In situ C-13 solid-state polarization transfer NMR to follow starch transformations in food

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In situ ^{13}C solid-state polarization transfer NMR to follow starch transformations in food

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Abstract

Convenience food products tend to alter their quality and texture while stored. Texture-giving food components are often starch-rich ingredients, such as pasta or rice. Starch transforms depending on time, temperature and water content, which alters the properties of products. Monitoring these transformations, which are associated with a change in mobility of the starch chain segments, could optimize the quality of food products containing multiple ingredients. In order to do so, we applied a simple and efficient in situ ^{13}C solid-state magic angle spinning (MAS) NMR approach, based on two different polarization transfer schemes, cross polarization (CP) and insensitive nuclei enhanced by polarization transfer (INEPT). The efficiency of the CP and INEPT transfer depends strongly on the mobility of chain segments—the time scale of reorientation of the CH-bond and the order parameter. Rigid crystalline or amorphous starch chains give rise to CP peaks, whereas mobile gelatinized starch chains appear as INEPT peaks. Comparing ^{13}C solid-state MAS NMR experiments based on CP and INEPT allows insight into the progress of gelatinization, and other starch transformations, by reporting on both rigid and mobile starch chains simultaneously with atomic resolution by the ^{13}C chemical shift. In conjunction with ^{1}H solid-state MAS NMR, complementary information about other food components present at low concentration, such as lipids and protein, can be obtained. We demonstrate our approach on starch-based products and commercial pasta as a function of temperature and storage.

KEYWORDS

^{1}H, ^{13}C, convenience food, CP, gelatinization, INEPT, MAS, solid-state NMR, starch-rich food products

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1 | INTRODUCTION

In 2015, the World Health Organization reported an increased consumption of processed food.[†] This trend is mirrored in an increased development of convenience food products, which are usually composed of at least one starch-based ingredient, that is, rice or pasta. Starch is often the main source of energy in the food and thus a necessary component of a meal.[1,2] Furthermore, starch-based ingredients commonly define the texture of the meal, determining the meal's appeal.[3–6]

On a molecular level, starch is composed of D-glucose units forming the two different polymers, amylose and amylopectin.[7] Amylose is a linear polymer with α(1–4) linkages whereas amylopectin contains α(1–4) and α(1–6) linkages enabling branching.[7] Water content and temperature induce changes in the multiscale organization of a starch granule: granules swell, starch gelatinizes and granules disintegrate. These changes might have a positive or a negative influence on texture and nutrition of starch-rich food products. For example, staling of bread is caused by recrystallization of starch with time and lowers the bread's flavour and appeal.[8] Other examples are annealing,[9] occurring in non-gelatinized starch and retrogradation[10,11] in gelatinized starch. Retrogradation is desired for food products such as breakfast cereals and for slowing down the enzymatic digestion.[10] Hence, characterizing starch is a prerequisite to improve the quality of starch-based food products.

Common, destructive methods to study starch are transmission electron,[12] atomic force[13] and scanning electron microscopy,[14] observing, for example, the surface of a material. Other techniques, such as differential scanning calorimetry and small angle X-ray scattering, provide information about static bulk properties and/or report solely on crystalline starch domains.[11] One of the most commonly used non-destructive method is ^{1}H NMR, including magnetic resonance imaging. It has been extensively applied to food to monitor water[15] or other components in vegetables and fruits,[16–19] dairy products,[20,21] honey,[22] pasta,[23–25] dough[26,27] and wheat.[28,29] A drawback of a ^{1}H (liquid- or solid-state) spectrum of a food product is that it is often complex and crowded or lacking features, complicating the analysis of starch. One solution to mitigate the shortcomings of ^{1}H NMR is to use ^{13}C solid-state magic angle spinning (MAS) NMR. It enables direct observation of the carbons in starch, and due to the ^{13}C chemical shift range, the signals are spread, which ease analysis. A disadvantage of ^{13}C NMR, when compared with ^{1}H NMR, is lower signal intensity, but it can be countered by polarization transfer from ^{1}H to ^{13}C.

The mobility of a polymer chain segment—the time scale of reorientation of the CH-bond—and the order parameter determines the efficiency of the polarization transfer from ^{1}H to ^{13}C. Many starch transformations are associated with a change in mobility of chain segments. The polarization transfer based on cross polarization[30] (CP) is the 'golden standard' solid-state ^{13}C NMR method and has been applied extensively to starch[31,32] and food products.[33–35] This method fails, however, for mobile chain segments, for example, in gelatinized starch, because rapid motion averages the dipolar ^{1}H–^{13}C couplings used for the polarization transfer. Morgan et al. made exactly this observation on gelatinized starch samples and suggested to record a direct polarization ^{13}C NMR spectrum, that is, without any polarization transfer.[36] Indeed, the resulting spectrum includes all peaks independently on the mobility but suffers from long experiment durations.

An alternative approach is insensitive nuclei enhanced by polarization transfer (INEPT),[37] which enhances solely peaks originating from mobile chain segments, using the scalar ^{1}H–^{13}C coupling (*J*-coupling) for polarization transfer. The INEPT transfer is enabled for a CH-bond reorientation time faster than 100 ns and an order parameter lower than approximately 0.2.[38] Hence, the comparison of ^{13}C solid-state NMR based on CP and INEPT allows independent observation of mobile and rigid polymer chain segments within the same sample, in contrast to other methods. This approach has already been successfully applied to study surfactant phase behaviour,[39] protein–lipid interactions[40] and the dissolution of cellulose.[41–43] A detailed description of the polarization transfer methodology using CP and INEPT can be found elsewhere.[38]

Here, this approach allows following both gelatinized, that is, mobile, and crystalline/amorphous, that is, rigid, starch chains concurrently in situ with atomic resolution. This method was applied to dry and soaked commercial pasta strands, to assess the state of starch. Then, the process of starch gelatinization was monitored in situ, for two different pasta-to-water ratios with increasing temperature, and subsequently, the storage at room temperature in contact with water. ^{1}H solid-state MAS NMR experiments with water suppression were also conducted providing complementary information about lipids and proteins present in the pasta strands. Our results show that starch is still rigid in soaked pasta and that a water-to-pasta ratio of more than 1 is needed to efficiently gelatinize starch in pasta. Furthermore, the results suggest that using ^{13}C solid-state MAS NMR based on CP and INEPT can be applied to investigate the state of starch and other molecules in food products. Line shapes and peak positions, as well as the interplay between the CP

and INEPT intensities, provide information concerning crystallinity, mobility and the simultaneous presence of rigid and mobile fractions of molecules.

2 | RESULTS AND DISCUSSION

^{13}C solid-state MAS NMR experiments based on the CP and INEPT transfer were used to (i) determine the states of starch in dry and soaked pasta, cooked rice and wheat starch and (ii) monitor starch transformations in pasta immersed in water, as a function of temperature in situ (for experimental details, see the last section).

2.1 | Uncooked

Figure 1 shows ^{13}C and ^{1}H solid-state MAS NMR spectra of an uncooked, dry pasta strand (a). The inset in Figure 1a (top) depicts a schematic illustration of a rigid (blue) and a mobile gelatinized (red) starch domain. This rigidity contributes to a boost of the CP transfer while mobile segments enhance INEPT transfer. The CP spectrum in Figure 1a (blue) reveals broad peaks of all carbon atoms of rigid starch domains. INEPT peaks appear when the requirements for the INEPT transfer are met, and small INEPT peaks are only visible for lipids. Sharp peaks in a ^{1}H MAS NMR spectrum are obtained when the molecular segment reorientation time is faster than 10 μs averaging the homonuclear dipolar ^{1}H couplings. The narrow peaks in the ^{1}H spectrum arise from mobile proteins[44] and lipids[33] in dry pasta, which is in agreement with ^{1}H spectra of dough and gluten.[26]

Furthermore, the peak line shapes observed in a CP spectrum, in particular for the C1 carbon, provide a clue about the crystallinity and the molecular structure of starch. A three-peak pattern of the C1 carbon peak is linked to an A-type crystallinity found in native starch, whereas a two-peak pattern refers to a B-type crystallinity formed during recrystallization.[34,45] The C1 peak of dry pasta shows a complex pattern indicating a combination of the A and B types. The mixed crystallinity most probably originates from common pasta production steps such as mixing flour with water, extruding the blend to obtain its desired shape and drying in an oven.

To assess the influence of water immersion at room temperature, ^{13}C solid-state MAS NMR experiments of a pasta strand, soaked in water for 1 h, were acquired (Figure 1b). The CP peaks arising from rigid starch chain segments narrowed, revealing more features compared with dry pasta. Although the soaked pasta strand is soft, which indicates that water is present between the starch granules, only small INEPT peaks were observed in the starch region, originating most likely from a 'mobility' introduced by a small fraction of dissolved starch or leakage of amylose. Broad and featureless starch peaks appeared also between 3 and 4 ppm in the corresponding ^{1}H spectrum (Figure 1b right). Also, peaks assigned to

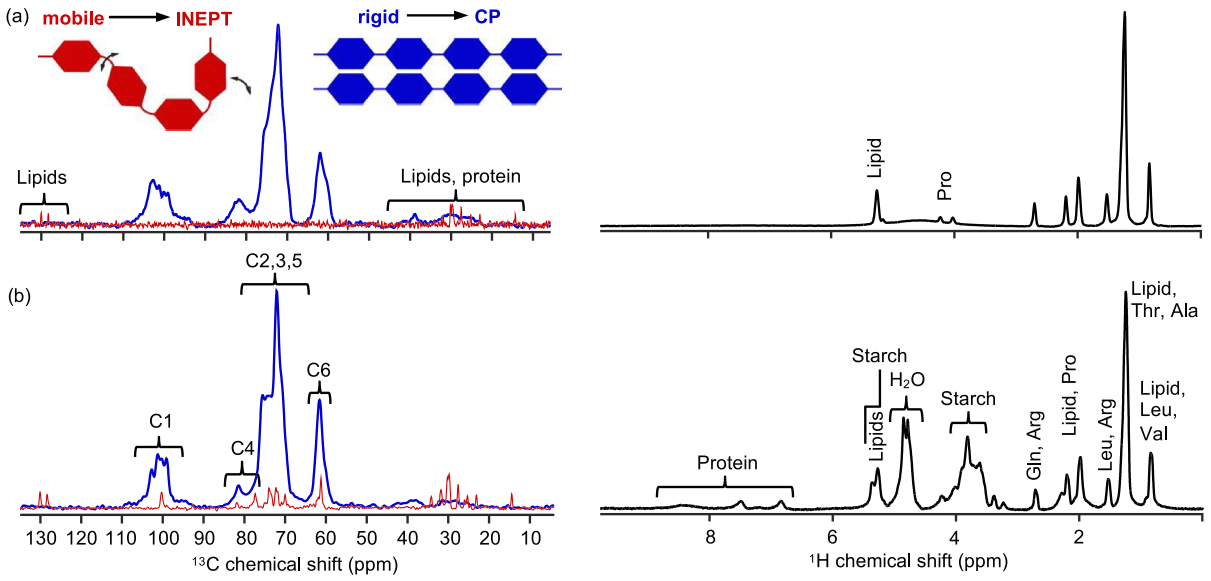

FIGURE 1 ^{13}C solid-state MAS NMR spectra using the CP (blue) and INEPT (red) transfer of the uncooked and dry (a) and soaked (b) 1.7-mm-diameter pasta strand and the corresponding ^{1}H solid-state MAS NMR spectra recorded with water suppression to the right. Spectra were acquired at the spinning speed of 5 kHz at 25°C. Assignment of the spectra is based on Calucci et al.[33] The inset depicts schematic illustration of rigid (blue) and mobile (red) polymer chains, and the curved arrows show some possible chain motions in the gelatinized starch

gluten, a mixture of proteins, appear in the ^{1}H spectrum due to gluten being hydrated. The hydration of the peptide chains enables a molecular segment reorientation time on the μs scale.

2.2 | Function of temperature

^{1}H and ^{13}C solid-state MAS NMR spectra of a 1.7-mm-diameter pasta strand in the presence of a limited amount of water as a function of temperature are shown in Figure 2. At 30°C, observed peaks arise from the CP polarization transfer (Figure 2a, blue), confirming the presence of rigid starch domains. INEPT (Figure 2a, red) peaks, if any, barely exceed the noise level of the spectrum, while the corresponding ^{1}H spectrum (Figure 2b) reveals small broad peaks in the starch region, similar to the ^{1}H spectrum of the soaked pasta strand but less intense (Figure 1b right). ^{1}H NMR is more sensitive because of a higher natural abundance and gyromagnetic ratio and a spectrum with acceptable signal-to-noise ratio is obtained within less than a minute. The ^{13}C experiments were optimized to take the least experimental duration (each between 8 and 13 min) to minimize averaging over sample changes during acquisition.

Upon heating to 50°C, the intensity of the CP peaks decrease, and the peaks become narrower, revealing a decreasing amount of rigid starch chain segments. In case of a change in crystallinity, a pattern change of the C1 carbon would be observed. As expected, INEPT peaks gain in intensity, indicating an increase of mobile starch chain segments. Furthermore, the corresponding ^{1}H spectrum (Figure 2b) reports stronger starch and protein peaks.

At 70°C, the INEPT peaks become more intense than the CP. The further increase in INEPT signals might be associated with the onset of gelatinization, which agrees well with the reported gelatinization temperature of starch between 60°C and 80°C depending on the botanical origin.[46] The ^{1}H spectrum shows an increase of starch and protein peaks. The line shapes around 2 ppm and between 6 and 9 ppm corresponding to the amide protons alter, suggesting a change in the protein's secondary structure.[47,48]

Finally, at 90°C, there is barely any CP peaks left and a further intensity increase of the INEPT and ^{1}H starch peaks are observed. Furthermore, ^{1}H protein peaks between 6 and 9 ppm split, whereas the lipid peaks at 0.8 and 1.3 ppm remain mainly unaffected with increasing temperature.

CP and INEPT experiments were repeated on a thinner, 1.1 mm in diameter pasta strand and the comparison at 70°C is shown in Figure 3. Almost all CP peaks disappeared for the thinner pasta strand (Figure 3a), whereas for the thicker pasta strand, CP peaks are still visible (Figure 3b). The results might be ascribed to a different pasta-to-water ratio, which is 1:1.4 for the thinner pasta and 1:1 for the thicker one. Smaller amount of water in the sample with the thicker pasta strand may be fully consumed during gelatinization, prohibiting further gelatinization, whereas in the sample with the thinner pasta strand, there is enough water to allow for nearly complete gelatinization of the pasta.

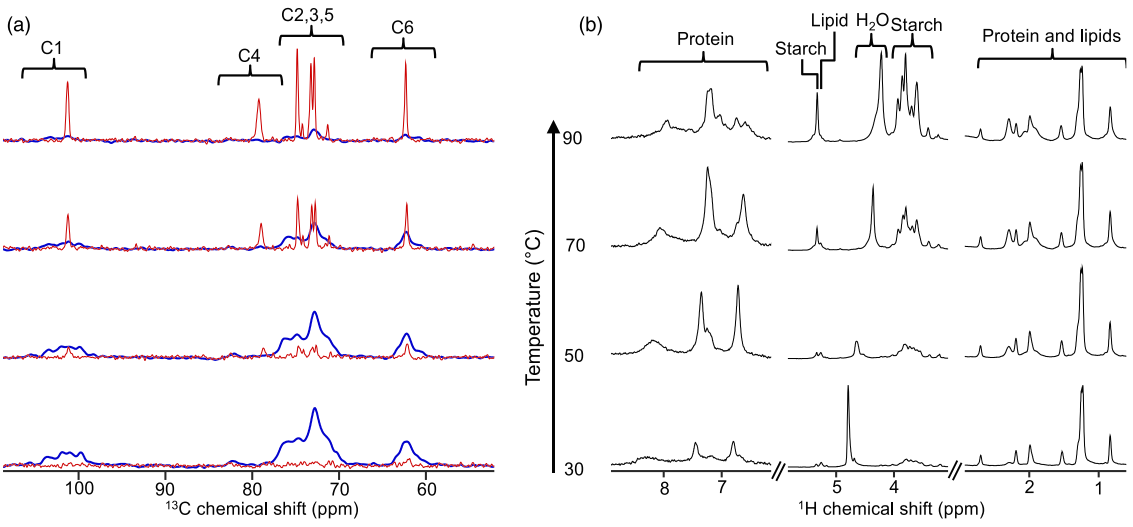

FIGURE 2 ^{13}C solid-state spectra MAS NMR using the CP (blue) and INEPT (red) transfer of a 1.7-mm-diameter pasta strand immersed in water with a pasta-to-water ratio of 1:1 as a function of temperature (a) and the corresponding ^{1}H solid-state MAS NMR spectra recorded with water suppression (b). The intensity of different regions, that is, protein or starch region of the ^{1}H spectrum, is scaled but held constant with temperature

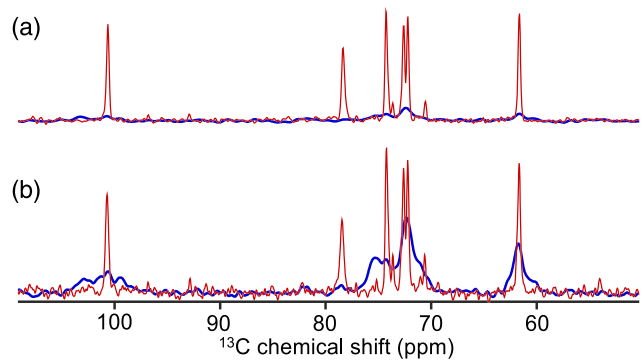

FIGURE 3 ^{13}C solid-state MAS NMR spectra using the CP (blue) and INEPT (red) transfer of a 1.1-mm-diameter pasta strand immersed in water at a pasta-to-water ratio of 1:1.4 (a) and a 1.7-mm-diameter pasta strand immersed in water at a pasta-to-water ratio of 1:1 (b) at 70°C

2.3 | Cooling and storage

Figure 4 shows ^{13}C solid-state MAS NMR spectra using the CP and INEPT transfer of a pasta strand immersed in water with pasta-to-water ratio of 1:1.4 at 30°C (a), after being heated to 90°C and cooled back to 30°C (b) and after additional 18 h of storage at 30°C (c). Upon cooling from 90°C to 30°C, CP peaks reappear, indicating a decrease of mobility of starch. However, the overall intensity of the CP peaks is much lower, compared with the results obtained before heating (a), where strong CP peaks dominated the spectrum. Most starch chains stay mobile upon cooling, as well as during the final measurement at 30°C, which was performed the following day (c).

The pasta strand was kept spinning overnight in the rotor in contact with water, which might have influenced the starch molecules to remain mobile. In case of recrystallization, which might take much longer than 18 h,[49] an increased CP intensity and/or an altered peak line shape would have been observed. The observed line shapes would shed light on the crystallinity of the re-emerging solid fraction.

2.4 | Additional spectral features based on the INEPT transfer

In Figure 5a, two unassigned INEPT peaks (open circles) were found for a heat-treated starch/water mixture and these INEPT peaks are also visible in Figures 2–4. To verify their origin, INEPT spectrum of cooked rice (Figure 5b) was recorded, revealing the same peaks confirming that these peaks arise from gelatinized starch.

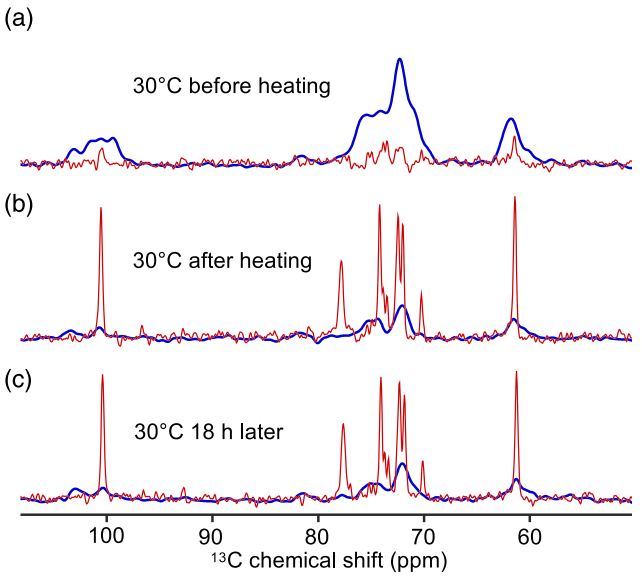

FIGURE 4 ^{13}C solid-state MAS NMR spectra using the CP (blue) and INEPT (red) transfer of a pasta strand immersed in water with pasta-to-water ratio of 1:1.4 acquired at 30°C (a), after heating to 90°C and cooling to 30°C (b) and 18 h later at 30°C (c)

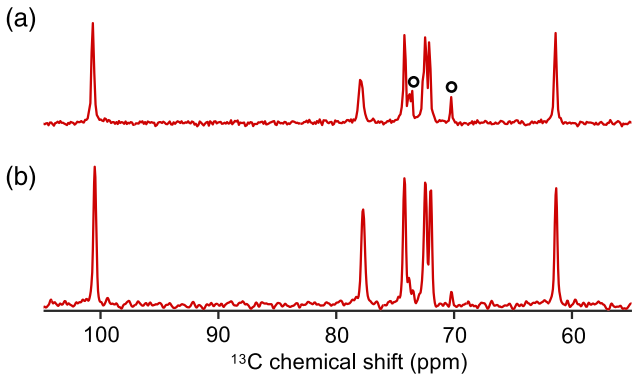

FIGURE 5 ^{13}C solid-state MAS NMR spectra using the INEPT transfer of a heat-treated starch/water mixture (a) and cooked rice (b). Open circles mark the unassigned peaks

A possible origin of the unassigned peaks may be the carbon atoms of the α(1–6) branches in amylopectin, which account for approximately 5% of the total linkages.[7] However, an INEPT spectrum is not quantitative, because the intensity of the observed peak depends on the efficiency of the ^{1}H–^{13}C polarization transfer.[38] Another possibility is reported by Falk and Stanek, who analysed amylose and amylopectin dissolved in dimethyl sulfoxide using high-resolution liquid-state NMR techniques.[50] They observed two additional peaks at similar chemical shifts and intensities, which they assigned to the non-reducing ends of the amylopectin chains. Comparable chemical shifts were reported by Bliard et al.[51]

underpinning the assumption that these peaks might arise from the non-reducing terminal units from amylopectin.

3 | CONCLUSIONS

The results presented above suggest that the comparison of CP and INEPT can be used to investigate the state of starch and other molecules in food products. Line shapes and peak positions, as well as the interplay between the CP and INEPT intensities, provide information concerning crystallinity, mobility and simultaneous presence of solid and mobile fractions of molecules. Our results show that starch remains rigid in soaked pasta and a water-to-pasta ratio of more than 1 is needed to efficiently gelatinize starch in pasta. Similar studies can be performed on starch-rich food products in a large variety of conditions, to mimic the processes occurring during food preparation and storage in situ. For example, products equilibrated at a precise relative humidity can be heated or cooled. Cooked, frozen or otherwise prepared products can be observed while cooling, aging or rewarming; spinning the sample could serve as stirring. In case a larger sample volume is advantageous, a larger rotor diameter could be used. Furthermore, our approach could elucidate the annealing and heat-moisture treating,[9] as well as retrogradation on a molecular level. Furthermore, this approach could be extended to study other food components such as fats or lipids, for example, in chocolate and cheese.

4 | EXPERIMENTAL

4.1 | Materials

Three starch-rich products were used: wheat starch, commercial parboiled rice and durum wheat spaghetti with the diameters of 1.1 and 1.7 mm. Wheat starch supplied by Lantmännen Reppe (Lidköping, Sweden) from soft wheat[24] was mixed with 11 μl deuterium oxide (D_2O, >99.88 Atom%D, Armar Isotopes) giving a starch-to-D_2O ratio of ∼1:1. The mixture was heated up to 90°C for 15 min in a rotor spinning at 5 kHz (see Section 4.2 for more details) before cooling down to room temperature at which the spectrum was recorded. This sample is called heat-treated starch/water mixture. Commercial parboiled rice was cooked according to the producer's instructions using deionized water. The water was removed immediately after the recommended cooking time had passed and the rice was blotted before being packed into the rotor. All ratios are by weight. Dry pasta was kept in place with Teflon tape inside the rotor during spinning. To study the effect of water immersion, a dry 1.1 mm pasta strand was soaked in excess water for 1 h until the pasta strand was soft. The total water uptake was 70 wt% of the dry weight. The soaked pasta strand was blotted before being packed into the rotor. A 3-mm-long piece of commercial durum spaghetti of the same brand as in Steglich et al.[23] with a carbohydrate content of around 77% was placed together with 11 μl deionized water in the rotor, which gave pasta-to-water ratio of ∼1:1.4 for the 1.1-mm-diameter pasta and ∼1:1 for the 1.7-mm-diameter pasta. To study the effect of cooling and storage, the pasta strand was immersed in water with a pasta-to-water ratio of 1:1.4 in the rotor. The rotor, which was spun at 5 kHz, was heated to 90°C and kept at this temperature for more than 30 min and then cooled back to 30°C by changing the temperature. A set of spectra was recorded after 18 h before the spinning was stopped.

4.2 | Methods

^{13}C solid-state MAS NMR based on CP[30] and INEPT[37] and ^{1}H solid-state MAS NMR experiments were performed on a 14.7 T Agilent Inova magnet (^{13}C and ^{1}H Larmor frequencies of −150.9 and −600.1 MHz) equipped with a 3.2 mm double-resonance MAS probe. All samples were spun at 5 kHz in a zirconia rotor.

^{13}C spectral width was set to 44.6 kHz. The repetition delay was 3 s; for CP, the τ_{CP} time was 1.2 ms and for INEPT, τ was 1.8 ms and τ' 1.2 ms. For more details about the experimental details, the reader is referred to Nowacka et al.[38] Spinal decoupling of 85 kHz was applied for all ^{13}C experiments. Two hundred fifty-six scans were accumulated for CP and INEPT for the 1.1-mm-diameter pasta and 160 scans for the 1.7-mm-diameter pasta. ^{1}H spectral width was set to 12 kHz with the repetition delay of 20 s for 1.1-mm-diameter pasta and 3 s for 1.7-mm-diameter pasta. A presaturation pulse of 2 s was used to suppress the water peak.

The experiments were performed at 30°C, 50°C, 70°C and 90°C on the same sample and the temperature was calibrated with potassium bromide.[52] After temperature stabilization, the sample was allowed to equilibrate for 15 min. The probe was tuned and matched prior to the acquisition at each temperature. For each temperature, one set composed of a ^{13}C CP and INEPT and a ^{1}H solid-state experiment with water suppression was acquired.

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NOTE

† http://www.who.int/mediacentre/factsheets/fs394/en/.

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