Multidimensional Solid-State NMR of Structure and Dynamics of Polymers

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SUMMARY: New developments in high-resolution multidimensional NMR of solids are described. Special emphasis is placed on double-quantum (DQ) methods employing fast magic angle spinning (MAS). This new technique allows structural elucidation with atomistic resolution including hydrogen positions in non-crystalline materials and the determination of the anisotropy of chain motions by probing residual dipolar couplings between adjacent groups along a macromolecule. Specific examples include hydrogen bonded systems, columnar structures with π-π interactions, polymer melts and block copolymers.

Introduction

Polymer science today heavily uses the concepts of supramolecular chemistry. Non-covalent interaction such as hydrogen-bonds, ionic forces, π-π interactions and the shape of the building blocks are exploited in order to generate complex structures for specific interactions[1,2]. In many, if not most cases, the so generated materials are not crystalline or single crystals are not available. Therefore, use of the most powerful methods for structure determination with atomic resolution, X-ray and neutron scattering, is limited and alternatives are needed.

High-resolution Nuclear Magnetic Resonance (NMR) spectroscopy of molecules in solution is widely used in order to elucidate the structures of synthetic and biomolecules alike[3]. Particularly attractive are methods which provide distance constraints by exploiting the dipole-dipole coupling between nuclear spins, such as the Nuclear Overhauser Effect (NOE). In solids[4], the spectral resolution is much lower, because of the severe line broadening resulting from the strong dipole-dipole coupling amongst the protons (^1H) and between ^1H and ^{13}C. Although the spectral resolution can be significantly reduced by Magic Angle Spinning (MAS), this approach was generally believed to be inadequate to achieve sufficient site resolution in ^1H solid state NMR. Therefore, structural studies of solids and solid

polymers focussed on measuring dipole-dipole couplings between ^{13}C-^{13}C and ^{13}C-^{15}N after selective isotope labeling [5-7].

With the advent of fast and ultrafast MAS[8] employing spinning frequencies in the range of 20 - 35 kHz and the availability of high magnetic fields with more than 10T the spectral resolution of ^{1}H significantly improved[9]. More important, the dipole-dipole coupling between the innumerable ^{1}H in a solid is immensely simplified by fast MAS. In fact, the behavior of the ^{1}H spins in rapidly rotating solids is largely dominated by ^{1}H-^{1}H pair correlations[10], which offer a new approach to structural elucidation of solids via ^{1}H-^{1}H homonuclear[11,12] and ^{1}H-^{13}C heteronuclear [13,14] Double-Quantum (DQ) NMR spectroscopy. In DQ NMR proximities of site resolved nuclei manifest themselves by peaks, whose intensities reflect the strength of the dipole-dipole coupling between them. Couplings between like spins lead to diagonal peaks in a suitably scaled two-dimensional DQ NMR spectrum and couplings between unlike spins manifest themselves in a pair of off-diagonal peaks at the *same* DQ frequency. As a rule of thumb, occurrence of such DQ signals require the two spins to be within 0.35 nm. This kind of DQ spectroscopy, therefore, can be considered as a solid-state analogue of the well-established NOESY spectroscopy in liquids[3], albeit considerably more quantitative. Moreover, for precise measurement of dipole-dipole couplings DQ sidebands can be recorded and analysed[12,15].

Hydrogen-Bonded Assemblies

Supramolecular polymers can be generated by exploiting hydrogen bonds, well-known from biomolecules, such as nucleic acids[1]. The hydrogen bonds can conveniently be studied by NMR spectroscopy, because the ^{1}H chemical shifts strongly depend on the position of the proton in a O···H···O or a N···H···O hydrogen bond[16]. As a first example we elucidated the hydrogen-bond structures in the benzoxazine building blocks of a new class of phenolic materials[17], whose unique properties are attributed to favorable hydrogen-bonding. Indeed, different arrangements could be identified, pairs of hydrogen-bonded dimers as distinguished from a linear arrangement of such dimers[18].

Hydrogen-bonds can also be used to link chain segments to form macromolecules via quadruple hydrogen-bonds imitating base-pairs in nuclei acids[19], see Fig. 1. As a function of temperature or solvent, these systems can reorganize, e.g. by automeric keto-enol rearrangements. Considering the hydrogen-bonded linkage alone, the keto-form is

thermodynamically considerably more stable than the enol-form. In the bulk, however, supramolecular packing of the disc-shaped linkages may favor the latter. As shown in Fig. 1 the DQ ^{1}H NMR of the two forms differ significantly, and indeed, the enol-form turns out to be more stable in the specific system studied[20].
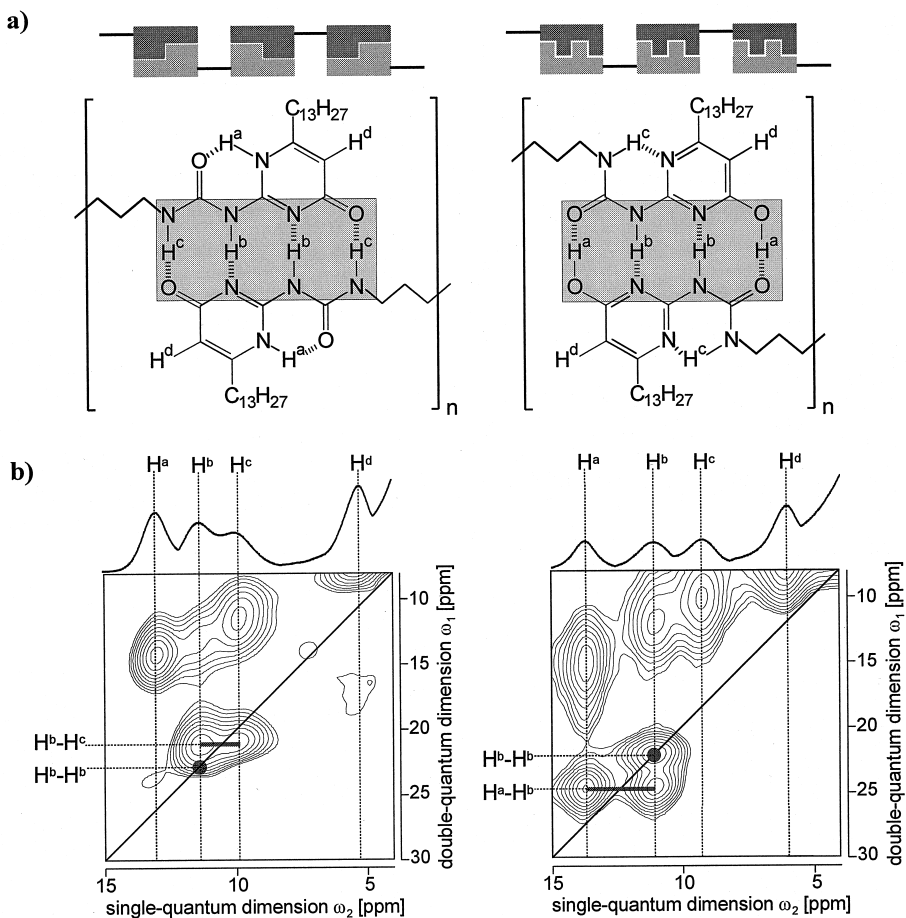
a)

b)

Fig. 1: Hydrogen-bonded supramolecular polymers: a) Scheme of different linkages with keto-form left and enol-form right. b) ^{1}H DQ MAS NMR spectra at 700 MHz, for details see[19,20].

Arrangement of Aromatic Rings in Columns

Columnar discotic liquid crystals[21] based on extended aromatic rings with flexible side groups are promising candidates for photonic applications[22]. Little is known, however, about the mutual arrangement of the rings within the columns, as these materials can usually not be prepared as single crystals suitable for X-ray structure determination. As described in detail elsewhere[23] fast MAS DQ ^{1}H NMR spectra allow us to deduce the staggered arrangement of hexabenzocoronene discs within the columns as depicted in Fig. 2. Homo- and heteronuclear DQ sideband patterns were recorded to distinguish different degrees of order within the columns resulting from chemical modifications[23,24]. The different packing arrangements resulting from the balance of optimizing π-π interactions and geometric factors, result in different values for charge carrier mobilities[25]. This shows that the unique information on the structure of such supramolecular assemblies now available from solid state NMR is highly valuable for optimizing the packing of tailored building blocks in order to achieve specific functions such as photo-conductivity.
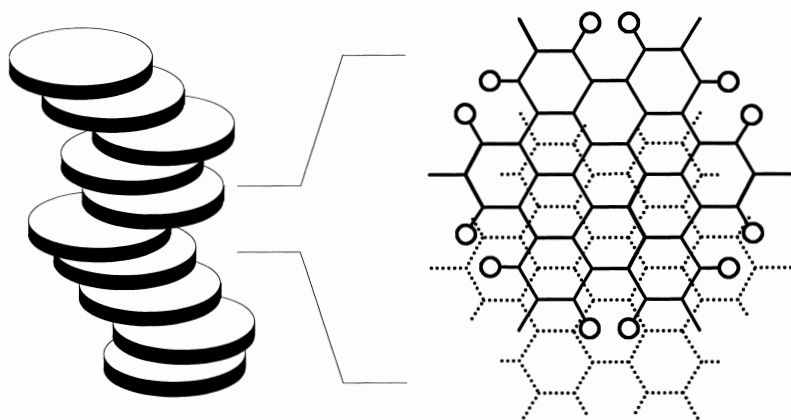

Fig. 2: Arrangement of discs in columnar structures as deduced from solid state NMR[23].

Chain Order in Polymer Melts

In the previous examples, DQ NMR was employed to elucidate the structure of complex materials. Yet, it is well-known from the study of liquid crystals that partial alignment of building blocks can be detected through time averages of anisotropic spin interactions, such as the dipole-dipole coupling [21]. At 50 K or more above T_g, the chain motions are rapid

enough to average the dipole-dipole coupling. Then, NMR can probe the motional behavior of the average chain structure. Contrary to low molar mass liquids the chain motion in polymers is not completely isotropic, resulting in residual spin dependent anisotropic couplings. Numerous ways have been proposed to relate these residual couplings to characteristic chain parameters[26]. Restrictions of the chain motion result from local chain order due to the presence of extended local conformations or stiffening structural elements on a shorter scale and entanglements as well as crosslinks on a longer scale. Then the autocorrelation function $S(t) = \frac{1}{2} \langle 3 \cos^2\theta - 1 \rangle$, where θ is the angle between the orientation of a vector $\mathbf{r}$ fixed to a structural unit of the chain at time zero, $\mathbf{r}(0)$ and time t, $\mathbf{r}(t)$, will not simply decay to zero, but at intermediate times level at some finite plateau value reflecting the anisotropy of the motion. On a longer time scale isotropisation occurs. The height of the intermediate plateau can then be considered as a dynamic order parameter of the chain motion, since it persists for a large number of conformational transitions. Such dynamic order parameters have mainly been considered in elastomers by measuring residual ^1H -^1H dipole-dipole couplings of CH_2 groups[26] or ^2H residual quadrupolar couplings[27,28] and it was concluded that they are typically very small, i.e. below 5%. All these methods, however, probe the chain order via anisotropic couplings whose primary directions are *transverse* to the local chain axis. Thus, they primarily probe the rapid axial chain motion.

The chain order can much better be characterized, if residual couplings *along* the carbon-carbon bonds can be determined. This has recently been achieved by determining the residual dipole-dipole coupling between the CH_2 and the adjacent CH group in the polybutadiene (PB) segment of a crosslinked poly(styrene-co-butadiene) (SBR) elastomer from 2D exchange NMR[29]. A much more complete dataset is provided by the double quantum spectrum of such systems recorded under fast MAS, see Fig. 3. With that technique the dynamic order parameter for the C=C double bond direction in a PB melt was determined to be S = 0.13 at T = T_g + 50 K. This value is considerably higher than anticipated[30]. Even more remarkable is the time dependence of the dynamic order parameter. As shown elsewhere[30] for long times S(t) probes the *translational* dynamics of the polymer. Based on current theories of chain dynamics[31,32], when a tagged segment leaves its initial environment the spin pairs will acquire a random orientation. Then, S(t) will reflect the probability that a segment at time t is between the same two entanglements as it was at t = 0 (return to origin probability)[33]. The natural unit for t will be t_e, the time a segment needs to move the distance

between two adjacent entanglement as determined, e.g., from the molar mass dependence of the bulk viscosity.
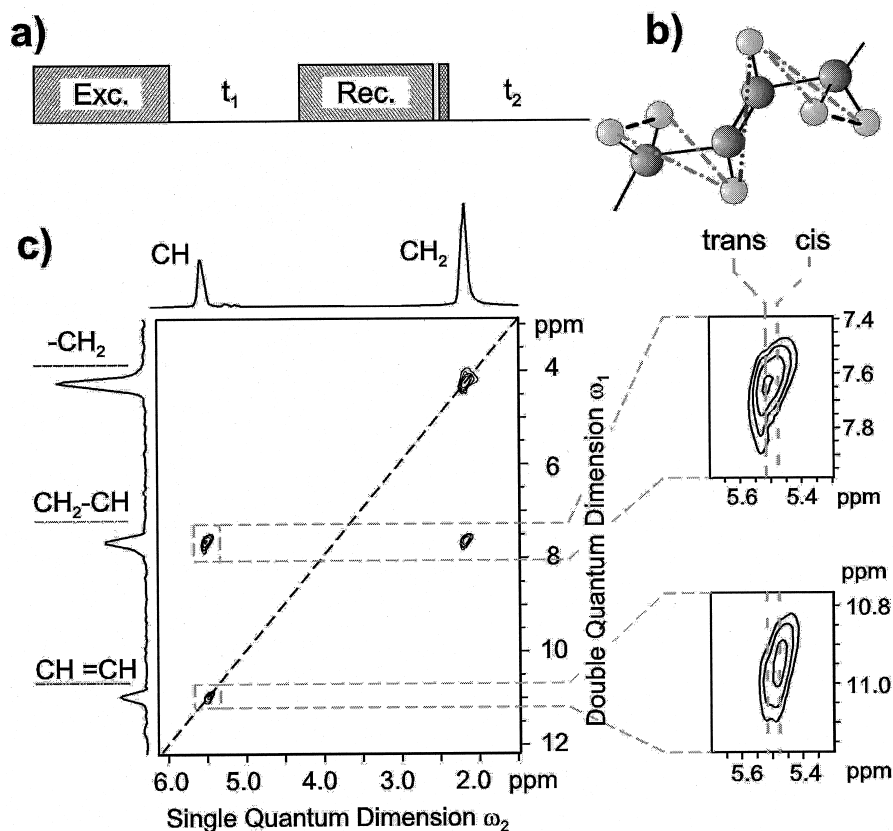

Fig. 3: Chain order in polymers as deduced from DQ NMR: a) Sketch of experimental scheme for measuring residual dipole-dipole couplings for selected proton-proton pairs. b) Trans-form of 1,4-polybutadiene. c) ^{1}H DQ MAS NMR spectrum of 1,4-polybutadiene at 500 MHz, for details see[30].

As shown in Fig. 4 the time dependence of S(t) for intermediate molar mass in the melt shows the scaling behavior expected from the reptation model[31,32], in particular the cross-over from $t^{-1/4}$ to $t^{-1/2}$ around 100 t_e. This means that the dynamic order parameter is defined on a length scale of the order of the tube diameter, i.e. on a nm scale. The dynamic order parameter can significantly be increased if the polybutadiene chain is incorporated as part of a lamellar block copolymer with rigid polystyrene (PS-b-PB), data also shown in Fig. 4. In the block copolymer the time scale where S becomes time dependent is shifted to longer

times. Similarly, for a ABA triblock-copolymer (PS-*b*-PB-*b*-PS), the dynamic order parameter is essentially time independent. This nicely corroborates our interpretation that the reduction of S is due to translational motion, which is quenched in the ABA triblock. The fact that S(t) significantly decays in the diblock means, that the chains are *not* aligned perpendicular to the plane of the lamellae, but assume more or less random orientations of their preferred chain axes, details will be published elsewhere[34].
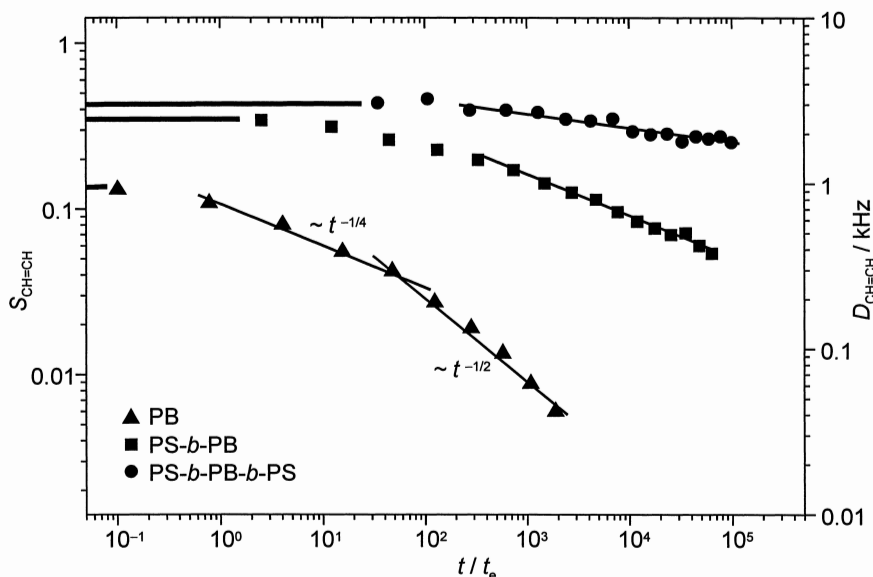

Fig. 4: Temperature dependent residual dipolar couplings and dynamic order parameters as determined from DQ NMR for a polybudadiene (PB) melt, a PS-*b*-PB diblock and a PS-*b*-PB-*b*-PS triblock copolymer. Two power laws observed for the melt are indicated. For details see[34].

This suggests that the dynamic order parameter for macromolecular chain units should be considered as a new parameter in order to get a better understanding of the rheological behavior of polymer melts on a molecular level. This parameter apparently strongly varies for different polymers. In fact, extremely high values were previously found in poly(n-alkyl methacrylates) by ^{13}C-NMR at temperatures about 50 K above T_g [35], S = 0.7 in poly(ethyl methacrylate) S = 0.35 and in poly(methyl methacrylate), which may be related to nanophase separation recently suggested for these systems[36].

Conclusion

Multidimensional solid-state NMR has in the past already shown its capability to provide hitherto inaccessible information about timescale and geometry of molecular motions, molecular order and phase separation in multicomponent polymers[4]. With the advent of fast MAS coupled with DQ NMR techniques, the versatility of solid-state NMR has further improved. It now provides detailed information about structure of complex supramolecular materials. In particular, two of the most important interactions governing supramolecular organization, i.e. hydrogen bonds and π-π interactions can be elucidated. The spectroscopic information can further be quantified by combination with *ab-initio* quantum chemical calculations[37]. Moreover, DQ NMR also provides new insight in the chain organization of amorphous polymers, which are apparently considerably more ordered than generally assumed so far. This then makes supramolecular polymers much easier to reconcile than often anticipated[38].

Acknowledgements

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