Solid-State NMR Studies of Environmentally Friendly Flame Retardants

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Introduction

For many applications, polymer based materials have to pass fire retardance tests. Frequently, brominated compounds are used as fire retardant additives, which suffer from the disadvantage of being environmentally hazardous under the influence of heat. Therefore it is of great interest to develop environmentally friendly flame retardants, which may be incorporated into polymers. A promising group of flame retardants is consid- ered to be melamine phosphates (MP). An important goal to improve flame retardation is to test their chem- ical composition and structure to their mechanism of functioning.

In a first step the approximate powder structure of MP was obtained by X-ray diffraction. Although the proton positions cannot be determined by X-ray diffraction, alternative models were proposed using a combined molecular modeling-MAS NMR approach. Although one model was favored, no conclusive answers could be drawn. A key issue is if and how the proton positions from the phosphoric acid bond to the melamine moiety.

A solid-state NMR is the ideal tool to gain detailed information about the proton positions, proximities and the hydrogen bonding network.

Here present solid-state NMR results which include high resolution H spectra obtained under magic-angle-spinning (MAS) conditions and different types of heteronuclear correlation spectra (H-1, T-1, T-2) of MP obtained on C-13 and N-15 enriched MP.

The solid-state NMR results confirm in parts the modeling results. The NMR results are consistent with a model of the proton positions obtained from the combined molecular modeling-MAS NMR approach.

In addition we present first results obtained on melamine pyrophosphates (MP22) and melamine polyphosphates (MP30).

Methods

Heteronuclear Correlation Spectra (HETCOR):

After the FSLG homonuclear decoupling sequence is applied to the 1 spin (H), the 15N-spin, the magnetization is transferred to the 1 spin (C, P) by Laue-Goldburg cross-polarization (LG-CP), during which the H spins are homonuclear decoupled. In the second step, the resulting 2D spectra represents the high resolution H spectrum, while the 15N-spectrums axes represents the direct 15N dimension. Cross-peaks indicate close heteronuclear through-space 1J-contacts.

Homonuclear Double-Quantum Spectra:

After ramped cross-polarization, the enhanced longitudinal 1spin (N) magnetization is converted into homonuclear double-quantum coherences using the POST-C2 homonuclear double-quantum recoupling sequence. The double-quantum coherences evolve during the interval t and are converted back into observable magnetization, which is detected in the interval t.

The diagrams on the right show the crystal structure of MP.

Discussion for MP

MP Heteronuclear Correlations:

All 2D experiments were performed in a field of 3T and a spinning frequency of 12.5 kHz.

The proton resonance in the 2D spectra is different in the different correlation experiments. This shows the advan-
tage of the heteronuclear correlation experiments compared to pure proton spectra.

The proton resonances could be improved by using different heteronuclear decoupling sequences. Tors on alime, using TPPI [2] and R2K [4] did not show an improved resolution.

However it is expected that these sequences result in better resolution at external fields (18.8 T) combined with high rf fields (200 kHz) [2].

N-15 Double-Quantum Spectrum:

On the right a 2D N-15 double-quantum spectrum of MP is shown. The spectrum was recorded at a field of 7.1 T and a spinning frequency of 600 kHz.

The assignment of the N resonances is indicated. The resonances for the N5/N8 and N6/N7 sites could not be uniquely assigned.

Results

The 1D H spectrum was obtained in an external field of 3T and a spinning frequency of 12.5 kHz.

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References


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