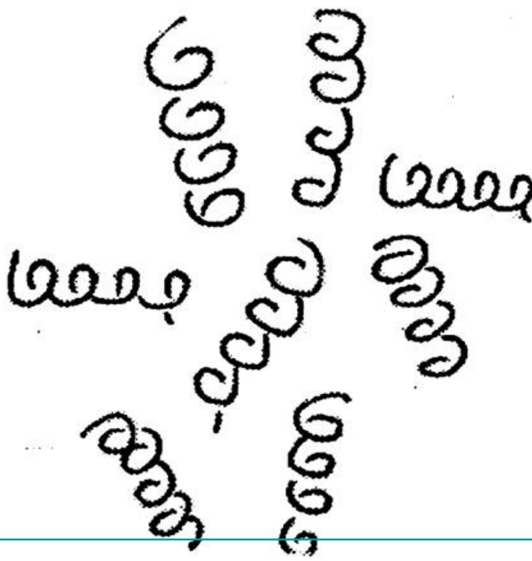
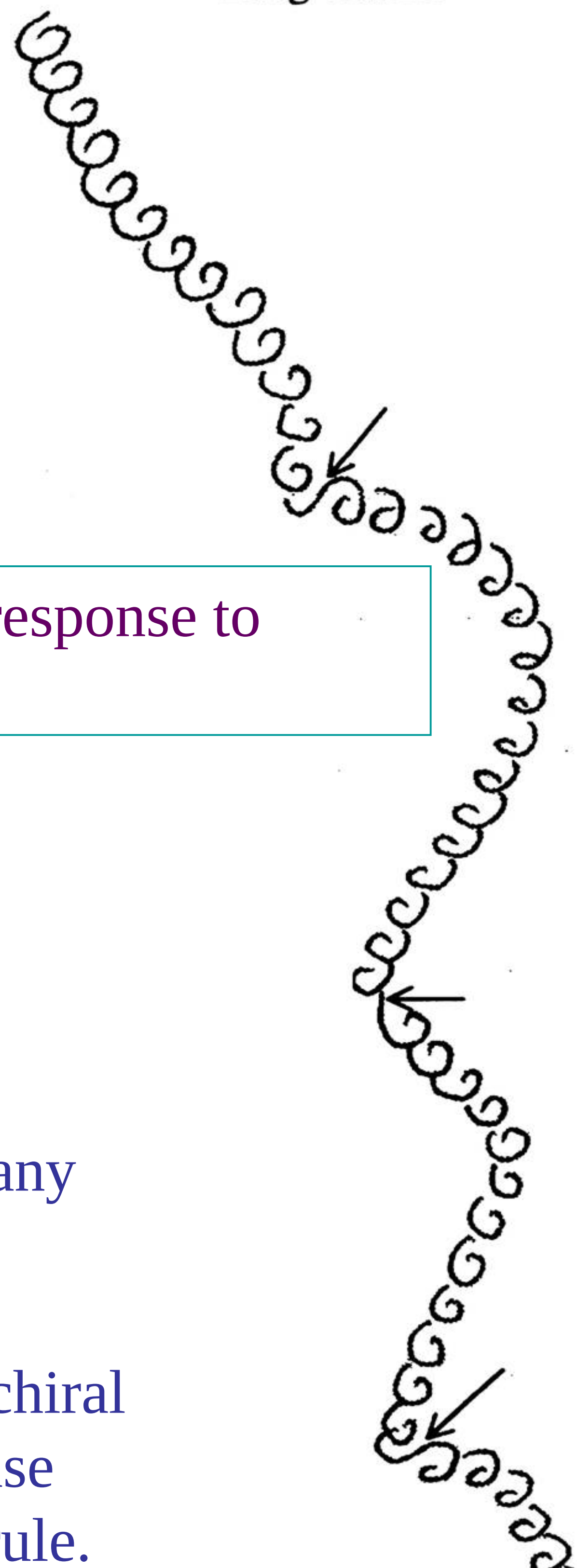
How can helical sense be chosen in a dynamically racemic polymer?

Short Chains



Long Chains



One can expect a cooperative response to chiral information so that:

Small chiral effects will be amplified.

As sergeants control soldiers,
few chiral units will control many achiral units along the chain.

When views conflict between chiral units with opposing helical sense preferences, the majority will rule.

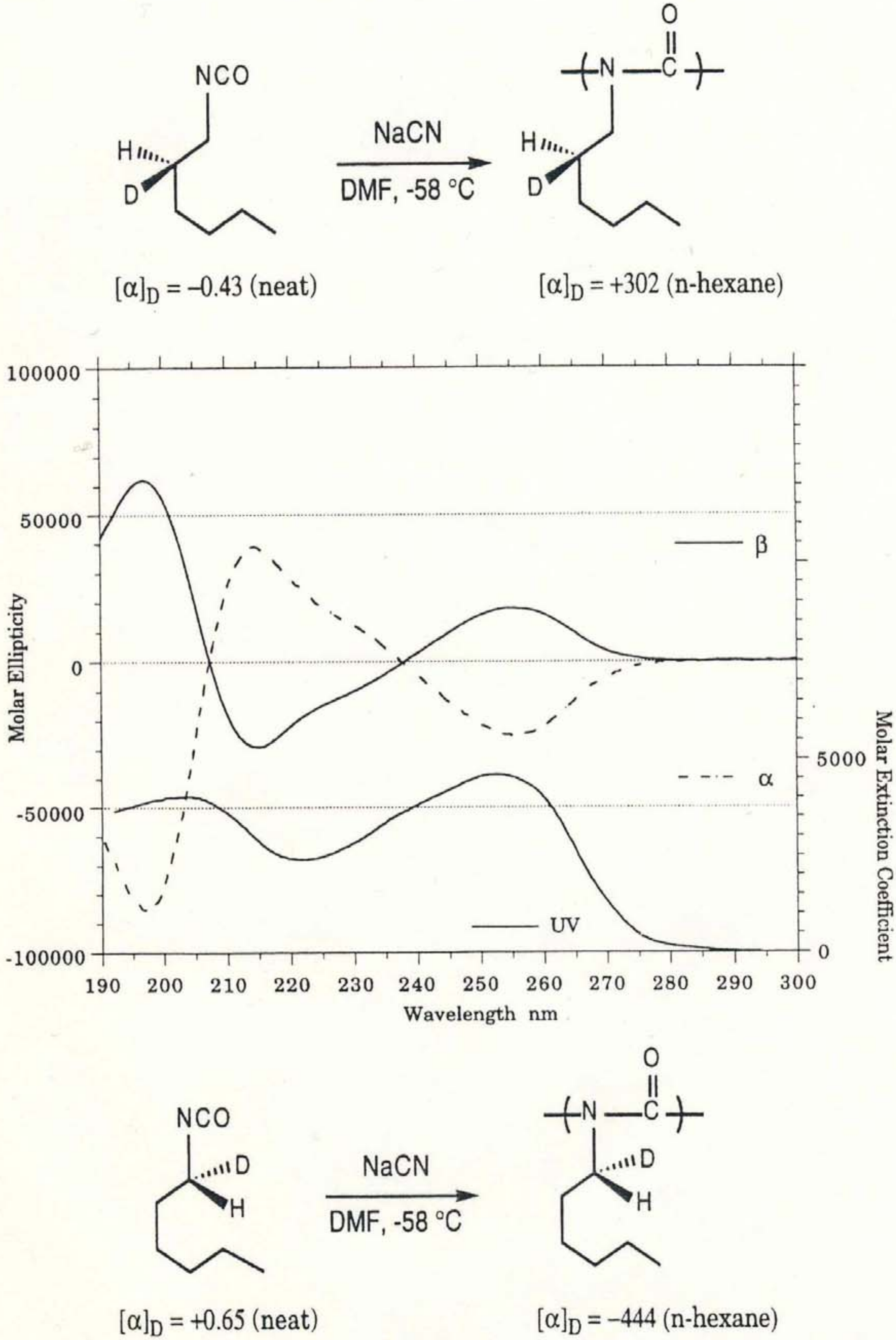
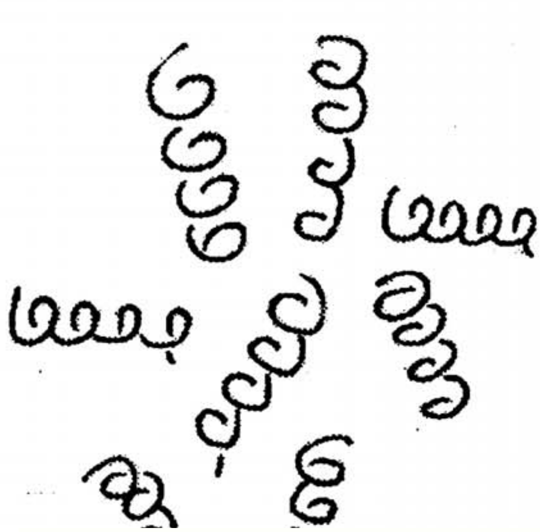
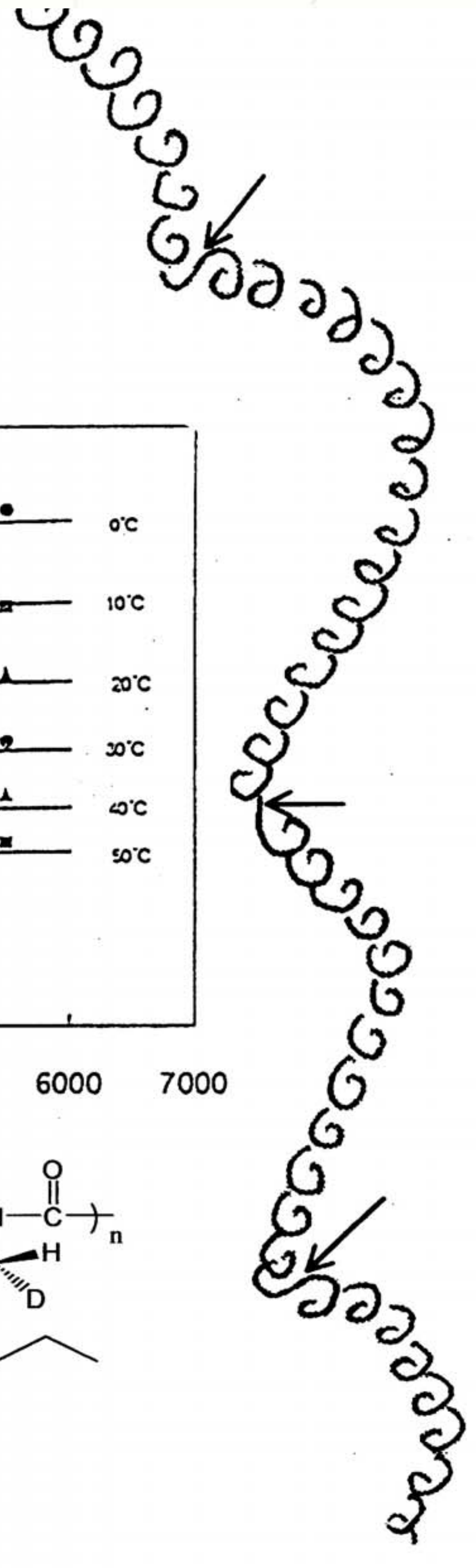


Figure 17.1 Circular dichroism spectra of poly(1-deuterio-*n*-hexyl isocyanate) and poly(2-deuterio-*n*-hexyl isocyanate) and the optical activities of their precursor monomers and also the ultraviolet spectrum of poly(*n*-hexyl isocyanate). (Taken in part from Ref. 36 with permission.)

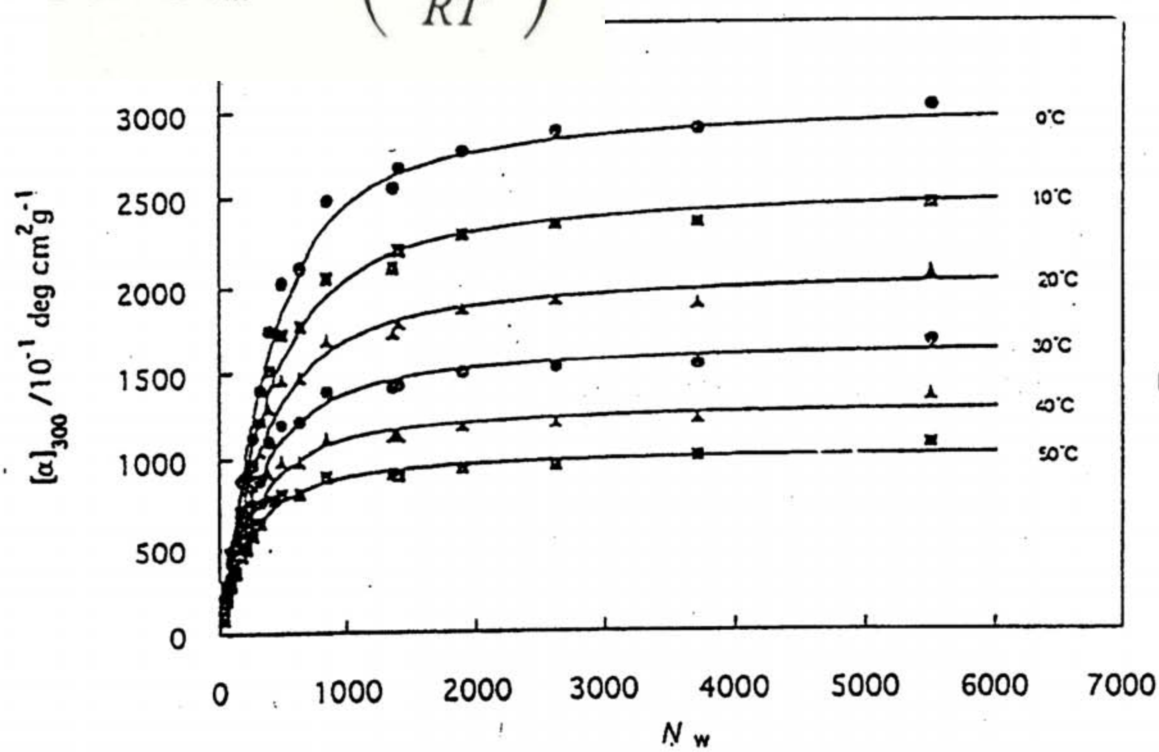
Short Chains **Long Chains**

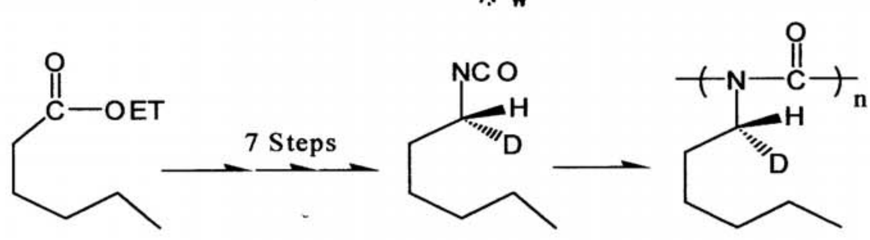
$$[\alpha] = [\alpha]_m \frac{(L\,\Delta G_\mathrm{h}/RT)}{((L\,\Delta G_\mathrm{h}/RT)^2 + 1)^{1/2}}$$





$$[\alpha] = [\alpha]_m \tanh\left(\frac{\Delta G_\mathrm{h} N}{RT}\right)$$

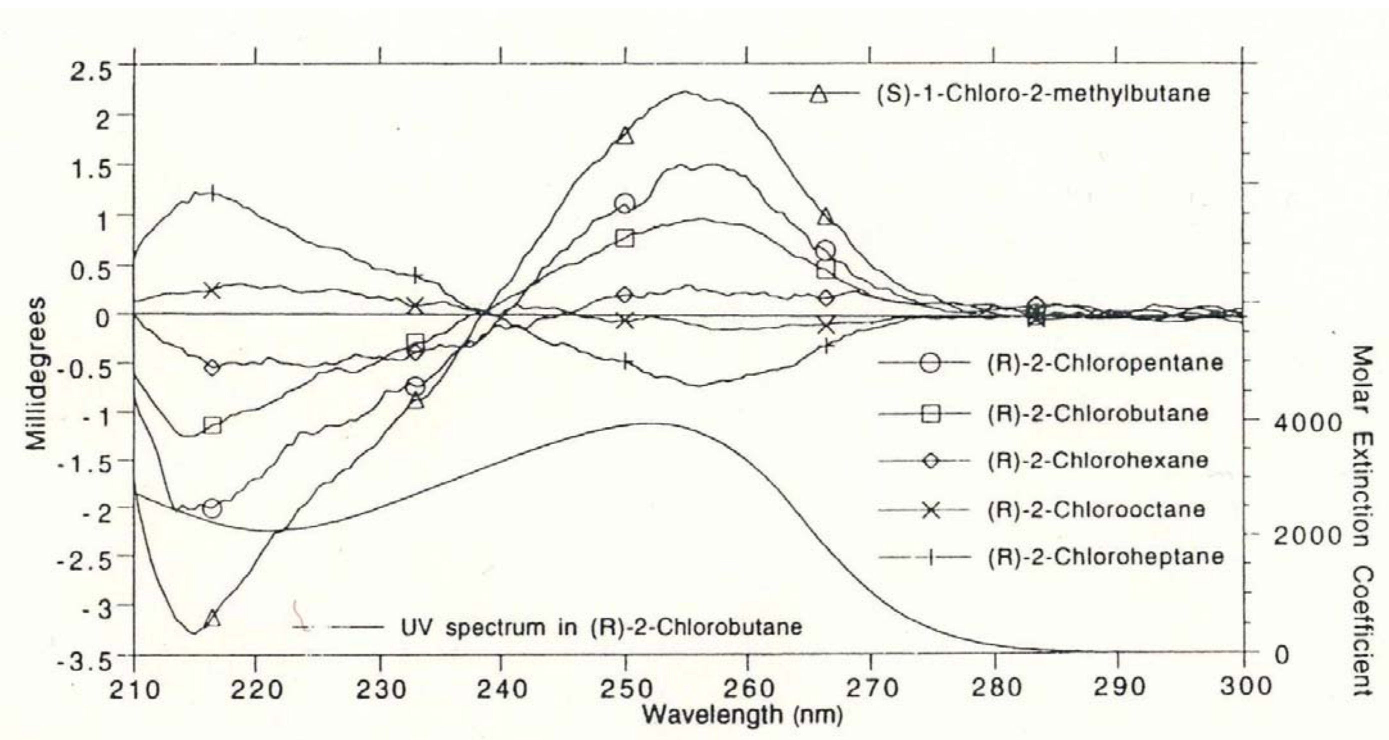




Ethyl Caproate

$[\alpha]_D^{25}$=+0.47°(neat)
1(R)-Deu-HIC

Chiral solvation demonstrates the inability of theoretical methods to interpret the energy changes associated with highly cooperative systems.



The same lesson arose from the results shown with the chiral influence of the deuterium substitution.

Sergeants and Soldiers Experiment

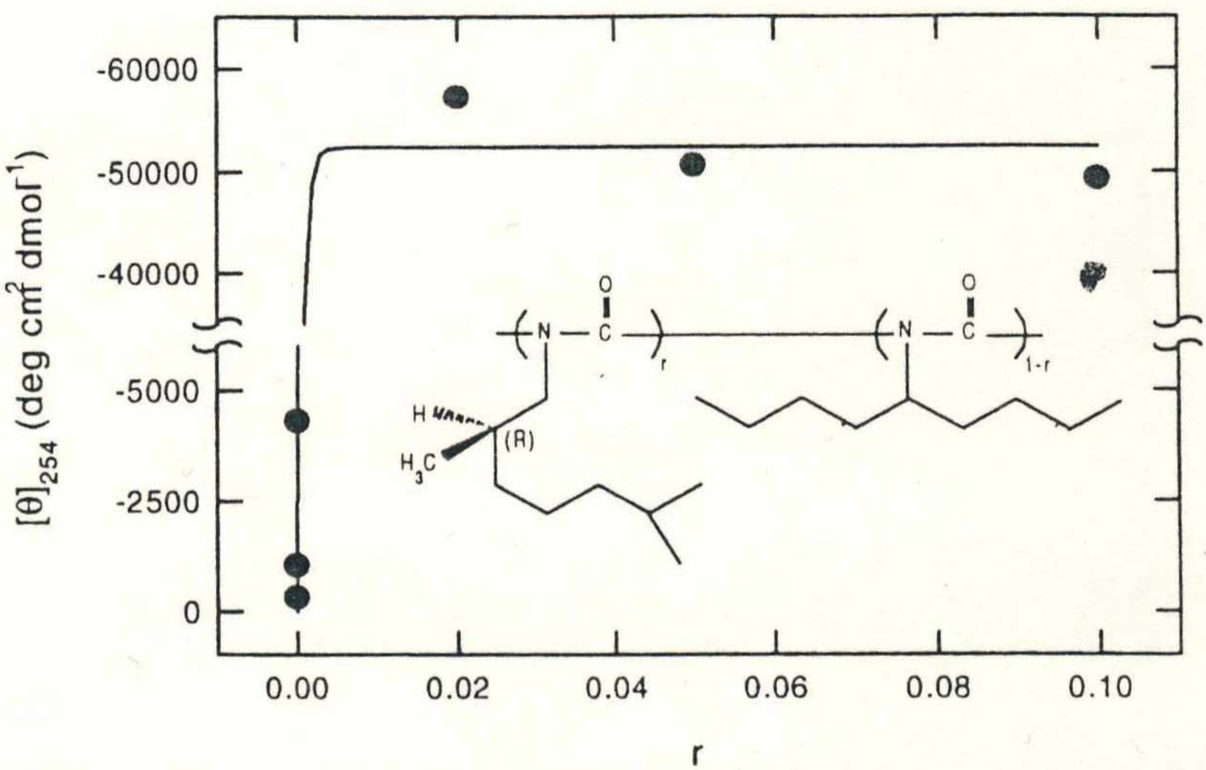


Figure 17.6 Circular dichroism molar ellipticity versus fraction of the chiral unit in the copolymer with the 2-butyl hexyl side chain shown in Fig. 17.5. (Taken from Ref. 27 with permission.)

A very few chiral pendants to the helical polymer can greatly influence the helical sense of the entire chain.

$$M = \tanh \frac{rL\,\Delta G_{\mathrm{h}}}{RT}$$

Majority Rules in Helical Polymers

$$M = erf\left[\sqrt{2Lr}\,(p - 1/2)\right]$$

Chiral order parameter

Cooperative domain size

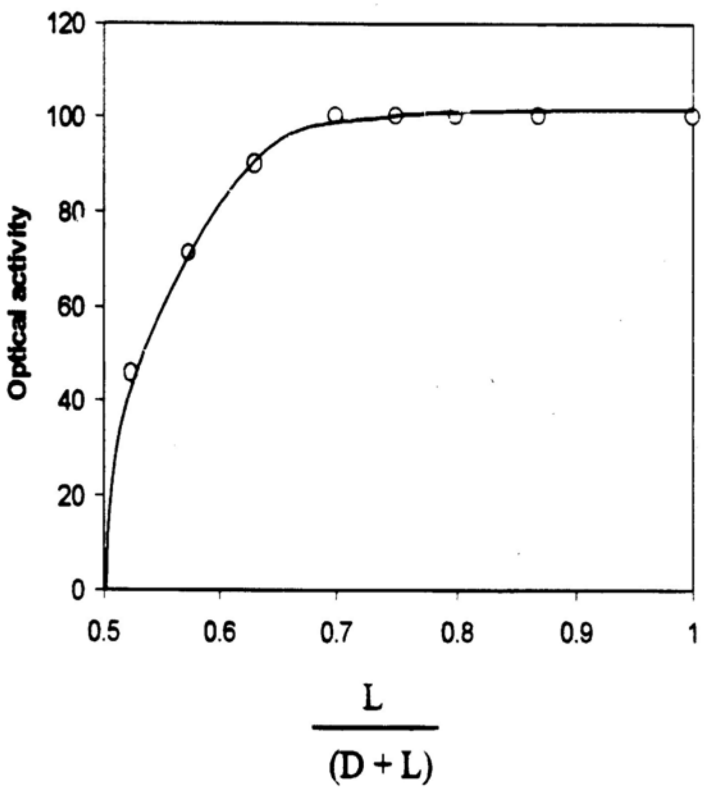
Chiral fraction

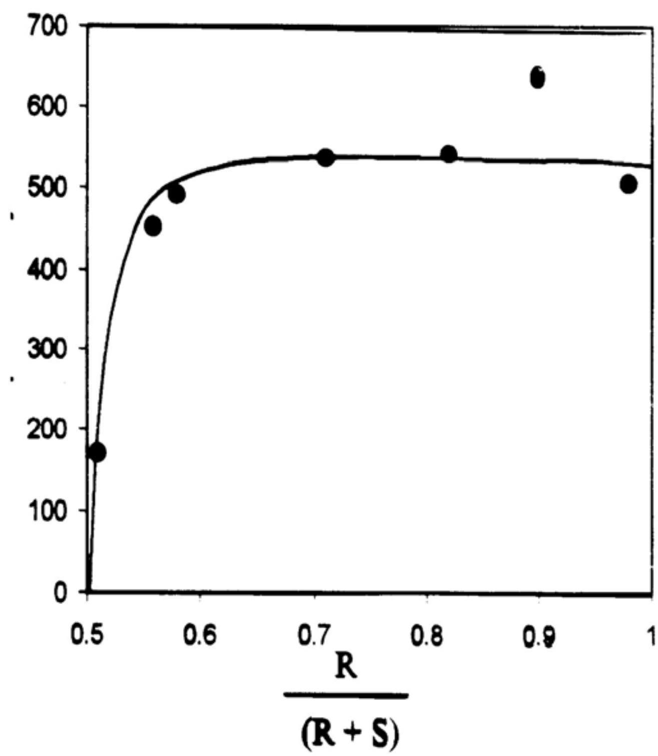
Chiral fraction of one enantiomer

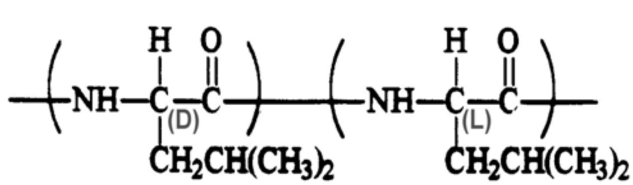
$$L_{rf} = \frac{1}{r}\left(\frac{\Delta G_r}{2\Delta G_h}\right)^2$$

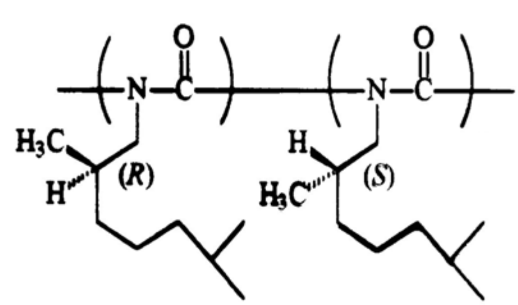
Helical reversal energy

Chiral bias energy









As predicted, Majority Rule is independent of the proportion of competing enantiomers under certain conditions.

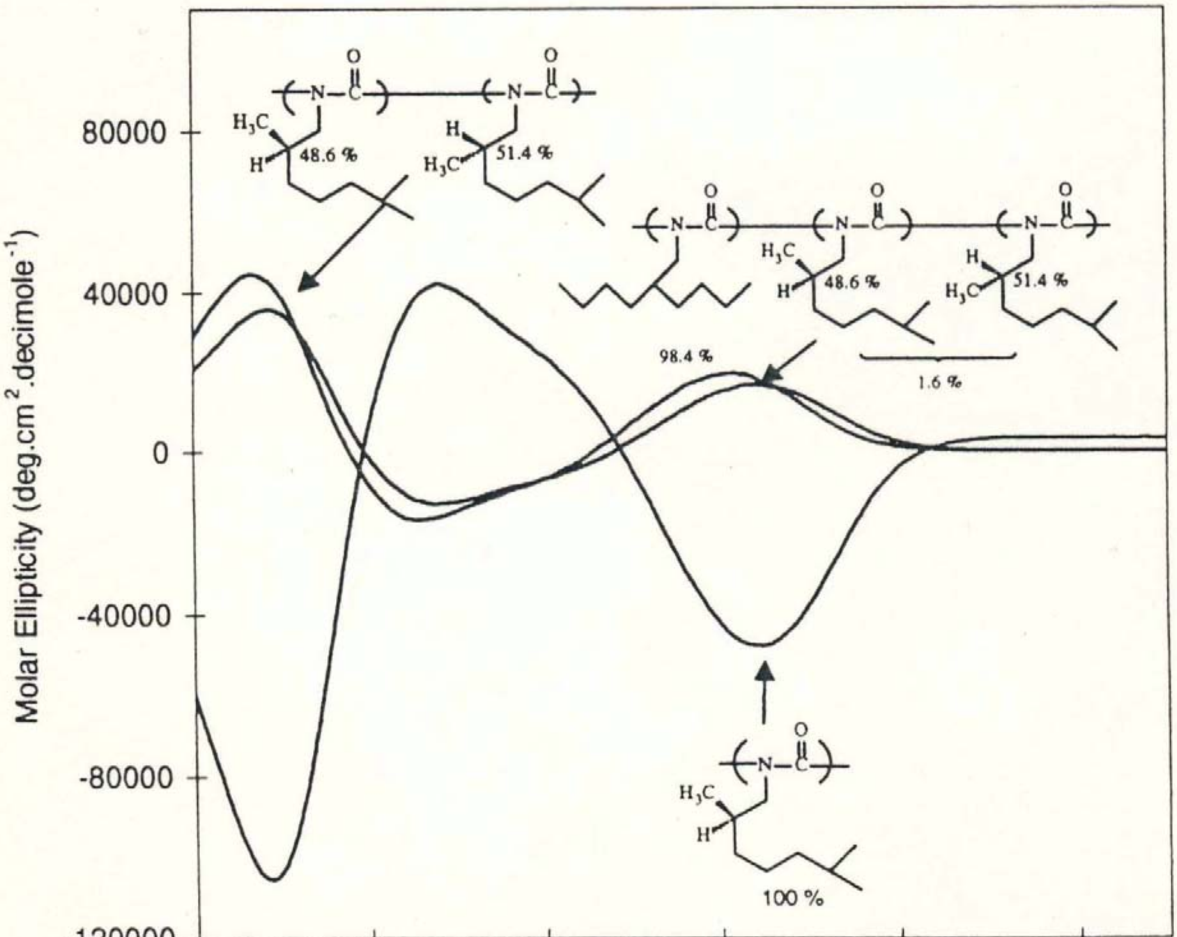
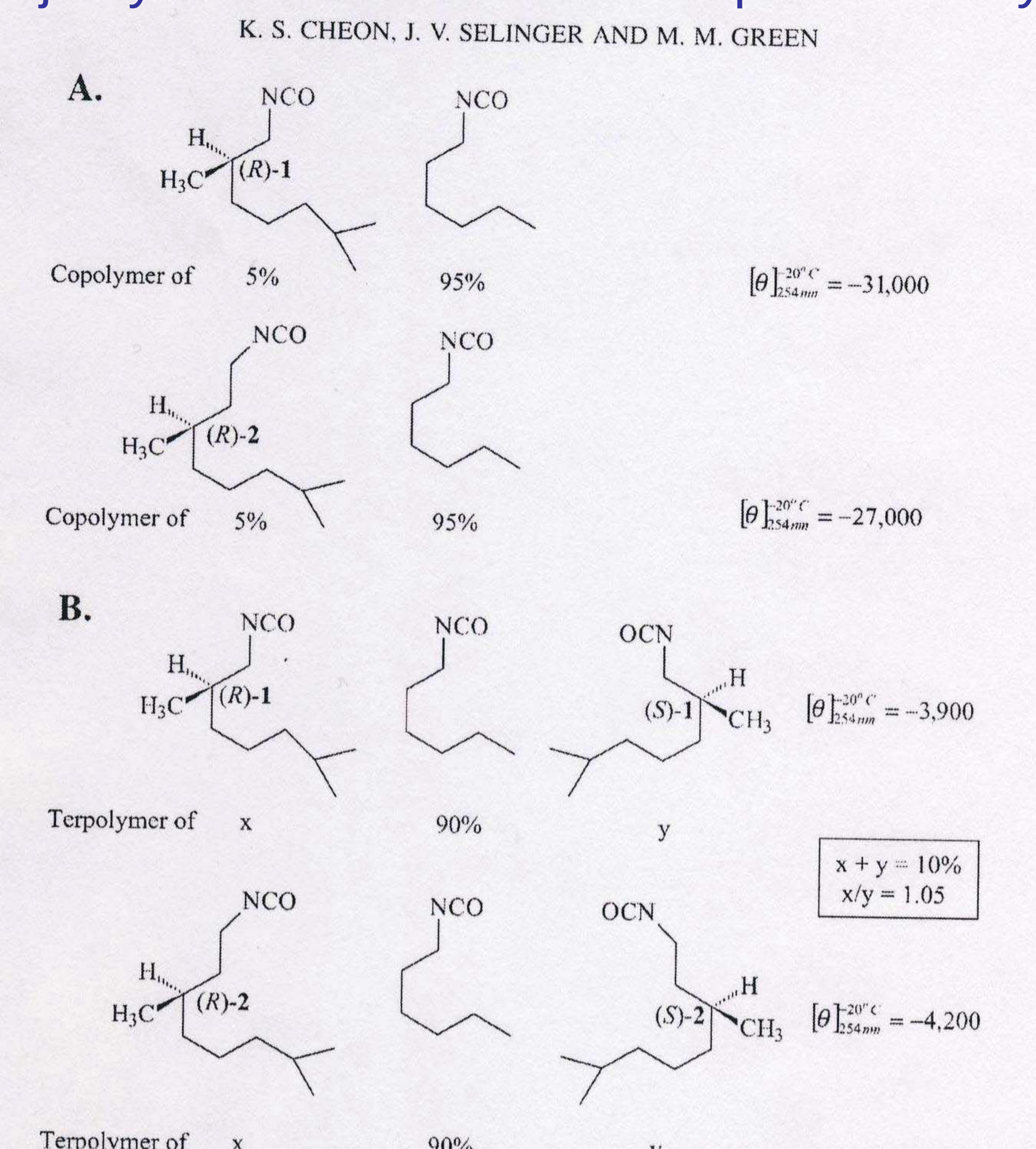


Figure 17.9 Circular dichroism spectra of poly((*R*)-2,6-dimethyl heptyl isocyanate) compared to a copolymer of the enantiomeric units in the ratio of 48.6/51.4 and to a terpolymer with the identical enantiomeric ratio diluted with 98.4% achiral units as shown on the figure. (Taken with permission from Ref. 27.)

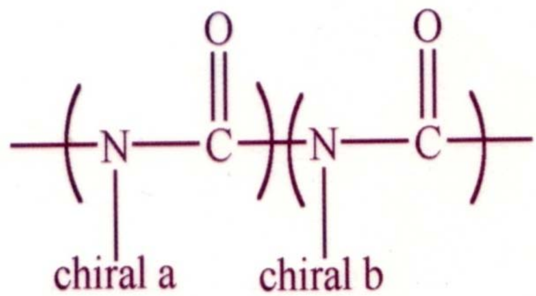
As predicted, under certain conditions:

An increased chiral influence in the Majority Rule experiment leads to a decrease in cooperativity and therefore to less helical sense control by the majority and therefore a lower optical activity.



Chiral Conflict for control of the helical sense of a polymer

$$[a] = [a]_{\max}\, erf\left[\sqrt{\frac{Lr}{2p^{*}(1-p^{*})}}\left(p-p^{*}\right)\right]$$



$p^* = \Delta G_a/(\Delta G_a + \Delta G_b)$ where a and b correspond to the chiral units that are competing with their respective chiral free energies, ΔG, to control the helical sense of the polymer they are appended to.

Case A: If a, b are enantiomers

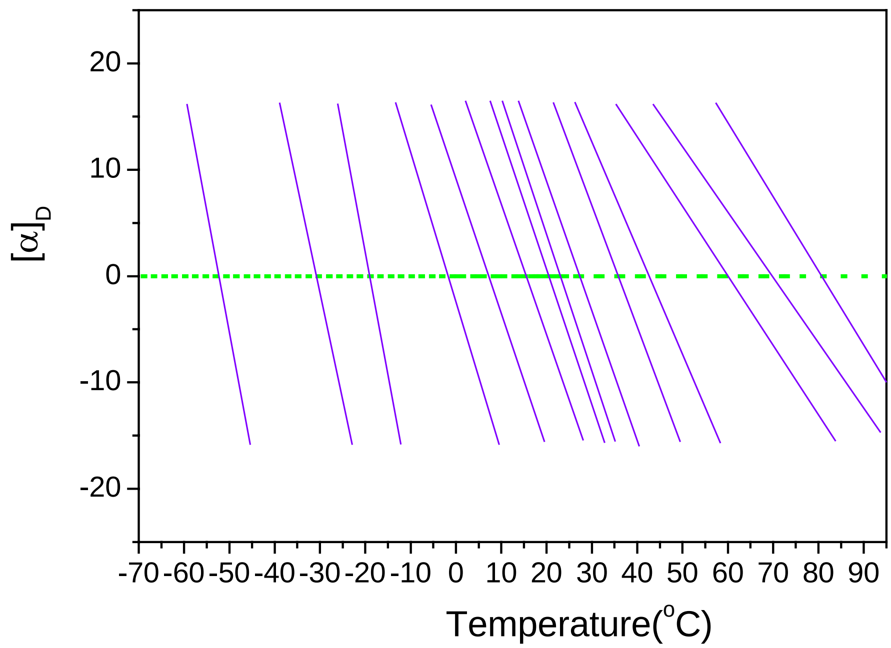
$\Delta G_a = \Delta G_b$, $p^*=1/2$, no temperature dependence

Majority Rule

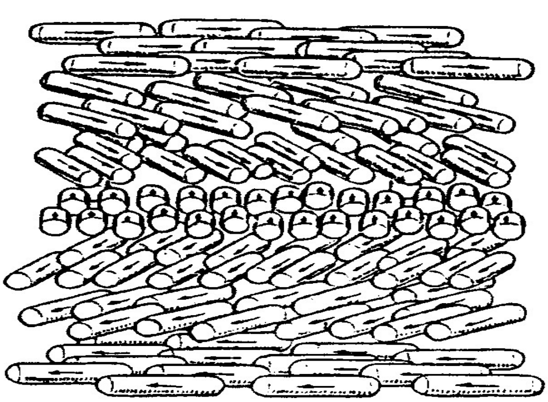
Case B: If a, b have different chemical structures, which favor opposite helical senses

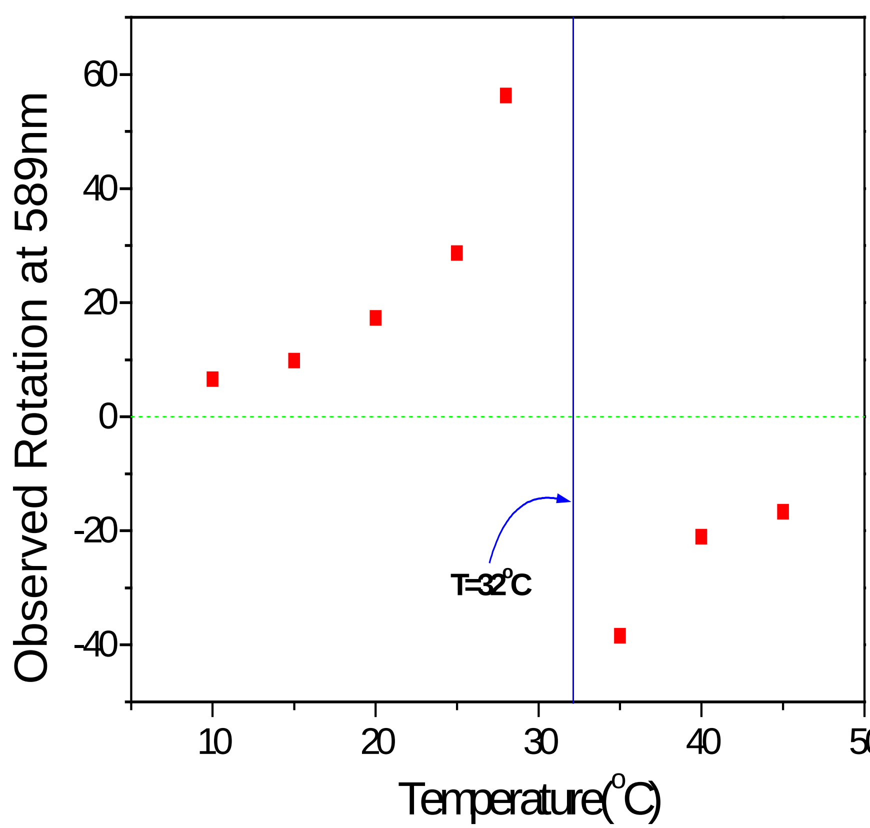
$\Delta G_a \neq \Delta G_b$, $p^* \neq 1/2$ and may be temperature dependent

If the chiral units competing to control the helical sense are not mirror images of each other then their competition will be temperature dependent. And by changing the proportion of these competing units they will balance each other at different temperatures.



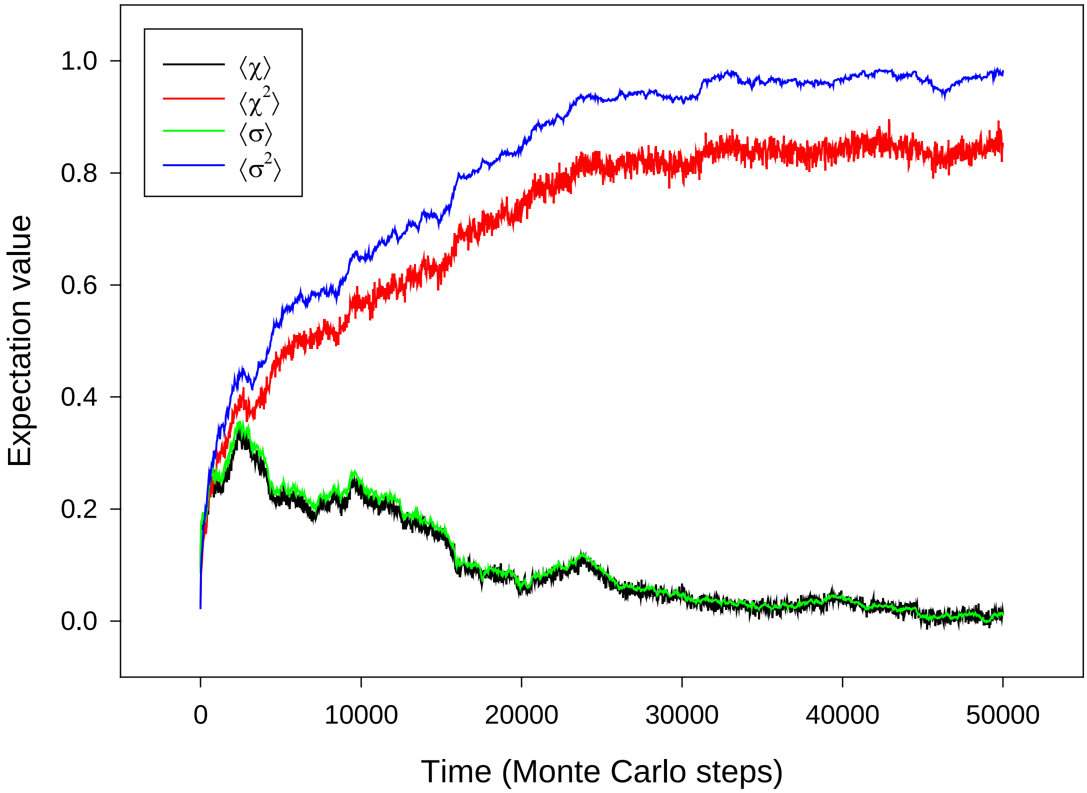
Translation to liquid crystals yields very large temperature dependent chiral optical effects.





Majority Rule experiment in which the competing R and S side chains can interconvert (epimerize).

Epimerization model



The excess of left or right helices averaged over all chains

The excess of R or S side groups averaged over all chains

The excess helical sense within each chain, left or right

The excess of one chiral side chains within each chain, R or S

In starting with a mess and ending up with a true racemic mixture, this result offers an explanation for the origin of homochirality in life: “Two equal runners, one tripped.”

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Philosophy

"What we have to learn we learn by doing."

-*Aristotle*-

"I see and I forget. I hear and I remember. I do and I understand."

-*Confucius*-