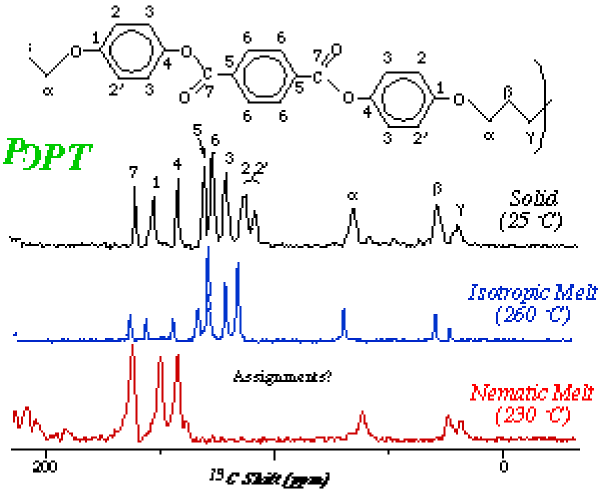
DYNAMIC DIRECTOR ^{13}C NMR OF LIQUID CRYSTALS

General Objectives

During liquid crystal NMR analyses, particularly ^{13}C NMR measurements at natural abundance, problems arise upon trying to ascribe the different nematic resonances to particular chemical sites. This is so due to the onset of chemical shift anisotropy (CSA) contributions; e.g. .



We present here an approach capable of elucidating the chemical origin of the resonances, and discuss some interesting dynamic features that arise from its use.

Dynamic-Director NMR:

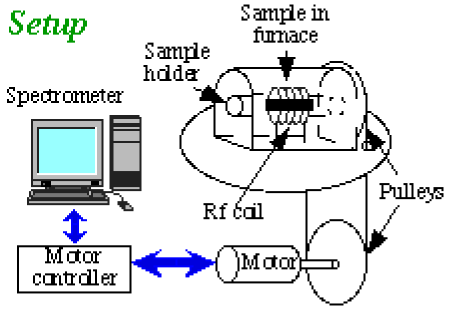
We distinguish isotropic and anisotropic chemical shift contributions in LCs by exploiting the CSA orientation dependence upon reorienting the liquid crystalline director by an angle beta:

total shift = isotropic shift + shift anisotropy·$P_2(\cos\beta)$

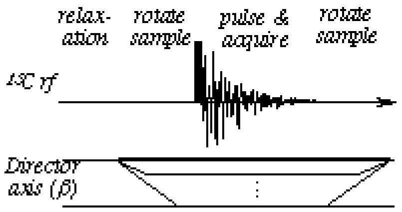
$$P_2(\cos\beta) = (3\cos^2\beta - 1)/2$$

⇒ a *total shift* vs P_2 least square analysis separates the two components

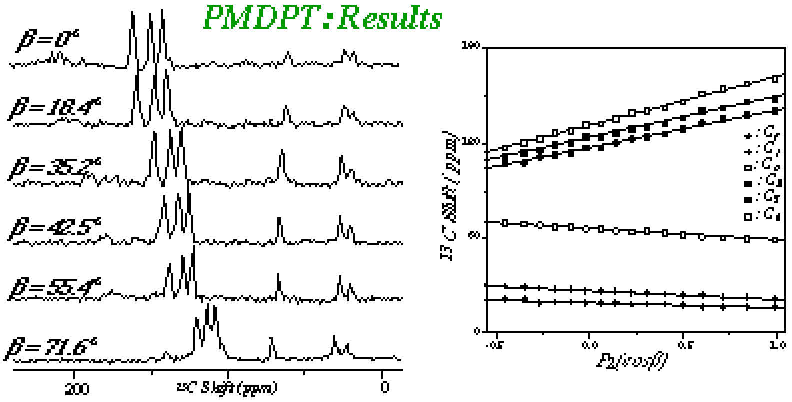
Setup



Sequence



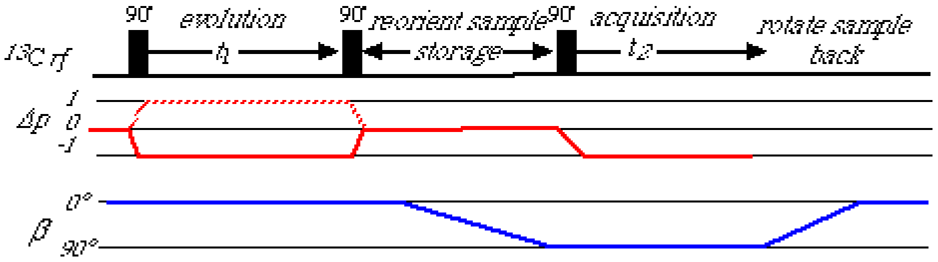
PMDPT: Results



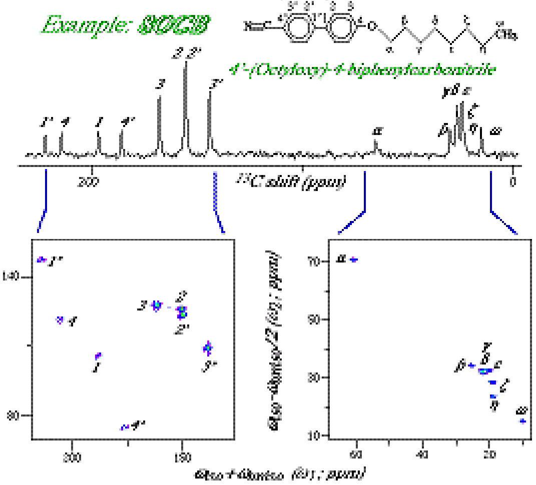
The peaks assignments can then be made on the basis of the isotropic shifts extracted from linear least square plots.

An alternative: record 2D correlation spectra between directors aligned parallel and perpendicular with respect to the external magnetic field:

The Pulse Sequence

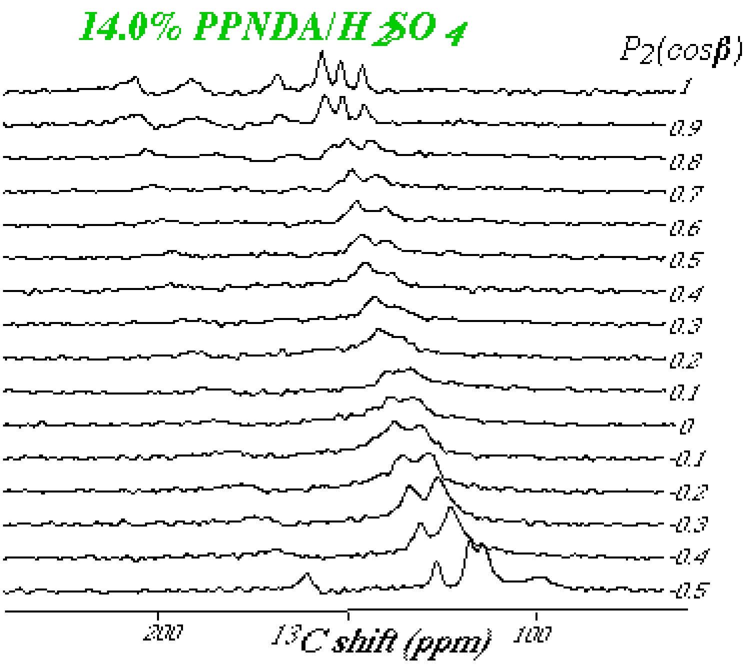


Some of the ^{13}C NMR results observed on applying this technique to smectic liquid crystals

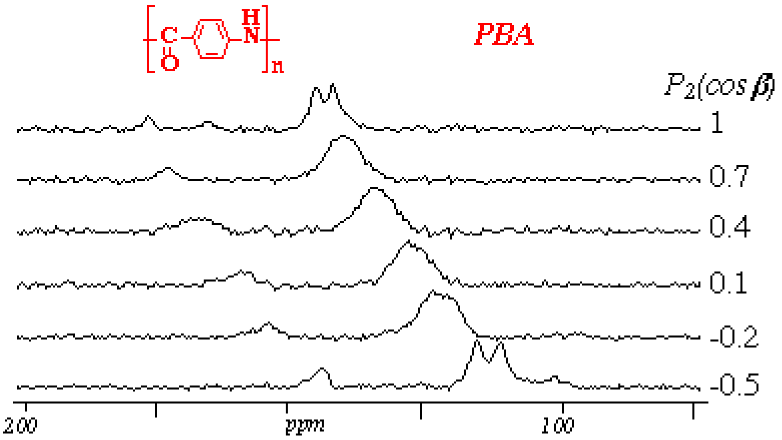


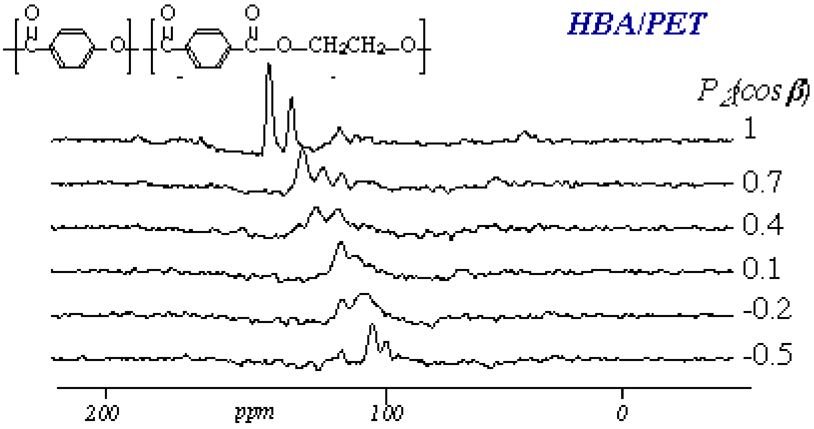
Applications of Dynamic Director to High Mw Liquid Crystalline Polymers:

When applying this approach to the analysis of Liquid Crystals with ca. 10 times higher Mw than these thermotropics, not only a shift but also a broadening of the peaks is observed:

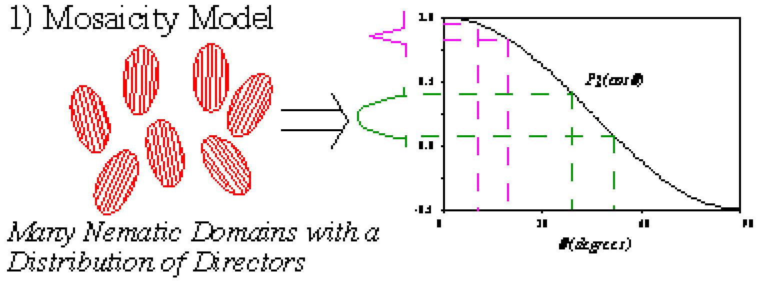


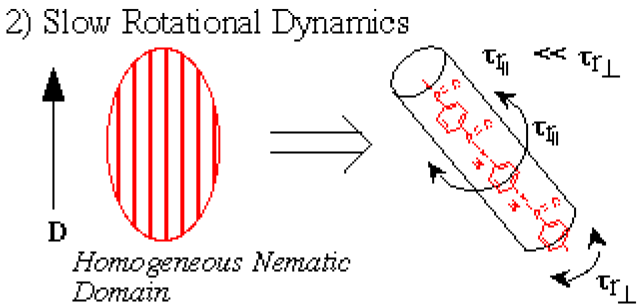
A similar behavior is observed in simpler lyotropics and in commercial thermotropics:



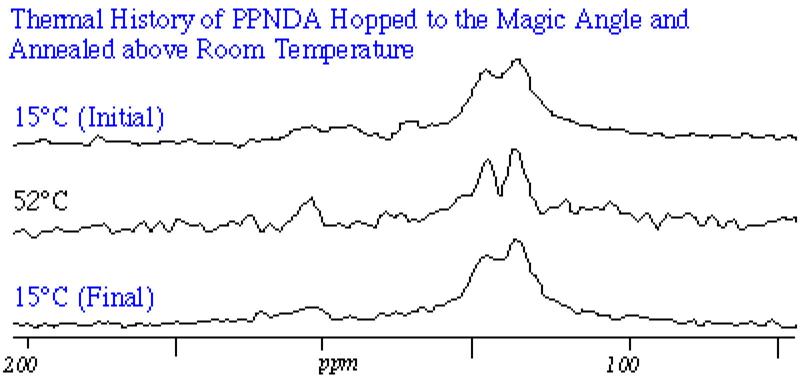


This could be due to a **polydispersity** in the orientations of local liquid crystalline domains (mosaicity; a defect common in certain liquid crystals), or due to **molecular tumblings that are slow in the NMR timescale** of either the macromolecules themselves or of the microscopic LC domains they aggregate into about their main axes of inertia





In order to ellucidate among these 2 possibilities, we are carrying out a series of variable-temperature line shape analyses: mosaicity is a defect that should anneal upon cycling temperatures, while kinetic phenomena should be reversible upon increasing and then decreasing temperature



These preliminary results favor the second (kinetic) of the models.