Macromol. Symp. **2003**, *201*, 85—88

Supramolecular Aspects of Polymer Science: A Challenge for Solid State NMR

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Summary: Recent developments in structural elucidation of supramolecular systems by advanced solid state NMR are described. Special emphasis is placed on hydrogen-bonded sytems and columnar stacks of aromatic moieties. In imidazole-based proton conductores spatially separated regions of high and low mobility are identified. In stacks of alkyl-substituted hexabenzocoronenes maximum charge carrier mobility is observed for crystal-like stacking of the discs.

Keywords: charge transport, NMR spectroscopy, proton transport, solid-state structure, supramolcular structure

Introduction

In advanced synthetic as well as in biological systems self-assembly of carefully chosen building blocks is of central importance.[1] Hydrogen bonding and aromatic π-π-interactions are key features of supramolecular chemistry. Despite being highly ordered on a local scale, such systems often do not crystallize. Therefore, their structures cannot be determined by conventional X-ray crystallography or neutron scattering. Alternatives are needed which should provide structural and dynamic information, preferably requiring only small amounts of as-synthesized samples. High resolution solid state ^{1}H-NMR can meet these requirements,[2] provided that sufficiently selective information can be extracted from the corresponding spectra.

Over the last years we have systematically pursued the development of solid state ^{1}H NMR for that purpose by combining fast Magic Angle Spinning (MAS) and Double-Quantum (DQ) NMR spectroscopy, which makes use of the homonuclear dipole-dipole coupling between protons.[3] The spectral resolution can be increased by use of similar methods exploiting

DOI: 10.1002/masy.200351109

heteronuclear ^{1}H-^{13}C dipole-dipole couplings.[4] These techniques have provided new insight in

- hydrogen bonded structures in the solid state[5]
- columnar stacking and molecular dynamics of discotics[6]
- chain order and translational motion in polymer melts[7]
- chain organization on surfaces.[8]

Solid state NMR probes the structure at the molecular level. Self-assembly, however, often leads to structures which are partially ordered on the nanometer scale. There, pulse EPR techniques[9] are better suited to determine their structure after introduction of spin labels. This technique has provided new insight in the nanostructure of polymers[10] including block copolymers with ionic groups.[11]

Hydrogen Bonded Systems

Protons in hydrogen bonded structures exhibit ^{1}H chemical shifts well away from the aliphatic peaks. Therefore, high resolution ^{1}H solid state NMR is ideally suited for investigating such systems as noted early on in our study of the unusual hydrogen bonded structures in benzoxazine dimers.[5] These dimers are of interest as model compounds for a new class of phenolic materials, the polybenzoxazines prepared by Ishida and coworkers.[12] These systems combine several favorable properties, such as near-zero shrinkage on polymerization as well as low water absorption, which are attributed to their favorable hydrogen-bonding. Application of improved methods have meanwhile allowed us to locate the protons in these compounds with high precision[13] and evidence for helical structures has been found in benzoxazine oligomers.[14] Further examples are collected in a recent review.[15]

Imidazole Based Proton Conductors

Recently, the new techniques were applied to study proton conductivity.[16] The materials of interest, ethylene oxide tethered imidazole heterocycles[17] (Imi-nEO), are characterized by variable temperature experiments, as well as 2D homonuclear DQ NMR and 2D exchange spectroscopy.[2] Quantum chemical calculations provide a full assignment and understanding of the ^{1}H chemical shifts, based on a single-crystal structure obtained for Imi-2EO. Three types of hydrogen bonded N-^{1}H resonances are observed. Double quantum NMR experiments identify those hydrogen-bonded protons that are mobile on the time scale of the experiment, and thereby, are able to participate in charge transport. In addition, evidence for locally ordered domains within all the Imi-nEO materials is provided. Disordered (mobile) and ordered components in Imi-2EO dramatically differ in their ^1H spin-lattice relaxation times. At lower temperatures and in absence of excess protons 2D NOESY spectra[2] show no evidence of chemical exchange processes between the ordered and disordered domains. These results indicate that the highly ordered regions of the materials do not (or only poorly) contribute to proton conductivity, which is rather taking place in the disordered regions.

Photonic Materials

Advanced solid state NMR is also highly suited for elucidating columnar stacking and its relation to function.[6] Solid columnar discotic and liquid crystalline (LC) phases formed by alkyl-substituted hexabenzocoronene (HBC) mesogens have been investigated by a combination of X-ray scattering and a variety of advanced solid state NMR methods. Correlations between chemical structure, molecular packing and dynamics are established. Maximum charge carrier mobility is observed for a crystal-like stacking of the discs in the column with optimized π-π-interactions.[18]

Self-assembly of fluorinated tapered dendrons can drive the formation of supramolecular liquid crystals with promising optoelectronic properties from a wide range of organic materials. Attaching conducting organic donor or acceptor groups to the apex of the dendrons leads to supramolecular nanometer-scale columns that contain in their cores π-stacks of donors, acceptors or donor–acceptor complexes exhibiting high charge carrier mobilities. Moreover, functionalized dendrons and amorphous polymers carrying compatible side groups co-assemble so that the polymer is incorporated in the centre of the columns through donor–acceptor interactions and exhibits enhanced charge carrier mobilities. The mutual arrangement of the functional groups was determined by solid state NMR.[19]

Conclusions

The development of the technique is far from being complete. Major advances are expected in the years to come. This includes in particular increased sensitivity through inverse detection in heteronuclear solid state NMR. Thus solid state NMR is envisaged to become an indispensable tool in the field of supramolecular polymer chemistry.

Acknowledgements

The author would like to thank his coworkers and visiting scientists involved in this work, in particular, I. Fischbach, G. Goward, H. Ishida, A. Rapp, K. Saalwächter, D. Sebastiani, I. Schnell. Financial support by the Deutsche Forschungsgemeinschaft (SFB 625) is gratefully acknowledged.

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