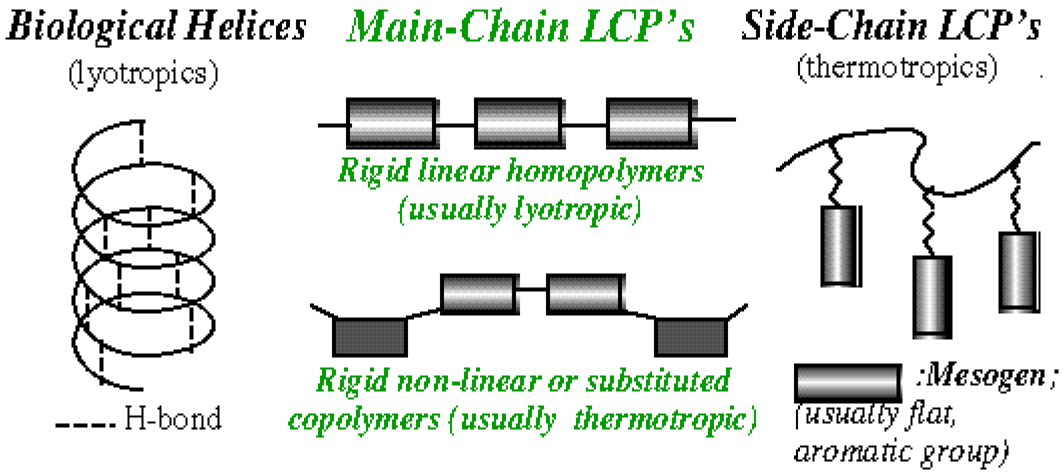
NMR ANALYSES OF LYOTROPIC POLYMERS

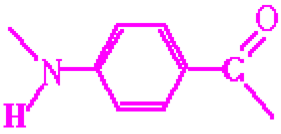
OVERALL OBJECTIVES:

We apply modern NMR methods for improving our understanding of static (alignment) and dynamic phenomena in liquid crystalline polymers (LCP's):



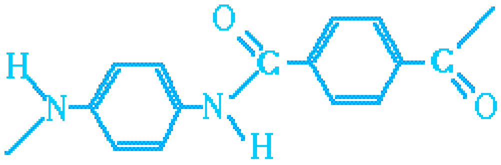
Main-chain LCP's have found the widest practical application owing to their superior mechanical properties. Our attention focuses on lyotropic aromatic polyamides:

PBA



DuPont (lyotropic)

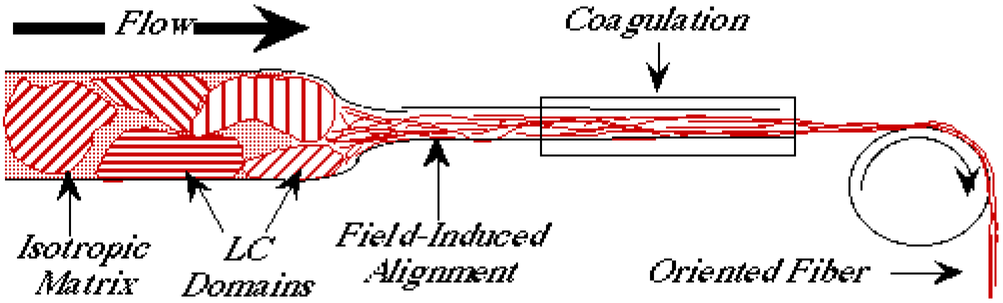
PPTA



DuPont
(Kevlar®, lyotropic)

These polymers are processed from the liquid crystalline phase to yield highly ordered materials.

Processing is usually done by wet-jet spinning:



We are attempting to answer questions regarding the nematic properties of these solutions, their ability to preserve order upon coagulation, and inter- intra-phase molecular migration using solution, solid phase and microimaging NMR

EXPERIMENTAL:

- Polymers are synthsized in our laboratory according to procedures described in the literature and patents.

- Polymers are dissolved in freshly prepared 99.8-100.2% H_2SO_4 (pale yellow solutions vs. black solutions from commercial polymer samples).

With the onset of liquid crystallinity, the solutions display a strong opalescence upon stirring:

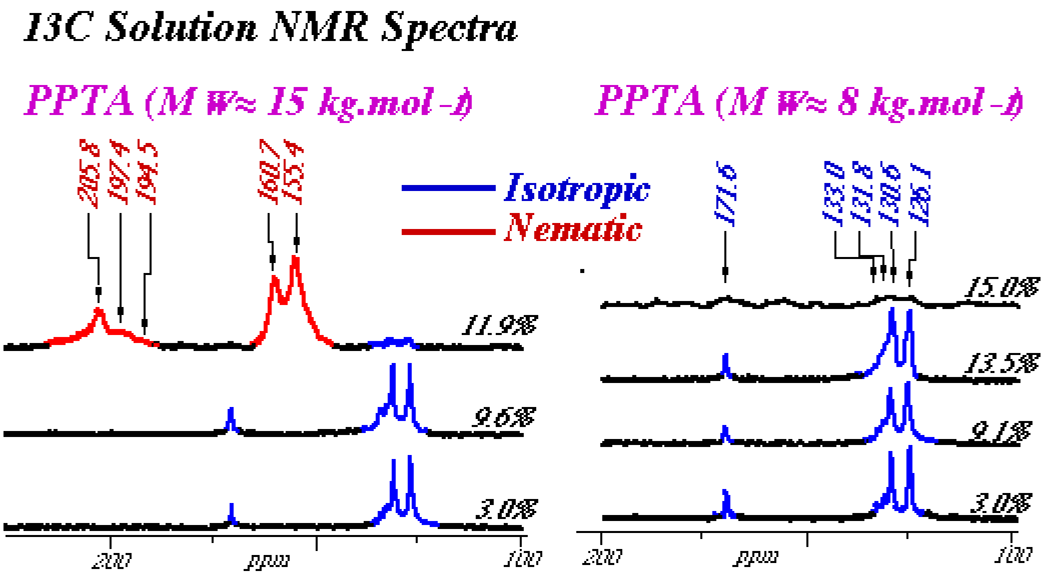
PBA/H2SO4 Nematic Solution

Nematic Upon Stirring

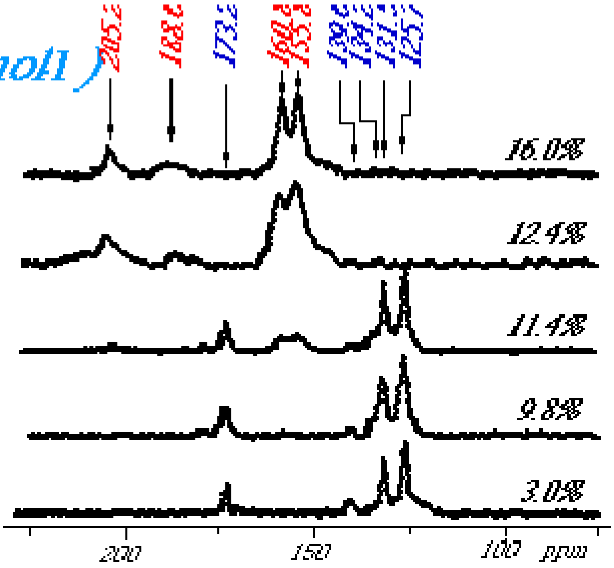
- Solution (WALTZ, no NOE), solid phase (CP) and microimaging (PGSE) NMR data are acquired on home-built 7.1 T instrument and probes

LC NMR RESULTS:

Spectral changes are observed in both polymers upon changing the polymer concentration

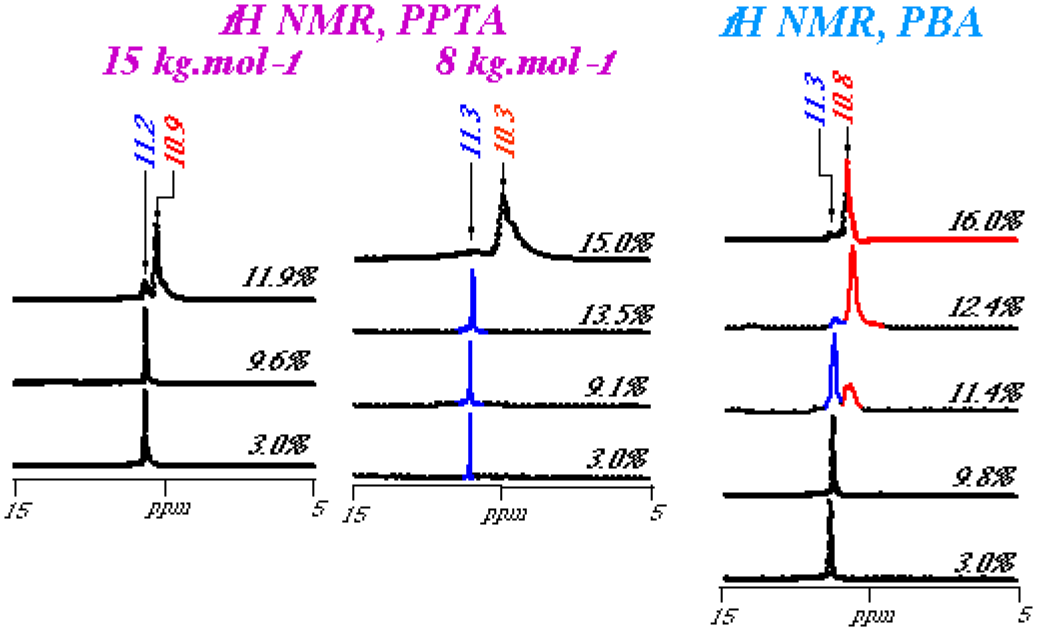


PBA (MW ≈ 12 kg.mol1)



In both cases, 13C NMR can successfully distinguish between molecules in the isotropic and nematic phase

The changes occurring in these solutions as a function of polymer concentration also affect the ^{1}H NMR solvent traces. There is a difference in the solvent shift between the phases, even though there are no anisotropic dipole couplings.



DATA ANALYSIS:

It is possible to analyze the anisotropic ^{13}C shifts in terms of Saupe's liquid crystal NMR formalism, which predicts:

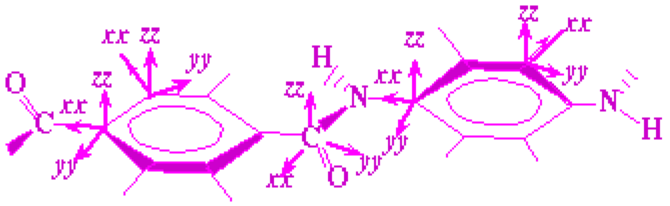
$$\boxed{\Delta\delta = \delta_{iso} - \delta_{lc} = 2/3 \sum_{i,j=1,2,3} S_{ij}\,\delta_{ij}}$$

S_{ij}: Saupe matrix
δ_{ij}: shielding tensor elements
i,j: arbitrary axis system

Since polymers possess nearly axial symmetry and their LC phase is nematic this expression can be recast in terms of a single order parameter S_{zz}; the average degree of chain alignment with respect to the external magnetic field.
To obtain S_{zz} from the ^{13}C NMR shifts, however, it is still necessary to know the magnitudes and orientations of the chemical shift tensors for each site in the monomeric unit.

Orientations can be placed with a good degree of confidence using literature guidelines resulting from single-crystal measurements:

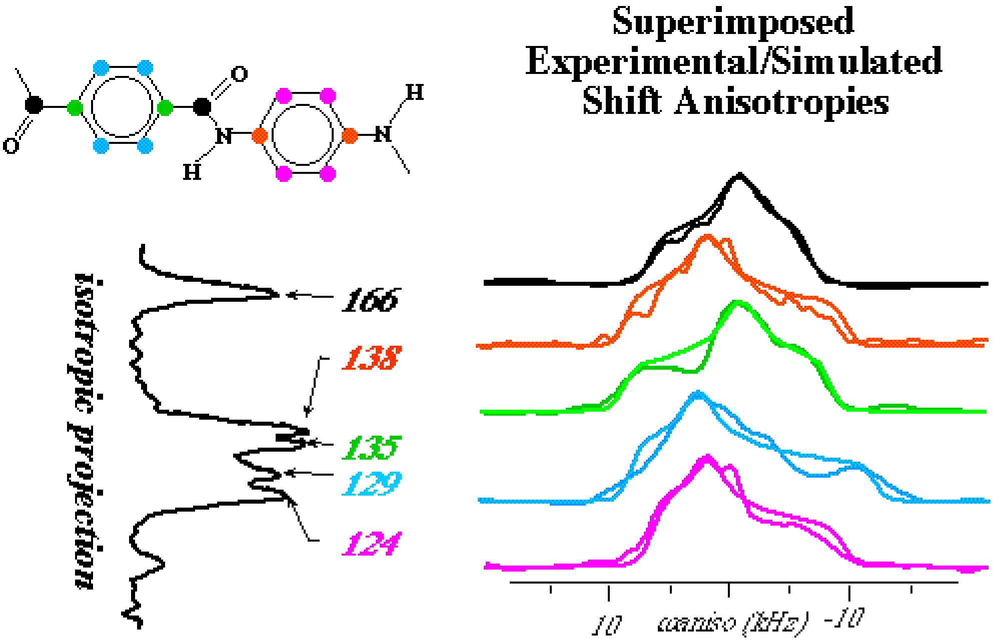
E.g., PPTA



In order to determine the principal values of the shielding tensors for each site we employ solid-state *Variable-Angle Correlation Spectroscopy (VACSY)* , a form of 2D NMR spectroscopy that separates anisotropic patterns of inequivalent chemical sites according to their isotropic shifts.

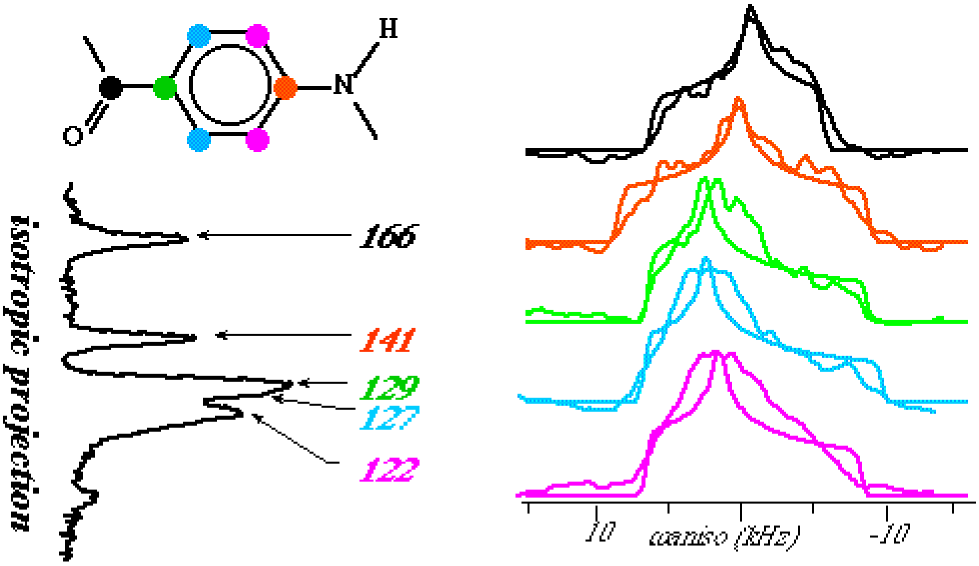
Solid-state NMR results obtained on polycrystalline LCP samples:

Polycrystalline PPTA: 2D VACSY NMR



Polycrystalline PBA: 2D VACSY NMR

(short CP and dipolar-dephased)



These data enable the quantitative analysis of the nematic NMR results. However, since polymer ^{13}C NMR resonances in anisotropic phases are broader than their isotropic counterparts while their T_2's are similar, we also allow for adistribution in the value of the order parameter S_{zz}. This leads to an overall NMR line shape expression

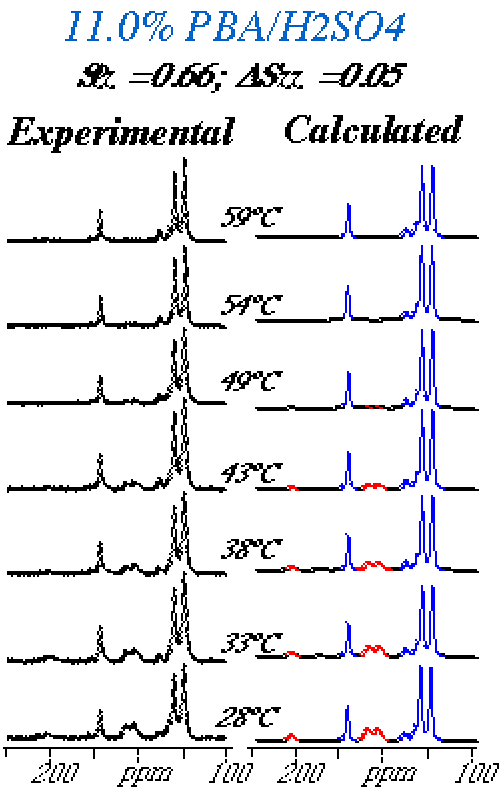
$$I(\delta) = I_o \int \{x_{iso} L(\delta - \delta_{iso}) + x_{lc} L(\delta - \delta_{lc})\} \exp[-(S_{zz} - S^0_{zz})^2 / 2(\Delta S_{zz})^2] \, dS_{zz}$$

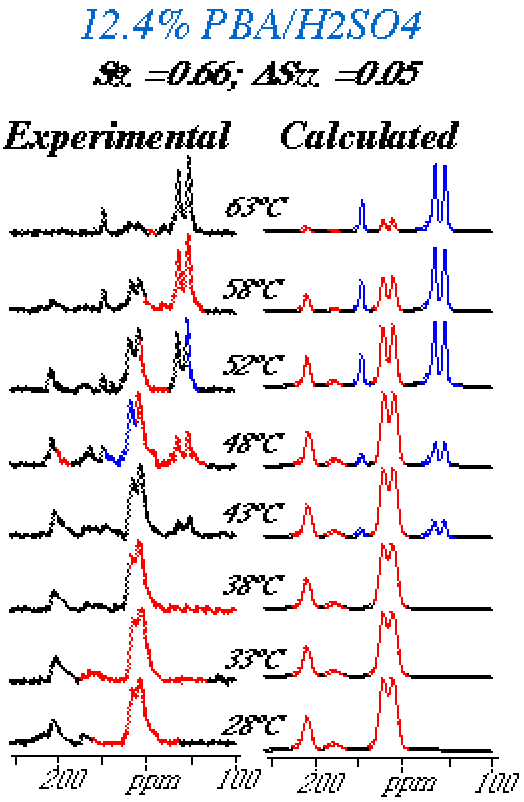
$L(\delta - \delta_i) = 1/[1 + 4\pi^2 (T_2^i)^2 (\delta - \delta_i)^2]$; I_o: **normalization constant;**

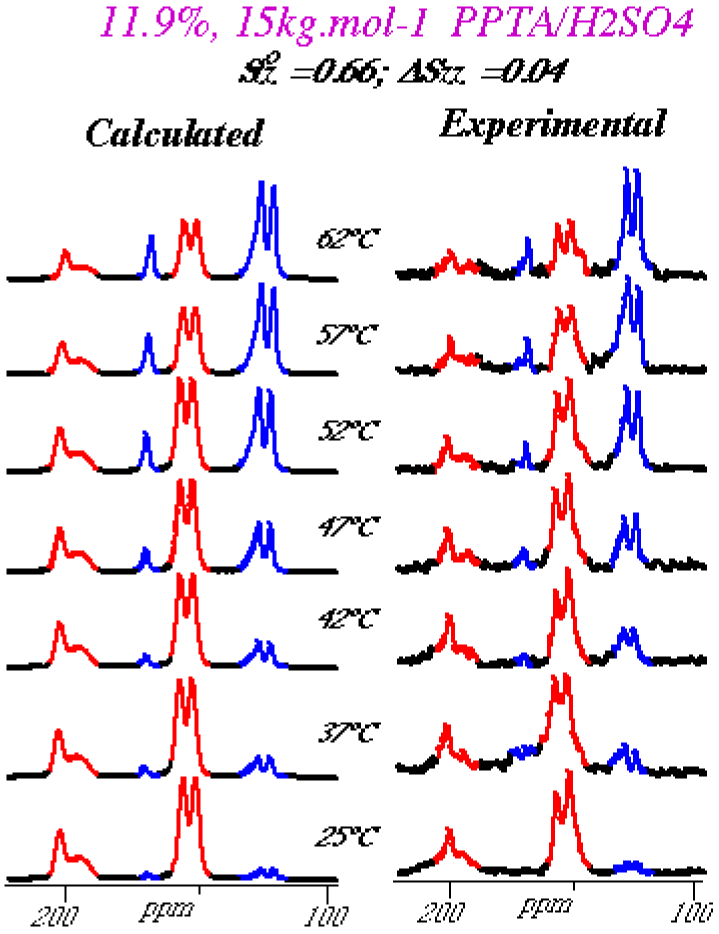
S^0_{zz}: **average order parameter;** ΔS_{zz}: **distribution in** S_{zz};

x_{iso}, x_{lc}: **fraction of molecules in each phase**

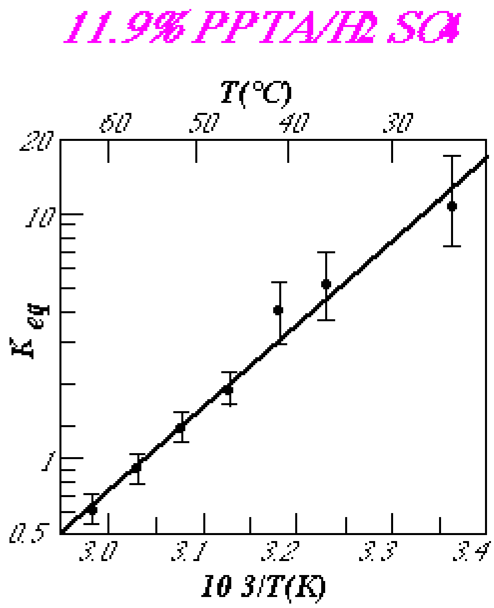
Simulations can then account very accurately for the changes observed in the various ^{13}C NMR spectra, leading to average values of liquid- crystalline alignment:





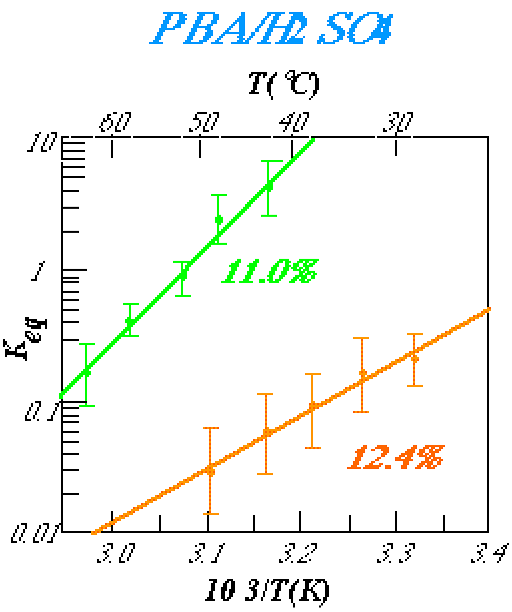


The relative abundance of each phase at the different temperature can also be used to characterize the thermodynamic behavior of each system:



$\Delta H = 1.7$ kcal/mol

$\Delta S = 4.7$ cal/K•mol



$\Delta H = 3.8$ kcal/mol

$\Delta S = 10.6$ cal/Kmol

$\Delta H = 2.0$ kcal/mol

$\Delta S = 6.3$ cal/Kmol

Although these data reflect an expected temperature (Van't Hoff) and concentration dependence for the isotropic<--->nematic equilibrium constant (K_{eq}), they display a remarkable independence of the average order parameter S_{zz} on concentration and temperature.