Electronic Supplementary Information

to

Probing self-assembled 1,3,5-benzenetrisamides in isotactic polypropylene by ^{13}C DQ solid-state NMR spectroscopy†

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Experimental Section

Materials and Preparation

The *i*-PP homopolymer grade Profax PH 350 was purchased from LyondellBasell. The polymer contained about 0.05 wt% of the antioxidant Irganox 1010, 0.10 wt% Irgafos 168 and 0.1 wt% Ca-stearate. The polymer pellets were pulverized in a freezer mill (Retsch ZM100, Schieritz & Hauenstein AG, Switzerland) before usage. The ^{13}C labelled 1,3,5-tris(2,2-dimethylpropionylamino)benzene was synthesised and characterised as described in Ref 1.

The *i*-PP/additive material was prepared by compounding a dry-blended powdery mixture of *i*-PP and the additive using a laboratory, co-rotating mini-twin-screw mixer (Technical University Eindhoven, The Netherlands) at 280 °C under nitrogen blanket for 5 minutes. The concentration of the additive was directly adjusted to 0.09 wt%. The extruded strand was mechanically cut and pulverized in a freezer mill (Spex CertiPrep 6750, Metuchen, NJ 08840, USA) using two cycles of 3 minutes each.

Solid-State NMR

The ^{13}C chemical shifts are reported with respect to TMS. The ^{1}H-^{13}C CP MAS spectrum, the ^{13}C double quantum build-up curve, and the ^{13}C 2D DQ-SQ spectrum of the *i*-PP/additive material were recorded at $B_0 = 7.04$ T using a standard ZrO_2 rotor on a Bruker Avance II 300 spectrometer with a 4 mm triple resonance probe. For the 1D CP MAS ($\nu_{rot} = 12.5$ kHz) spectrum a contact time of 6 ms was used. The 90° pulse on the proton channel and the recycle delay were set to 3.0 μs and 2 s, respectively. The number of scans accounted for 4096 leading to a total experiment time of 6 h.

For the double quantum experiments, the symmetry-based pulse sequence $SR26^{11}_{4}$ was used. Before exciting DQ coherences, a ramped shaped cross polarization from proton to ^{13}C with a ^{1}H 90° pulse length of 3.0 μs and a contact time of 6 ms was used for an increased signal-to-noise ratio. The recycle delay was set to 2 seconds which matched the full T_1 relaxation time for the aliphatic protons of the polymer as well as of the methyl groups of the additive. The 90° read-out pulse on the ^{13}C channel accounted to 3.0 μs. The MAS frequency was set to 6.25 kHz and the R-block was implemented as a 90°-270° composite pulse corresponding to a nutation frequency of roughly 40.5 kHz ($\tau_{90°} = 6.15$ μs). The transmitter frequency offset was placed between the resonances of the polymer and the additive leading to an off-resonant excitation of roughly 6 kHz.

For the build-up curve, the establishing of the coherence pathway 0 ±2 0 -1 was performed with the conventional 16-fold phase cycle.[2] An additional standardisation experiment was performed with the zero-quantum coherence pathway 0 0 0 -1. From both data sets the normalised DQ intensity is calculated according to equation S1. The number of repetitions for each of the nine 1D experiments was set to 4096. The step size for incrementing τ_{exc} was set to 52 corresponding to 2.56 ms accounting for a maximum excitation time of 20.48 ms. During excitation and reconversion CW decoupling with a nutation frequency of roughly 120 kHz was performed.

For the 2D DQ-SQ ^{13}C spectra excitation times of 6.4, 15.36 and 20.48 ms (shown in Figure 1 and S2) were established. The quadrature along the indirect dimension was obtained using the STATES procedure.[3] For τ_{exc} = 15.36 ms the 50 t_1 increments were set rotor synchronised with two times τ_{rot} (t_1 = 320 µs) while for τ_{exc} = 6.4 and 20.48 ms, respectively, only one time τ_{rot} (t_1 = 160 µs) was applied. During t_1 a heteronuclear CW decoupling with reduced power irradiating a nutation frequency of roughly 85 kHz was applied. Each t_1 increment was repeated 3072 times resulting in a total experimental time of 4d. During excitation and reconversion a heteronuclear broadband decoupling was necessary to gain signals with acceptable intensities beyond the noise level. To avoid Hartmann-Hahn conditions a strong decoupling during the DQ blocks following $\nu_{nutation}(^1H) = 3 \cdot \nu_{nutation}(^{13}C)$ was used.[4] The strong irradiation on the proton channel with roughly $\nu_{nutation}(^1H)$ = 120 kHz is thereby the power-limiting factor of the probe.

For all experiments, a broadband SPINAL64 proton decoupling with a nutation frequency of about 85 kHz was used during data collection.

Experimental ^{1}H-^{13}C CP MAS spectrum

The signals of the polymer are quite broad reflecting the partly crystalline and amorphous nature of *i*-PP with different chemical environments. The S/N ratios in the range of the signals account for 675.4 (*i*-PP) to 10.6 ($^{13}C=O$) reflecting the weak intensity of the additive signal despite of the ^{13}C enrichment.

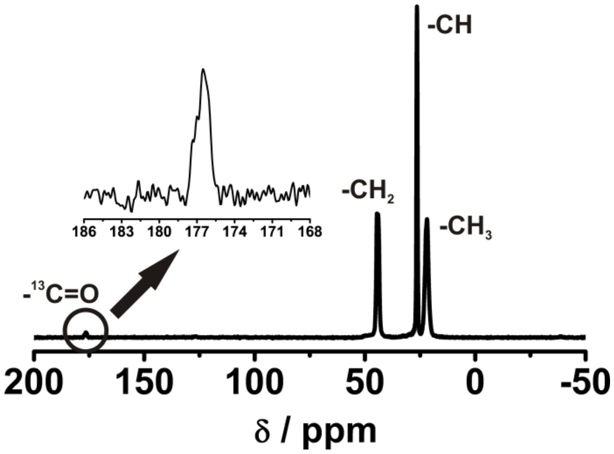

Figure S1 Experimental ^{1}H-^{13}C CP-MAS spectrum (B_0 = 7.04 T, ν_{rot} = 12.5 kHz) of the binary mixture (1,3,5-tris(2,2-dimethylpropionylamino)benzene in isotactic polypropylene, $c_{additive}$ = 0.09 wt%) with a signal assignment for *i*-PP ($\delta \approx 22$ - ≈ 45 ppm) and the carbonyl signal ($\delta \approx 177$ ppm) of the enriched $^{13}C=O$ group of the additive.

Comparison of the DQ-filtered ^{13}C signal of neat BTA and i-PP/BTA mixture

Both the SQ ^{13}C CPMAS (not shown) and the DQ filtered ^{13}C MAS (Figure 3, black circles) spectra of the neat BTA were measured at a external magnetic field of B_0 = 7.04 T and a spinning speed of ν_{rot} = 6.25 kHz. They exhibit a distinct fine structure which arises from the second-order quadrupolar interaction of neighboured ^{14}N nuclei (I = 1) mediated by the $^{13}C^{14}N$ dipole interaction. The experimental DQ filtered ^{13}C MAS spectrum was deconvoluted using the freeware program WSOLIDS1.[5] For getting reasonable starting values a comparable OC=NH system was taken from literature.[6] Here the quadrupolar coupling constant (C_Q = -3.2 MHz), the asymmetry parameter (η = 0.22), the angle between the V_{xx} component of the ^{14}N electric field gradient (EFG) and the projection of the internuclear ^{13}C-^{14}N vector into the equatorial plane (α = 43 °) and the angle between the V_{zz} component of the ^{14}N EFG and the internuclear ^{13}C-^{14}N vector (β = 90 °) were extracted. From the data presented in Ref. 1 the isotropic chemical shift and the direct dipolar coupling constant ($d^{13}{}_{C-}{}^{14}{}_{N}$ = 840 Hz) was used. For the indirect scalar dipolar coupling between ^{13}C and ^{14}N ("*J*-coupling") 11 Hz were chosen which is typical for peptide bonds. The values of β, $d^{13}{}_{C-}{}^{14}{}_{N}$ and $J^{13}{}_{C-}{}^{14}{}_{N}$ were not varied, all other values were refined during the simulation. All relevant parameter for the simulation are given in Table S1.

In accordance to the crystallographic data[1] the simulated spectrum (Figure 3, black line) can be described as a superposition of three sub-spectra (Figure 3, coloured lines). Each of the resonances is split due to the influence of the ^{14}N quadrupolar interaction on a dipolar coupled ^{13}C-^{14}N spin pair. For a more detailed description of the theoretical background the reader is referred to Ref. 6.

Table S1 Summary of the parameters used for the simulation of the three sub-spectra; the superscripted numbers in brackets (1-3) represent the three different carbonyl groups.

	$^*C{=}O^{(1)}$	$^*C{=}O^{(2)}$	$^*C{=}O^{(3)}$
δ_{CS} / ppm	176.65(1)	176.53(1)	176.08(1)
$d^{13}{}_{C-}{}^{14}{}_{N}$ / Hz	840	840	840
$J^{13}{}_{C-}{}^{14}{}_{N}$ / Hz	11	11	11
C_Q / MHz	-3.18(2)	-3.18(2)	-3.18(2)
η	0.40(2)	0.40(2)	0.40(2)
α / °	51(1)	51(1)	52(1)
β / °	90	90	90

To increase the signal-to-noise ratio of the DQ-filtered signal of the *i*-PP/BTA mixture all 1D spectra extracted from the DQ build-up curve (Figure 3, brown line) were summed up.

Evaluation of 2D ^{13}C DQ spectra

For the *i*-PP/additive material a series of 2D ^{13}C DQ spectra with different excitation times were measured and processed using standard procedures within the software package TopSpin™ and further handled using Matlab scripts.[7] Exemplarily, Figure S2 reveals the spectra for τ_{exc} = 6.4 and 20.48 ms representing excitation times below and above the one shown in the main article. The sweep width in the F1 domain - in comparison to the spectrum with τ_{exc} = 15.36 ms - is doubled (83 ppm) due to the halved t_1 increment. This leads to a reduction of the refolding problematic as discussed in the main article. In addition, since the t_1

increment is halved but the numbers of transients in the F1 domain are equal, the spectral resolution is reduced by a factor of two. Still all relevant DQ coherences are resolved. For τ_{exc} = 6.4 ms all signals according to the polymer as well as the autocorrelation signal oft the carbonyl group are observed (in analogy to the spectrum in Figure 1). At higher excitation times the signals including the CH_2-group are missing due to T_2 effects. However, a correlation signal between the carbonyl group of the additive and the polymer matrix could not be observed for any excitation time.

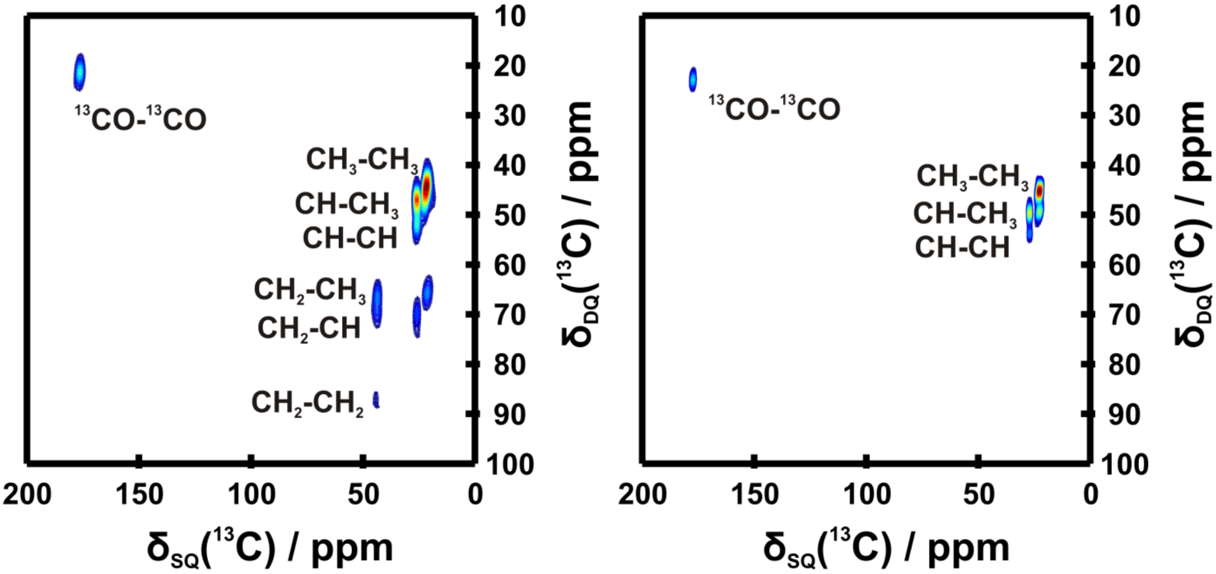

Figure S2 Two dimensional ^{13}C DQ-SQ spectra at excitation times of 6.4 ms (left) and 20.48 ms (right) with assignment of the correlation signals in the spectrum. In comparison to the spectrum with τ_{exc} = 15.36 ms (see Figure 1 in the main article) the spectral width in the indirect domain is doubled to 83 ppm since t_1 was set only one time τ_{rot}. Therefore, only the ^{13}CO-^{13}CO autocorrelation signal was refolded into the spectrum.

For the spectrum with τ_{exc} = 15.36 ms (see Figure 1) four signal groups were refolded into the spectrum. In Table S2 the expected and the observed chemical shifts in the indirect dimension are summarised.

Table S2 Summary of expected and observed signals including assignment in the 2D DQ-SQ ^{13}C spectrum at τ_{exc} = 15.36 ms (see Figure 1); the subscripted figures in brackets represent how many times the correlation signal is refolded into the spectrum.

Correlation	$\delta_{DQ,exp}$ /	$\delta_{DQ,obs}$ / ppm
CH_3 - CH_3	45	45
CH_3 - CH	49	49
CH - CH	53	53
CH_3 - CH_2	66.5	$25_{(-1)}$
CH_2 - CH	70.5	$29_{(-1)}$
CH_2 - CH_2	88	$46.5_{(-1)}$
^{13}CO - ^{13}CO	354	$22_{(-8)}$

Data Evaluation of the DQ build-up curve of the *i*-PP/additive system

The DQ build-up curve of the carbonyl group within the composite material was extracted using a self-written Matlab script.[7] For both the double-quantum filtered (DQF) and the reference experiment filtering the zero-quantum intensities (ZQF) of the neat BTA the *C=O signal and the first two sidebands were taken into account for extracting the intensities. For the *i*-PP/BTA mixture only the main signal could be resolved. The ZQF experiment is necessary to normalise the build-up curve and to eliminate relaxation effects. For more information the reader is referred to Ref. 8. The normalised double quantum efficiency is therefore given by

$$DQ_{\mathrm{norm}} = \frac{I_{DQF}}{I_{DQF} + I_{ZQF}} \qquad \text{(S1)}$$

where I_{DQF} and I_{ZQF} are the absolute intensities extracted from the DQF and ZQF experiments, respectively, and the error Δy can be defined through

$$\Delta y = \sqrt{\left(\frac{\partial DQ_{norm}}{\partial I_{DQF}}\right)^2 \cdot \left(\sigma I_{DQF}\right)^2 + \left(\frac{\partial DQ_{norm}}{\partial I_{ZQF}}\right)^2 \cdot \left(\sigma I_{ZQF}\right)^2} \qquad \text{(S2)}$$

where the partial derivative of S1 leads to

$$\Delta y = \sqrt{\left(\frac{I_{ZQF}}{(I_{DQF} + I_{ZQF})^2}\right)^2 \cdot \left(\sigma I_{DQF}\right)^2 + \left(-\frac{I_{DQF}}{(I_{DQF} + I_{ZQF})^2}\right)^2 \cdot \left(\sigma I_{ZQF}\right)^2} \qquad \text{(S3)}$$

For every 1D spectrum of both the DQF and the ZQF experiments the signal-to-noise (S/N) ratio was directly calculated using the TopSpin^{TM} software. The error of the absolute intensity for the experiment with the highest absolute DQ intensity (τ_{exc} = 12.8 ms) was set to 10 %. Based on the different S/N ratios the errors of the intensities - σI_{DQF} and σI_{ZQF} - were calculated separately. In Table S3 the errors Δy for every excitation time are summarised.

Table S3 Summary of the experimental errors Δy for all data points for the experimental DQ build-up curve of the *i*-PP/additive material according to equation S3 and the corresponding signal-to-noise ratios for each 1D experiment.

τ_{exc} / ms	S/N$_{(DQF)}$ / %	S/N$_{(ZQF)}$ / %	Δy · 10^{-2}
0	---	---	---
2.56	1.84	22.4	4.57
5.12	5.16	18.8	3.12
7.68	6.50	18.5	3.08
10.24	7.63	14.1	3.02
12.80	8.13	7.0	3.70
15.36	8.24	9.0	3.31
17.92	5.56	7.6	4.26
20.48	3.30	14.9	6.27

Validating the existence of supramolecular aggregates in the binary mixture

The DQ build-up of the neat BTA and the BTA/*i*-PP mixture is very similar. Within the experimental error both curves match perfectly. We take this as a strong indication that in both samples the BTA molecules are arranged in similar structural motifs. The characteristic feature of the crystal structure of the neat BTA is the pseudo-hexagonal rod packing of BTA molecules. As demonstrated in ref. 1 by applying a DQ filtered ^{13}C NMR experiment for the BTA molecules which are fully ^{13}C enriched at the carbonyl position we are able to probe the columnar arrangement of the molecules but not the alignment of neighbouring rods. To stress this point we used the concept of the root-sum-squared dipolar coupling (d_{rss}) as introduced by Zorin et al.[9] We calculated d_{rss} for three different models: i) isolated molecules in the case when no self-organization would occur, ii) one infinite molecular strand and iii) the crystal structure taken from ref. 1. For one molecule, the d_{rss} accounts to roughly 36.7 Hz corresponding to a mean distance of about 5.9 Å. For the two models mentioned in ii) and iii), however, both coupling constants converge at values of 127.3 Hz and 128.4 Hz, respectively, corresponding to mean distances of 3.91 and 3.90 Å.

Consequently, in the case of single molecules, the progression of the build-up for the binary mixture would be much slower compared to the one of the neat BTA. The other two scenarios lead to nearly identical build-up curves which cannot be distinguished experimentally. In both compounds - the neat BTA and the BTA/*i*-PP mixture - therefore, columnar arranged supramolecular aggregates exist. The d_{rss} values, however, demonstrate that no information about the size of these aggregates can be derived based on the DQ build-up curves.

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