

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

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**Using  $^{13}\text{C}$  double quantum solid-state NMR spectroscopy, we were able to observe nuclei of a supramolecular BTA based additive on the nanoscale in a matrix of *i*-PP at a concentration of only 0.09 wt%. These nuclei exhibit the analogous structural features as the crystalline phase of the neat additive.**

As 1,3,5-benzenetrisamides (BTAs) are well known to form supramolecular structures *via* self-assembly,<sup>1</sup> BTAs become more and more important in many research fields.<sup>2</sup> Their accessibility together with their supramolecular behaviour renders BTAs into a versatile class of advanced materials with potential to be used as hydrogelators<sup>3</sup> and organogelators.<sup>4</sup> Besides, several research groups demonstrated the benefits of BTAs as nucleating agents in semi-crystalline polymers such as isotactic polypropylene (*i*-PP),<sup>5,6</sup> poly(ethylene-co-propylene),<sup>7</sup> polybutylene terephthalate,<sup>8</sup> polylactides,<sup>9</sup> and polyvinylidene fluoride.<sup>10</sup> In addition, some derivatives of this class are highly efficient as electret additives<sup>11</sup> or as clarifying agents for *i*-PP.<sup>5</sup> In contrast to other nucleating agents such as inorganic salts, clays and organic pigments,<sup>12</sup> supramolecular polymer additives are soluble in the polymer melt and self-assemble upon cooling into supramolecular nano-objects, which act as heterogeneous nuclei initiating the crystallisation of the polymer.

In particular, 1,3,5-tris(2,2-dimethylpropionylamino)benzene has been proven to feature outstanding clarifying properties for *i*-PP.<sup>5</sup> The crystal structure of this BTA has been recently determined by NMR-crystallographic strategies revealing a hydrogen-bond mediated pseudo-hexagonal columnar rod-packing where every molecule possesses a high intrinsic dipole moment.<sup>13</sup> This dipole moment gains rapidly within one rod leading to a markedly increased potential energy which can be stabilised in strong electric fields.<sup>14</sup> In the crystalline phase the potential energy due to the macroscopic dipoles,

however, is balanced by neighboring rods which are aligned anti parallel. The possibility to compensate dipole moments due to the rod-packing is supposed to play a crucial role in the nucleating process of the polymer since it allows an extremely fast one dimensional crystal growth process.<sup>13</sup> However, there is practically no experimental evidence of the nucleation mechanism within the polymer melt since standardised techniques like X-ray diffraction, for example, fail due to the small size of the nuclei and the low additive concentrations.

Here, we communicate the *first experimental data* on the structural properties of this special BTA in a matrix of *i*-PP by means of  $^{13}\text{C}$  double quantum (DQ) solid-state NMR. For this purpose we first synthesised and characterised 1,3,5-tris(2,2-dimethylpropionylamino)benzene  $^{13}\text{C}$  labelled at all three carbon atoms of the amide linkage (**1**).<sup>13</sup> Subsequently, 0.09 wt% of the additive was incorporated into *i*-PP using a twin screw mini compounder at 280 °C. The extrudate of the binary mixture was finally crushed in a cryogenic laboratory mill at low temperature to generate powder for the solid-state NMR experiments.

From a  $^1\text{H}$ - $^{13}\text{C}$  CP-MAS spectrum of the binary additive-*i*-PP mixture all signals corresponding to *i*-PP and one of the  $^{13}\text{C}$  enriched carbonyl groups of the additive molecules ( $\delta \approx 177$  ppm) can be observed (Fig. S1, see ESI†). The  $^{13}\text{C}=\text{O}$  chemical shift in the solid state does not show any difference compared to the chemical shift in the liquid state. As a consequence, the occurrence of the resonance in the MAS spectrum cannot give sustainable evidence whether it belongs to single molecules being randomly distributed in the polymer matrix or to the supramolecular columns that are known from the crystal structure of the bulk material.<sup>13</sup>

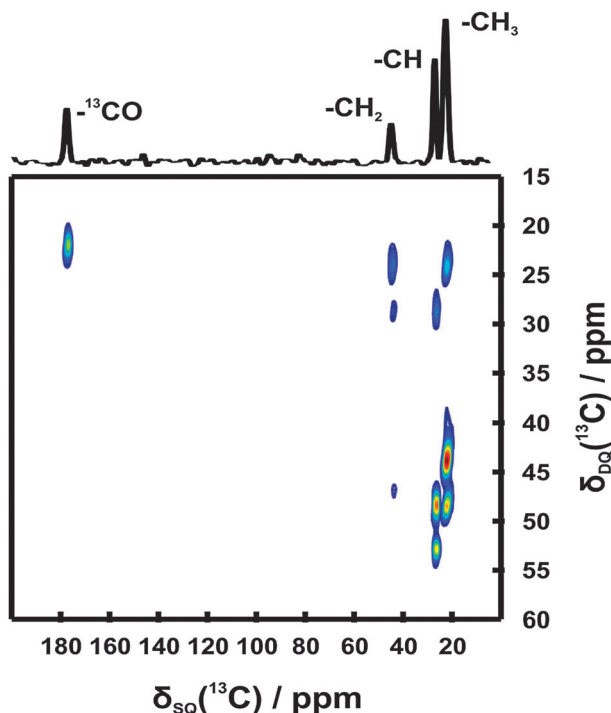
For this reason  $^{13}\text{C}$  DQ experiments were performed. These experiments are based on the dipolar coupling between two spins which is proportional to  $1/r^3$  where  $r$  represents the spin-spin distance. To identify the closest connectivities between the additive molecules and the polymer matrix, if existent, we recorded several 2D DQ spectra with different excitation times. Here, every correlation signal can clearly be assigned to its distinct chemical shift in the indirect dimension.

Since the  $^{13}\text{C}$  resonance frequencies of the polymer matrix and the additive ( $^{13}\text{C}=\text{O}$ ) are spread over roughly 12.5 kHz, the transmitter

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**Fig. 1** Experimental 2D DQ-SQ  $^{13}\text{C}$  spectrum of the additive-*i*-PP mixture using the SR26 $_4^{11}$  sequence at  $B_0 = 7.04$  T,  $\nu_{\text{rot}} = 6.25$  kHz and  $\tau_{\text{exc}} = 15.36$  ms. The F2 projection is the sum of all signals in the SQ domain – signal assignment included. Additional information is given in the ESI†

frequency offset was placed in the middle of these resonances. This leads to an off-resonant excitation of about 6 kHz which does have only a minor influence on the spectrum due to the robustness of the pulse sequence against offset effects.<sup>15</sup> A rotation frequency of 6.25 kHz was used with the non- $\gamma$ -encoded SR26 $_4^{11}$  sequence<sup>16</sup> (see ESI†) since previous results showed that faster spinning does not lead to an efficient DQ build-up, especially for large distances of  $\approx 5$  Å which we expect from the structure model of the neat additive. In addition, to obtain pure absorptive 2D spectra without any rotational sidebands in the DQ-domain,  $t_1$  must be an integer multiple of the rotor period and, moreover, possess equal values in the direct and indirect dimension (in our case two times  $\tau_{\text{rot}}$ ). As a consequence the spectral width in the indirect domain is just 41.5 ppm (19.5–61 ppm) causing a refolding of the DQ signals in the indirect dimension which were theoretically placed outside the Nyquist frequencies (Nyquist theorem<sup>17</sup>).

Fig. 1 displays the DQ-SQ  $^{13}\text{C}$  spectrum of the *i*-PP-additive material at  $B_0 = 7.04$  T,  $\nu_{\text{rot}} = 6.25$  kHz and  $\tau_{\text{exc}} = 15.36$  ms. The spectrum exhibits DQ correlations between all resonances corresponding to the *i*-PP and the auto-correlation signal of the  $^{13}\text{C}=\text{O}$  group of the additive. The auto-correlation peak of the CH-group served as internal shift calibration.

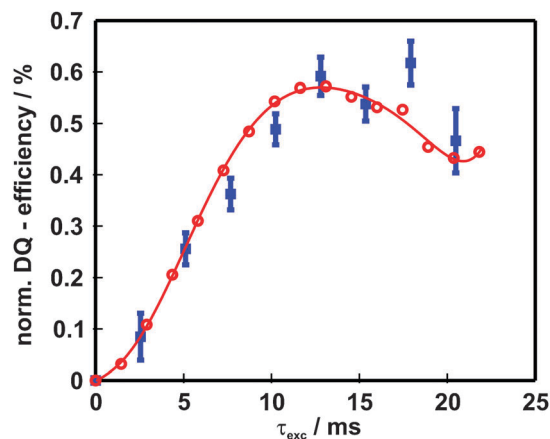
The chemical shift of the  $\text{CH}_3$ -group in the direct domain of  $\delta_{\text{SQ}} \approx 22.5$  ppm leads at the same time to a signal at  $\delta_{\text{DQ}} \approx 45$  ppm in the indirect dimension. This can also be observed for the CH-group where the peak in the DQ domain at  $\delta_{\text{DQ}} \approx 53$  ppm corresponds to the signal at  $\delta_{\text{SQ}} \approx 26.5$  ppm in the SQ domain. The signal at  $\delta_{\text{DQ}} \approx 49$  ppm can be identified as the one-bond correlation between the methyl and the methine group. The auto-correlation signal of the  $\text{CH}_2$ -group with a chemical shift

$\delta_{\text{SQ}} \approx 44$  ppm ( $\delta_{\text{DQ,exp}} \approx 88$  ppm) occurs at  $\delta_{\text{DQ,obs}} \approx 46.5$  ppm after being refolded once into the spectrum. However, the intensity of this signal at  $\tau_{\text{exc}} = 15.36$  ms is very weak, in comparison, for instance, with the auto-correlation peak of the CH-group. We additionally observe refolded correlation peaks between the  $\text{CH}_2$ -group of the polymer and the CH- and  $\text{CH}_3$ -group at  $\delta_{\text{DQ}} \approx 25$  ppm and  $\delta_{\text{DQ}} \approx 29$  ppm. At  $\delta_{\text{SQ}} \approx 177$  ppm, a signal corresponding to the carbonyl group of the additive occurs. After an eightfold refolding of the signal into the spectrum, the peak at  $\delta_{\text{DQ}} \approx 22$  ppm can clearly be identified as the auto-correlation signal of the  $^{13}\text{C}=\text{O}$  group ( $\delta_{\text{DQ,exp}} \approx 354$  ppm), while other correlations that include the carbonyl groups, *i.e.* interaction with the polymer matrix, are not observed. This fact can also be seen in 2D DQ-SQ spectra with lower and even higher excitation times, respectively (see Fig. S2 in the ESI†). In Table S2 (see ESI†) the expected and observed chemical shifts after refolding of all correlation signals in the indirect domain are summarized.

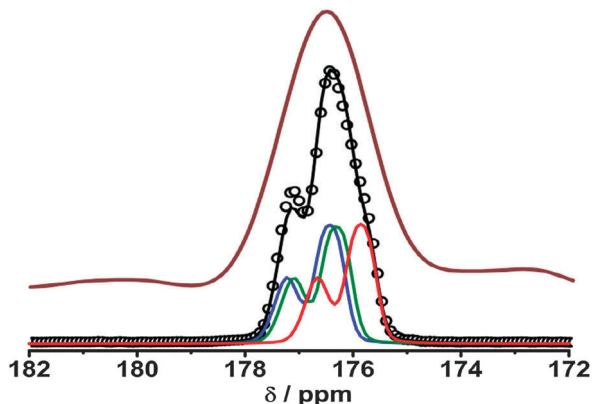
The existence of the  $^{13}\text{C}=\text{O}$  auto-correlation indicates a spatial connectivity of the additive carbonyl groups but, still, is no unequivocal evidence. To get a more detailed picture of the structural features of the additive clusters in the polymer matrix, we recorded a symmetric DQ build-up curve. The absence of correlations between the additive and the polymer matrix allows treating the signal of the carbonyl group independently. Thus, the intensities being extracted from the build-up curve of the *i*-PP-BTA material can be directly compared to one of the neat  $^{13}\text{C}$  labelled additive 1.

Fig. 2 displays the experimental symmetric  $^{13}\text{C}$  DQ build-up curves of the labelled carbonyl groups of the bulk material (red circles) and the additive within the polymer (blue squares with error bars according to equation S3 in the ESI†). Both build-up curves are normalised according to equation S1 (see ESI†).

Within the experimental error, the progression of both curves matches perfectly. In this respect, the slight shift of the maximum of the DQ build-up curve for the *i*-PP-additive mixture is negligible. As a consequence, the  $^{13}\text{C}$ - $^{13}\text{C}$  DQ data provide solid evidence that the structural motifs for the additive



**Fig. 2** Experimental symmetric  $^{13}\text{C}$  DQ build-up curves of the labelled carbonyl groups within neat 1,3,5-tris(2,2-dimethylpropionylamino)benzene (red circles,  $\nu_{\text{rot}} = 5.5$  kHz) and the *i*-PP-additive binary mixture (blue squares with error bars,  $\nu_{\text{rot}} = 6.25$  kHz). Both measurements were performed using the SR26 $_4^{11}$  pulse sequence ( $B_0 = 7.04$  T) with a maximum excitation time  $\tau_{\text{exc}}$  of 21.76 (bulk) and 20.48 ms (mixture), respectively. Further information is given in the ESI†



**Fig. 3** Bottom: experimental (black circles) and simulated (black line)  $^{13}\text{C}$  DQ filtered spectra of the neat BTA with deconvolution into three distinct resonances (blue, green and red lines). Their fine structure is caused by a second order  $^{14}\text{N}$  quadrupolar interaction on a dipolar coupled  $^{13}\text{C}$ - $^{14}\text{N}$  spin pair (compare ESI†). Top: experimental  $^{13}\text{C}$  DQ filtered spectrum of the binary mixture (as sum over all 1D spectra extracted from the build-up curve).

clusters in the polymer matrix and in the bulk material are similar. As demonstrated in ref. 13 the applied DQ filtered  $^{13}\text{C}$  NMR experiment is able to probe the columnar arrangement of the molecules but not the alignment of neighbouring rods. This could also be successfully demonstrated by evaluating the root-sum-square dipolar coupling  $d_{\text{RSS}}$  for different scenarios (see ESI†).<sup>18</sup> For diluted molecules,  $d_{\text{RSS}}$  accounts to roughly 37 Hz and thus a slower DQ build-up would be observed, while a single molecular strand and the rod packing in the crystal lead to nearly identical values of 127 Hz and 128 Hz.

The DQ-SQ spectra (Fig. 1 and Fig. S2, ESI†) display intensive peaks for all correlations with the exception of the signal between the BTA carbonyl group and the polymer units. Although a quantitative analysis is demanding due to the influence of the DQ intensity on the nuclear distances,<sup>19</sup> the geometry of the aggregates, the low additive concentration and possible motional processes its absence hints at the formation of larger clusters consisting of several rods. Nevertheless, the significant broadening of the DQ signal of the carbonyl groups in the BTA-*i*-PP mixture where the fine structure is masked – compared to the neat BTA (Fig. 3) – suggests a less well defined long-range order and crystallite sizes in the lower nanometre regime within the polymer matrix.

Our experiments demonstrate that the additive molecules form columns within the polymer matrix which are similar to the ones observed for the neat material. The compensation of the macrodipole arising in one rod requires a pseudo-hexagonal rod packing accounting also for the fast 1D growth behaviour. Thus, even at low concentrations the BTAs can form long and thin needle-like objects which provide enough surface area to initiate heteronuclear nucleation of the polymer. Interestingly, the spacing of the additive molecules within one rod leads to a surface modulation with similar characteristic distances (6.8 Å)<sup>13</sup> as compared to neat *i*-PP (6.5 Å) indicating that the growth mechanism of the *i*-PP is indeed epitaxial in nature.

In conclusion, we have presented a powerful approach to visualise nuclei on a nanoscale of an efficient BTA-based nucleating and clarifying agent for *i*-PP at a concentration below 0.1 wt% within

the polymer matrix. We successfully used  $^{13}\text{C}$  DQ solid-state NMR to clearly demonstrate the structural analogy of the supramolecular aggregates of the additive within the binary *i*-PP-additive material compared to the neat bulk material.

With this approach it will be possible to study nucleation processes from solutions and melts in an early stage for a wide range of molecular compounds including pharmaceuticals in the future. This is important especially for systems with polymorphism where probably small structural changes of the nuclei may lead to a different polymorph.

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