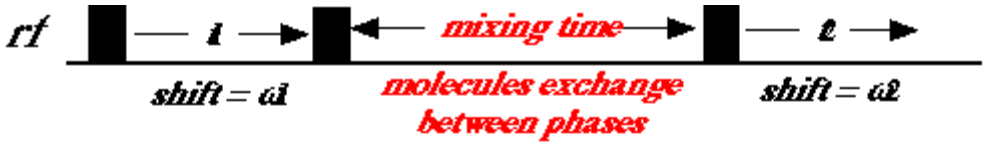
DIFFUSION IN LIQUID-CRYSTALLINE PHASES

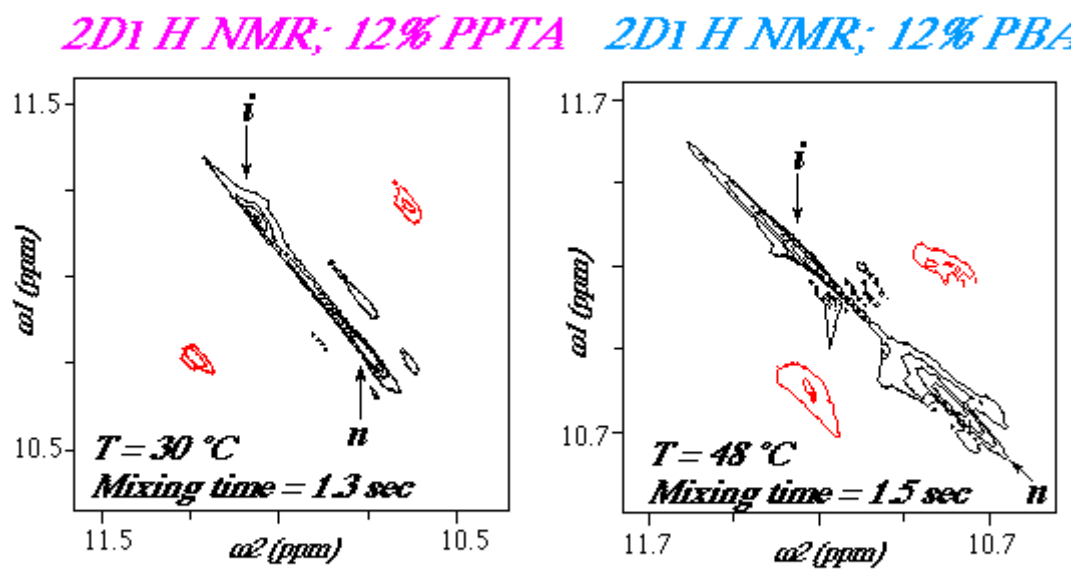
General Objectives

As part of our ongoing research in liquid-crystalline polymers. we attempt to characterize diffusion in these systems at a molecular level using various NMR methods. Once successful these investigations will yield valuable insight on how molecular diffusion and flow can help weld interphase defects during the processing of these systems.

2D Exchange NMR:

Inter-phase molecular diffusion between nematic and isotropic domains can be explored using 2D exchange NMR, a technique that monitors the chemical shift of the molecules at two different time intervals:





cross peaks intensities ≈ 10% of nematic diagonals

Solvent life times are consequently in the order of seconds.
Solute cross peaks could not be detected.

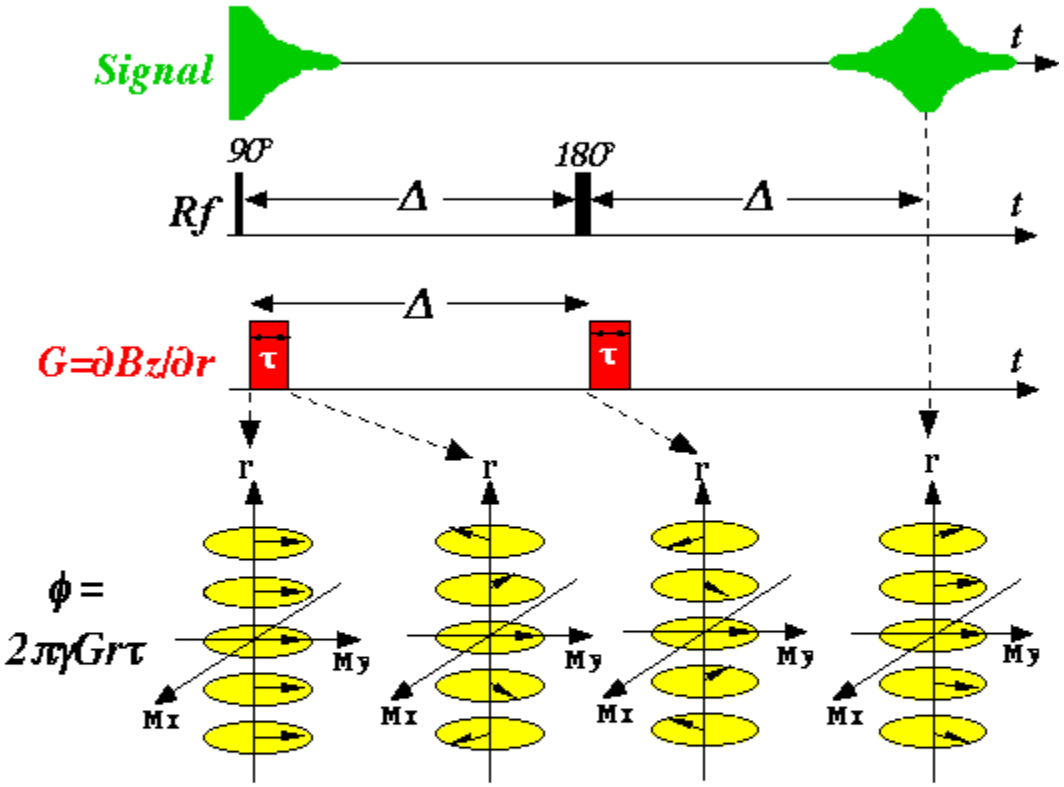
These investigations were succesfully applied to the characterization of solvent migration in PPTA and PBA solutions in H2SO4; but failed to reveal migration of solute molecules.

Pulsed-Gradient Spin-Echo Microimaging NMR:

We explored another option for the analysis of micrometer-scale migrations of both the inter- as well as the intra-phase kind:

An alternative for analyzing intra-phase diffusion:

PULSED-GRADIENT SPIN-ECHO (PGSE) MICROIMAGING NMR

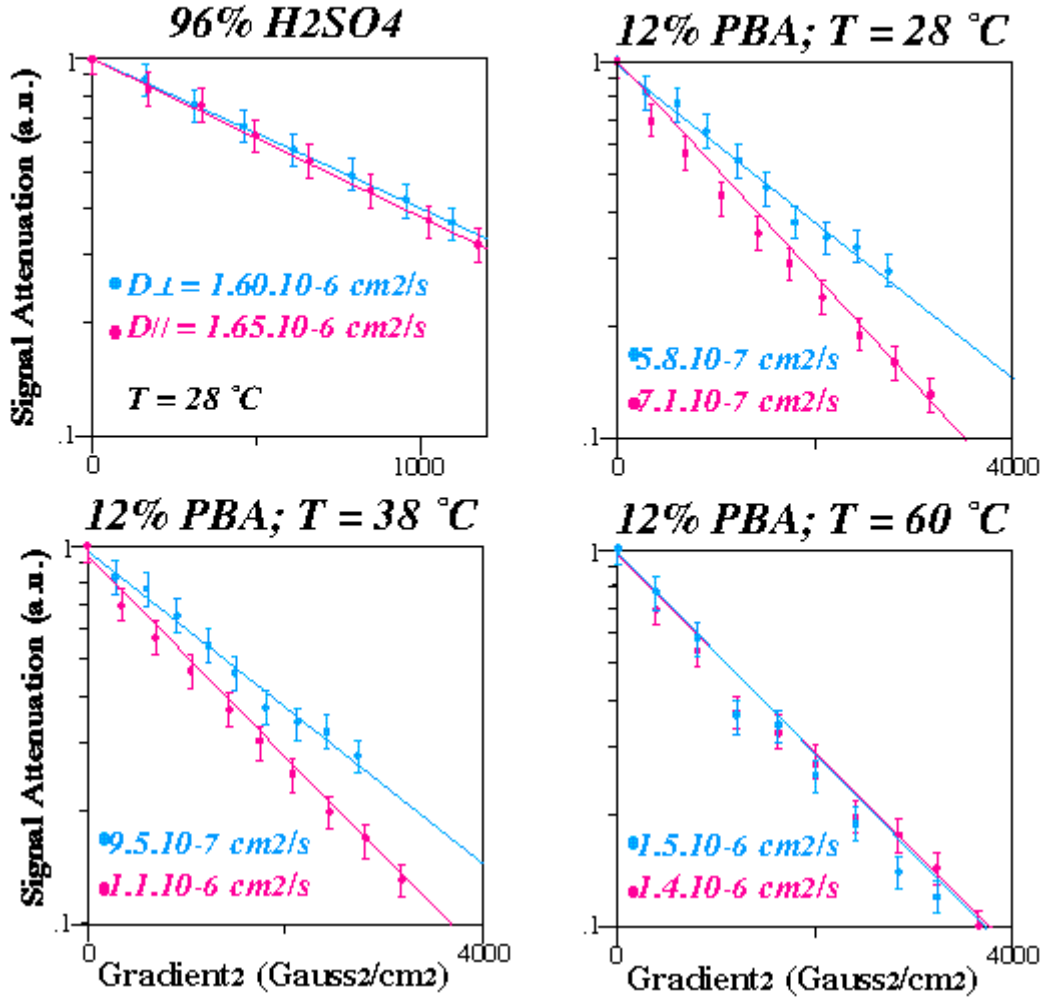


$$S(\mathbf{G})_{echo} = \langle \exp(i\phi_{echo}) \rangle = S(0).\exp[-\gamma^2\tau^2 \mathbf{G}.\mathbf{D}.\mathbf{G}(\Delta - \tau/3)]$$

$$\Rightarrow \quad \ln[S(\mathbf{G})/S(0)] = -\gamma^2\tau^2 G^2 \langle D \rangle (\Delta - \tau/3)$$

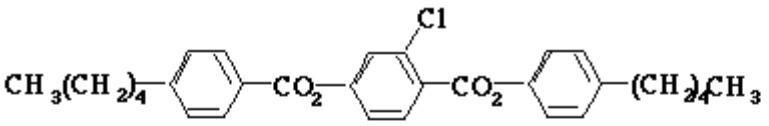
where

$G = |\mathbf{G}|$; $\langle D \rangle$ = average diffusion coefficient along $\mathbf{r}$

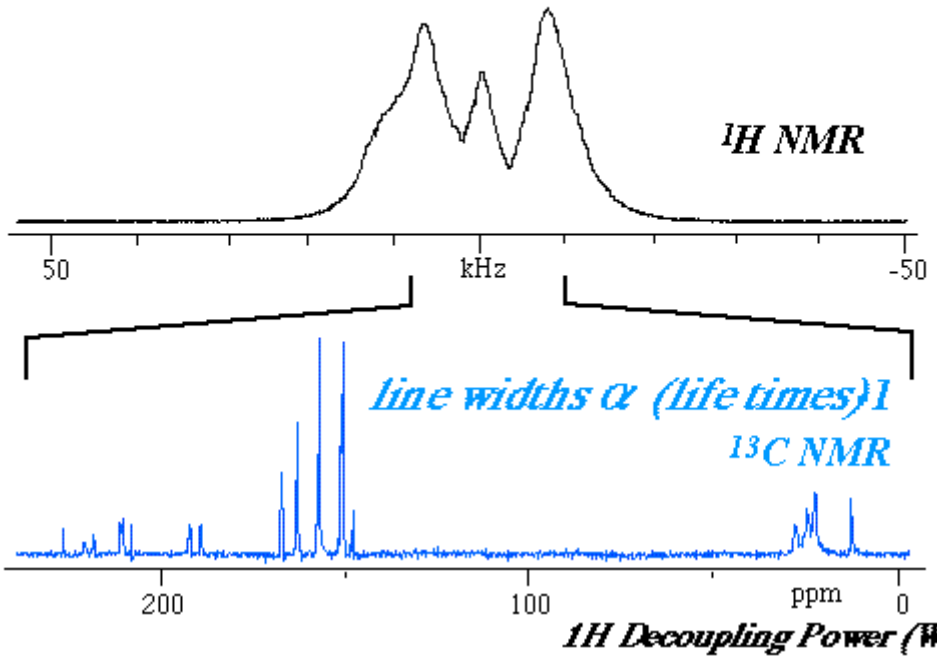


Pulsed-Gradient Spin-Echo 13C NMR:

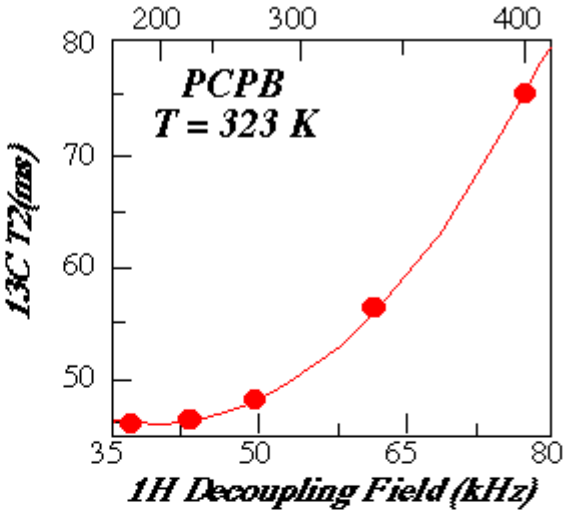
Now we would like to do the same but monitoring the solute's signal. Unfortunately the polymers T2's are too short for using conventional or even stimulated-echo PGSE. One possibility would be to extend the T2's by applying 1H multiple-pulse decoupling sequence. We chose an alternative option: Monitor the PGSE behavior of 13C signals under high-power 1H decoupling conditions.
The rationale:



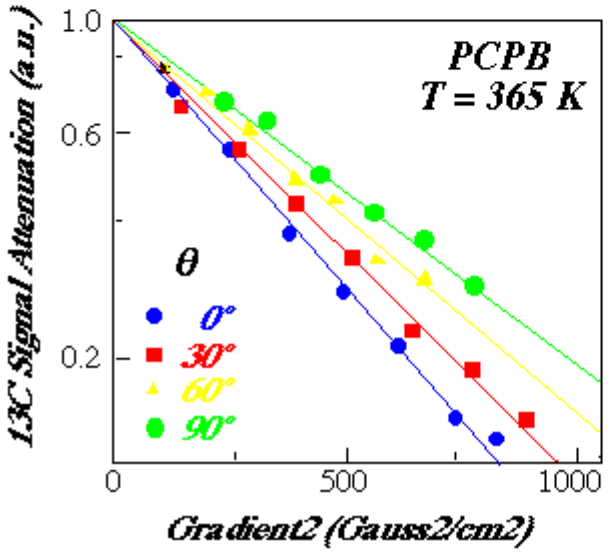
PCPB:
thermotropic LC



As shown by these CPMG spin-echo measurements, an important consideration in these liquid crystal NMR experiments is the level of 1H decoupling: the higher the field, the longer the FID



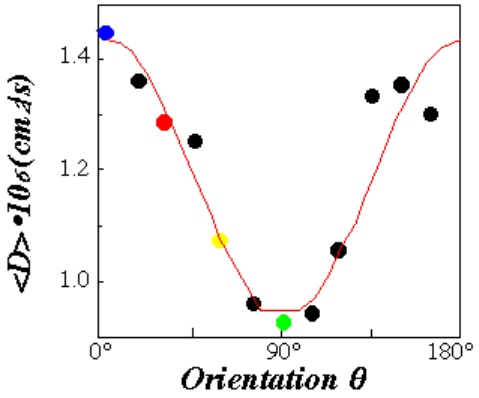
Appropriate decoupling levels enable the PGSE measurement of diffusion coefficients in these phases:



13C PGSE decay curves of PCPB resonances as a function of gradient orientation

The orientation-dependence observed in these measurements can be understood from the fact that in a liquid-crystalline phase molecules move faster along their main ordering axis. Data can then be fit in order to extract the individual components of the self-diffusion tensor:

$$\langle D(\theta)\rangle = D_{\parallel}.\cos^2\theta + D_{\perp}.\sin^2\theta$$
$$= D_{iso} + (\Delta D/2).(3\cos^2\theta - 1)/2$$



$D_{\perp} = 9.5.10^{7}$ cm²/s
$D_{\parallel} = 1.4.10^{6}$ cm²/s

We are beginning to apply this 13C PGSE methodology on liquid-crystalline polymers