



Solid State NMR Study of Molecular Dynamics in Oligofluorenes



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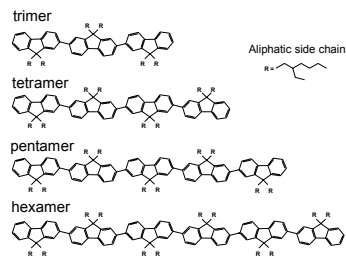
Introduction

The blue light emission of polyfluorenes stimulated intense recent investigation for device application in photonics and optoelectronics as organic electroluminescent materials. However, known keto defects can lead to a low energy emission band. Therefore conjugated defect free oligofluorenes with controlled properties provide excellent alternative candidates for purification, characterization and processing into thin films [1].

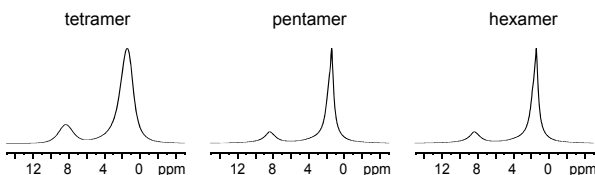
In contrast to the polyfluorenes, the oligomers form nematic meso-phases which can be used to improve the electroluminescence and the processing properties. The NMR studies of this presentation investigated the dynamic behavior of different oligofluorenes.

Characterization of Oligofluorenes: Basic Solid-State NMR Experiments

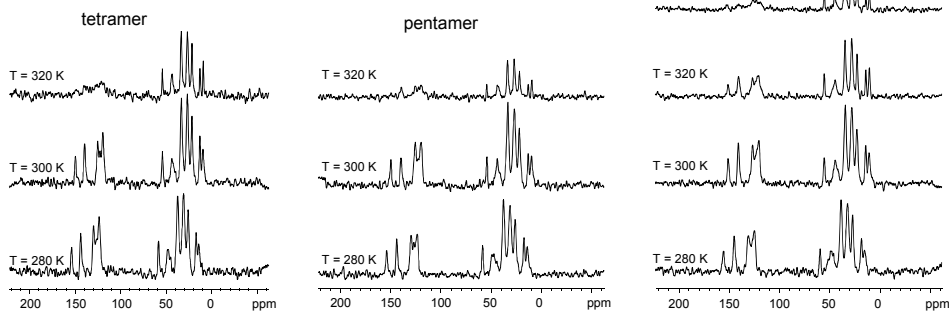
chemical structure of oligo-fluorenes



¹H MAS NMR spectra recorded at ambient temperature (T = 300 K), 30 kHz MAS spinning frequency and 700 MHz ¹H Larmor frequency (shown at the right), have a poor resolution and do not show any significant difference between the different fluorene oligomers.



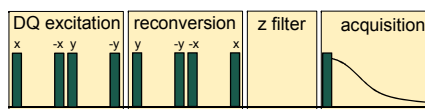
Temperature dependent ¹³C CP MAS measurements provide spectra with reasonable resolution. However, the ¹³C signal intensity drops significantly with increasing temperature.



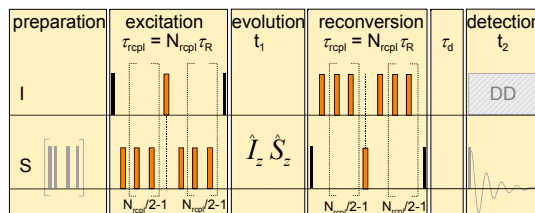
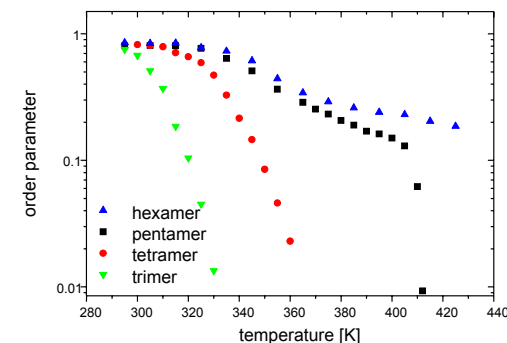
The reduced ¹³C signal cannot be attributed to reduced CP efficiency due to molecular dynamics, because the weaker signals of ¹³C single pulse experiments vanish in the same temperature range. Therefore, interference of molecular dynamics and NMR time scales may reduce the signals.

Dynamic Behavior of Oligofluorenes: Recoupling Experiments under fast MAS

Despite the poor resolution of ¹H MAS spectra, ¹H double quantum (DQ) measurements of the aromatic signal can be used to study dynamic order parameters along the main chain of the oligofluorenes. Spinning at 30 kHz, the BABA-recoupling scheme [2], shown below, has been applied to DQ coherences.

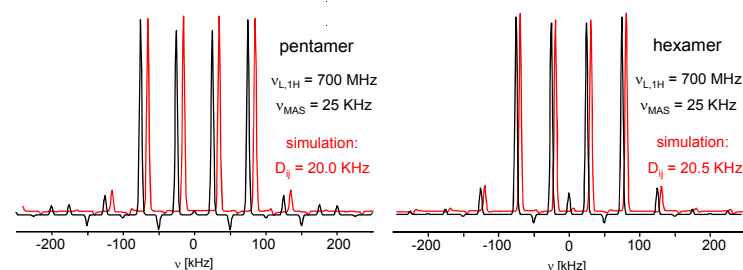


The order parameters obtained from the DQ experiments show a smooth decrease with increasing temperature attributed to the glass transition, which goes to zero for trimer and the tetramer. In the case of the pentamer the order parameter drops to zero at nematic-isotropic transition, known from DSC. Due to the limited temperature range of the NMR probe, the transition of the hexamer cannot be observed.



Order parameters perpendicular to the oligomer main chain can be obtained from ¹H-¹³C heteronuclear dipolar couplings. A rotor-encoded TEDOR scheme, named REPT-HDOR [3], has been used to determine the hetero-nuclear dipolar couplings via sideband pattern analysis. The comparison of experimental (—) and simulated (---) sideband pattern indicate that the oligomers do not reorient around their main chain at ambient temperature (T= 300 K).

The SIMPSON simulation package [4] has been used to compute the REPT-HDOR sideband pattern in order to take finite pulse length (v_{RF} = 100 kHz) and instabilities of the MAS rotation into account. The determined hetero-nuclear dipolar coupling are slightly below the static C-H bond coupling value of 21 kHz.



Conclusions

- Vanishing ¹³C (CP) MAS signals indicate the onset of molecular dynamics at temperatures above the static glass transition temperature.
- ¹H DQ spectroscopy can monitor the order parameters along the oligomer main chains, and thus is very sensitive to nematic-isotropic phase transition.
- In the case of the fluorene tetramer, the nematic-isotropic phase transition is obscured by the slow dynamics close to the glass transition.
- Rotational or flip motions in the glassy state and close to the glass transition temperature can be excluded by REPT-HDOR measurements.

References

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