

Citric acid cross-linking of centrifugally spun starch-based fibres

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Many research papers have demonstrated that the starch-based fibres showed poor water stability. In this work, it is proven that citric acid can cross-link starch and improve the water stability of centrifugally spun starch-based fibres. The effect of citric acid concentration on fibre morphology and water stability was studied. Fibre morphology was characterised by scanning electron microscopy and optical microscope. Fourier transform infrared analysis was used to investigate structure changes of fibres during cross-linking.

1. Introduction: Many attempts have been focused on developing starch-based products because of their potential applications in many areas, e.g. food packaging [1–3], textile industries [4–6], drug delivering [7] and so on. A number of methods for preparing starch films, slurries and microsphere from various starches have been developed. Among these, starch films drew an increasing attention in recent years, which is due to the great potential application in food packaging [2]. However, pure starch films are rather brittle, poor in water stability and mechanical properties, which limits them further scaling up for commercial production [8–10]. Starch-based fibre is also an important starch material and identified as a substitute for starch films. Unlike films, toughness and strength of the starch-based fibre could be easily improved by controlling fibre diameter and adding other polymers [11]. Kong and Ziegler [12, 13] prepared pure starch-based fibres by using electrospinning, and systematically investigated the relationship between electrospinnability of starch and spinning parameters (including rheological properties of starch, processing parameter and amylose/amylopectin ratio). In order to improve the water stability of the fibres, postprocessing treatments, like cross-linking, was often applied. Wang *et al.* [14] reported on cross-linking of electrospun starch-based fibres by vapour-phase glutaraldehyde. The tensile strength and water stability of the fibres were found to improve after cross-linking.

Due to advantages of non-toxic, environmental friendly and low in cost, citric acid has now been widely used to cross-link various materials for improving the properties. Quellmalz and Mihranyan [15] demonstrated that citric acid could cross-link cellulose and improve the wet strength of nanocellulose-based paper filter. In the processing of tissue adhesive, Aoki *et al.* [16] chose citric acid as cross-linker to shorten gelation time and increase mechanical strength of the adhesive. Additionally, many attempts have tried to cross-link starch-based materials by using citric acid. Ma *et al.* [17] reported a method for fabricating starch nanoparticles/plasticised-starch composites, and citric acid was used to modify starch nanoparticles by preventing gelatinisation and decreasing the size of particles. In the experiment of cross-linking starch films, researchers found that citric acid could improve the wet stability, thermal stability and strength of films [18]. The mechanism for cross-linking starch products by citric acid was based on esterification reaction between hydroxyl group in starch and carboxyl group in citric acid [18, 19]. After cross-linking, the water stability of starch products was improved by the decreasing of hydroxyl group.

In previous attempt, we have demonstrated that amylopectin rich corn and potato starch (amylopectin content > 68%) were suitable for centrifugal spinning [20]. The relationship between centrifugal

spinnability and entanglement concentration of starch solution has been discussed. However, the performance of obtained fibres (such as water stability, thermal and tensile properties) was not mentioned. In this work, we prove that citric acid can cross-link starch and improve the water stability of centrifugally spun starch-based fibres. The effect of citric acid concentration on fibres morphology and the water stability of fibres have been studied.

2. Experiments: Native corn starch was purchased from Zhengzhou Honest Business Co., Ltd (Henan Province, China). Native potato starch was self-prepared from potato. Citric acid, NaOH and ethanol were reagent-grade chemicals and provided by Aladdin (China). The amylopectin ratios of native corn and potato starches have been determined to be 68.89 and 73.35%, respectively [20].

Centrifugal spinning was carried out by the home-made centrifugal spinning apparatus, as shown in Fig. 1; the whole experiment was conducted at a controlled environment of $25 \pm 3^\circ\text{C}$ and relative humidity of <55%. About 2 ml starch solution was injected into spinneret for each complete centrifugal spinning process. A heat gun (temperature range: $50\text{--}650^\circ\text{C}$, wind velocity: 190 l/min) was applied to increase the evaporation rate of solvents. Other spinning conditions are shown in Table 1. For cross-linking treatment, corn-based and potato-based fibre membranes were placed in petri dishes containing 10 ml citric acid alcohol solution with different concentrations, respectively. The samples were then kept in a lab oven at 165°C for 10 min. To measure the water stability, the samples after cross-linking was immersed into water for 24 h and subsequently dried at 70°C in an oven.

The non-cross-linked and cross-linked fibres (immersed into water for 24 h and dried at 70°C) were measured by a portable

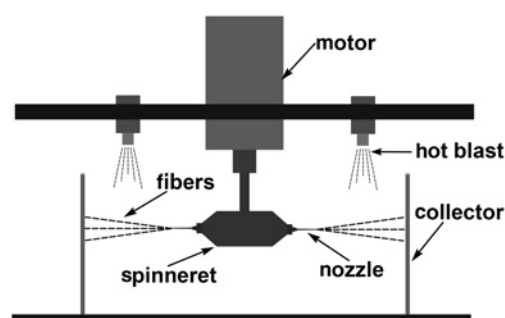


Fig. 1 Schematic drawing of the self-designed centrifugal spinning apparatus

Table 1 Spinning parameters

Starch	Aqueous sodium hydroxide as solvent % (w/w)	Concentration % (w/w)	Nozzle diameter (G)	Rotational speed, r·min ⁻¹	Nozzle-to-collector distance, mm	Hot blast temperature, °C
native corn starch	2	14	27	2000	110	350
native potato starch		12				

pH meter (PHB-1, Hangzhou Lei magnetic Analytical Instruments, China). Their pH values were compared to judge whether the residual NaOH in starch fibres reacted with citric acid during cross-link proceeding or not. Morphologies of obtained and treated fibres were observed by optical microscope (XM-30, Xingming Optical Instrument Co., Ltd, China) and scanning electron microscopy (SEM) (EDS/EBSD, Carl Zeiss, Germany). About 4 mm² fibre membranes were cut as SEM samples and coated with gold using an Emitech sputter coater for 50 s, and then observed in secondary electron mode with an electron acceleration voltage of 2 kV. Fourier transform infrared (FTIR) profiles were measured on an infrared spectrometer (Nicolet 5700, Thermo Electron Corporation, USA). The samples were prepared by mixing the fine powder with KBr and pressing. Spectra were obtained at a resolution of 4 cm⁻¹ in the range 4000–500 cm⁻¹. Typically, 32 scans were signal averaged to reduce spectral noise.

3. Results and discussions: The morphologies, diameter distributions and water stability of centrifugally spun starch-based fibres were displayed in Fig. 2. It could be observed that the corn-based (Fig. 2a) and potato-based fibres (Fig. 2b) were well formed under the spinning conditions, and both of the fibres were appeared as rough surface. As previous paper reported, we

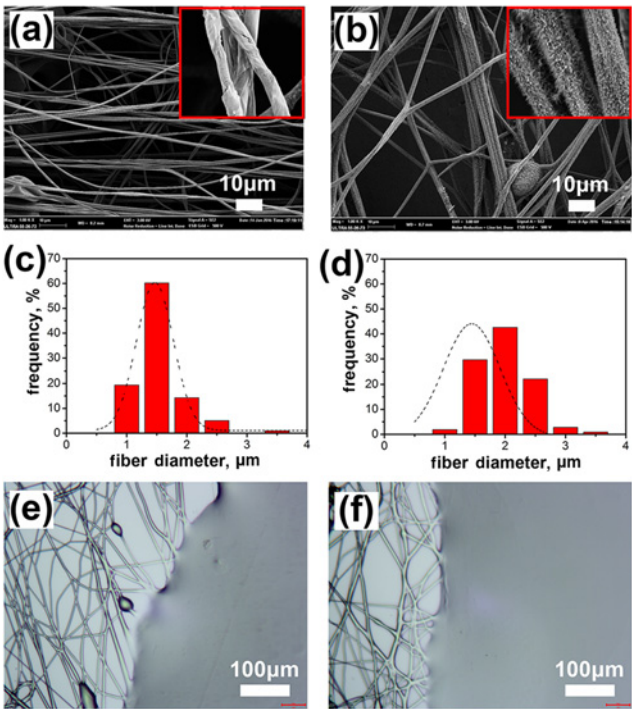


Fig. 2 Morphology and water stability of centrifugally spun starch-based fibres
a, b SEM images of corn-based and potato-based fibres
c, d Fibre diameter distributions
e, f Instantaneous changes of the corn-based and potato-based fibre immersed in water

concluded that the rough surfaces of starch-based fibres were caused by the phase separation between amylose and amylopectin [20]. For the distribution of fibres, we could observe that the corn-based fibres (Fig. 2c) were narrower than potato-based fibres (Fig. 2d), and had smaller diameters.

The starch-based films and fibres have been demonstrated to have a poor water stability, which could prevent their wide applications [9, 13, 18]. In this case, we first studied the water stability of

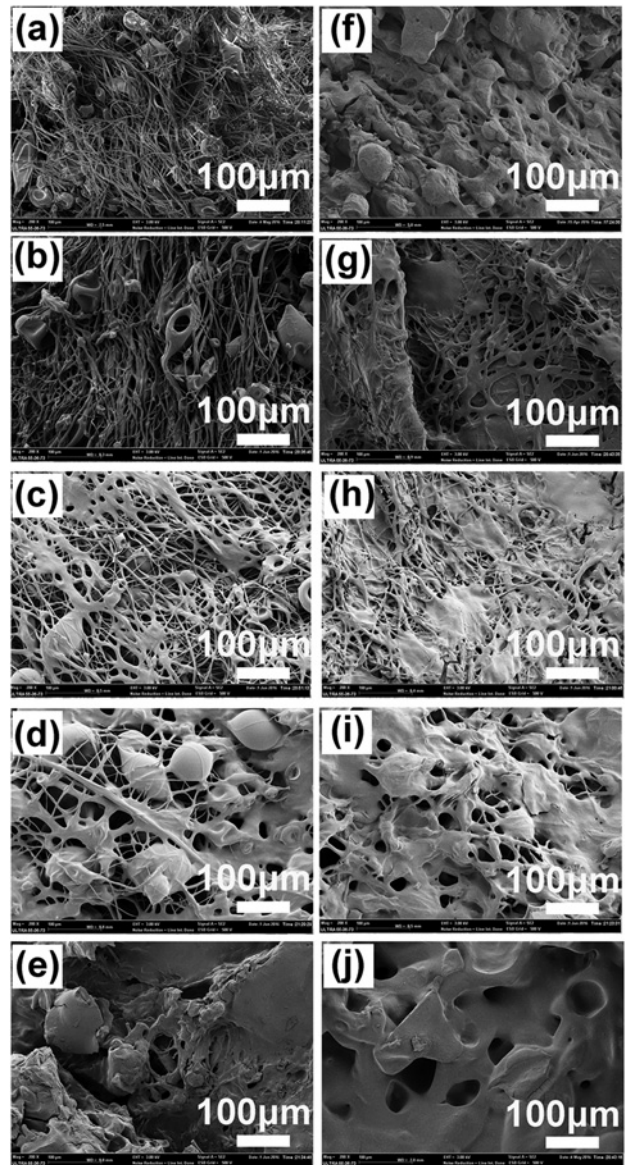


Fig. 3 SEM images of centrifugally spun corn-based fibres cross-linked at 165°C for 10 min using citric acid alcohol solution with concentration from 2 to 10% (w/w) at 2% (w/w) intervals
a–e Cross-linked corn-based fibres
f–j Fibres immersion in water for 24 h

centrifugally spun starch-based fibres and results are shown in Fig. 2. Obviously, both the corn-based (Fig. 2e) and potato-based (Fig. 2f) fibres could be dissolved immediately when water dropped on fibre membranes. Generally, the hydrophilic hydroxyl groups in starches induced the poor water stability of starch products. Here, another reason should be taken into consideration, namely, the water solubility of residual NaOH in obtained fibres.

In the present research work, the citric acid was selected as the cross-linker to substitute the hydroxyl groups of the fibres, on the one hand, and remove the extra sodium hydroxide, on the other hand. The effects of citric acid concentration on water stability of corn-based and potato-based fibres were shown in Figs. 3 and 4, respectively. Interestingly, after cross-linking, both of corn-based and potato-based fibres were swelled in the radial direction and enlarged with the increasing concentration of citric acid. More significantly, as citric acid concentration increased to 10% (w/w), corn-based fibres were completely dissolved after cross-linking (Fig. 3e). The similar phenomenon occurred for potato-based fibres when citric acid concentration increased to 12% (w/w)

(Fig. 4e). As we have mentioned in previous sections, the mechanism of cross-linking was based on the esterification reaction between starch and citric acid. The water, which is generated during esterification reaction, caused fibres swollen in diameter or even dissolution.

Figs. 3f–j and 4f–j depicted the effect of citric acid concentration on water stability of corn-based and potato-based fibres, respectively. When cross-linking corn-based fibres with 2% (w/w) citric acid, the treated fibres had barely changed in morphology (Fig. 3a). However, the cross-linked fibres were completely dissolved after immersed in water for 24 h (Fig. 3f). Increasing citric acid concentration caused the diameter swelling of corn-based fibres (Figs. 3b–d), but the dissolution of treated fibres in water was decreased (Figs. 3g–i). For potato-based fibres, similar results were obtained. Therefore, we could conclude that the water stability of cross-linked fibres was increased with the increasing of citric acid concentration. However, considering the ability of cross-linked fibres to maintain fibrous structure of before and after immersed water, the optimal concentration for cross-linking corn-based and potato-based fibres should be 4% (Figs. 3b and g) and 8% (w/w) (Figs. 4c and h), respectively. Many attempts have demonstrated that corn starch had shorter chain length than potato starch [21, 22], which suggested more hydroxyl groups contained in potato-based fibres. The optimal concentration of the citric acid for potato-based fibres is therefore higher than that for corn-based fibres.

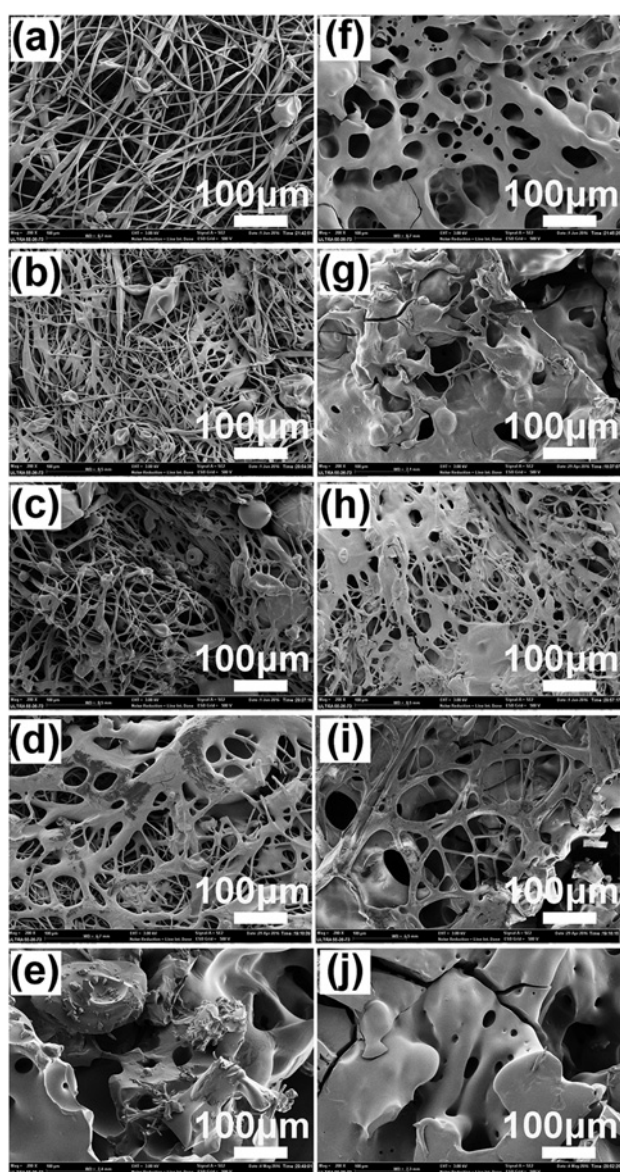


Fig. 4 SEM images of centrifugally spun potato-based fibres cross-linked at 165°C for 10 min using citric acid alcohol solution with concentration from 4 to 12% (w/w) at 2% (w/w) intervals
a–e Cross-linked potato-based fibres
f–j Fibres immersion in water for 24 h

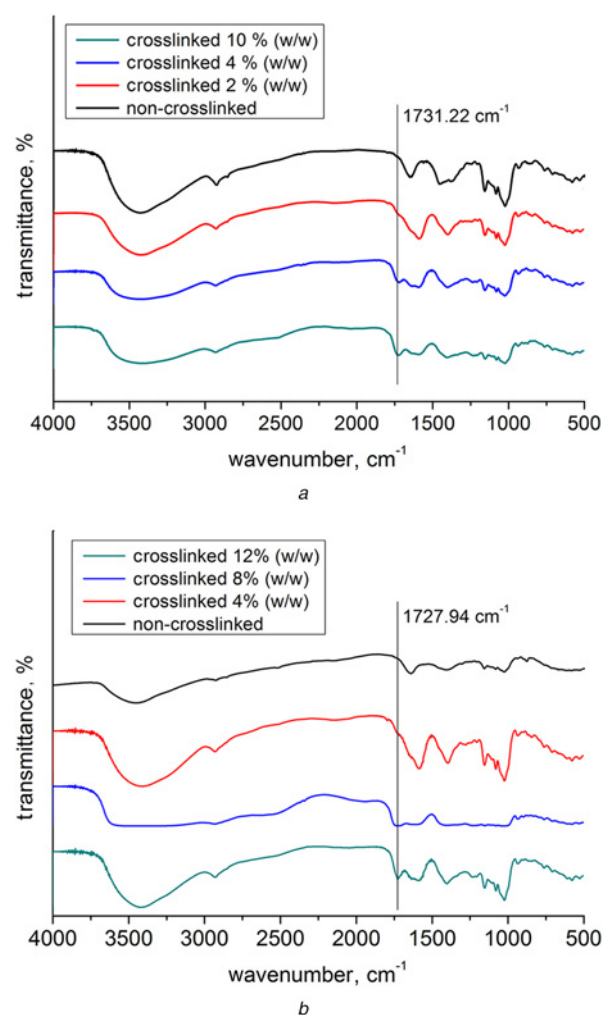


Fig. 5 FTIR spectra of the before and after cross-linked starch fibres
a Corn-based fibres
b Potato-based fibres

The pH of non-cross-linked and cross-linked fibres (after immersing water for 24 h) was decreased from 8.17 and 8.51 to 4.91 and 5.26 for corn-based and potato-based fibres, respectively. It was suggested that the neutral reaction between citric acid and NaOH was occurred during cross-linking proceeding.

Fig. 5 showed the FTIR spectra of non-cross-linked fibres and fibres cross-linked with different citric acid concentration. We could observe that the FTIR spectra of corn-based fibres showed the similar peaks, except for a new absorbance peak formed on cross-linked fibres at 1731.22 cm^{-1} (Fig. 5a). The intensities of peaks were increased with the increasing of citric acid concentration, which suggested the reactivity of starch and citric acid improved. For the cross-linked potato-based fibres, new absorbance peak formed at 1727.94 cm^{-1} (Fig. 5b), and the intensities of peaks showed same trend with those corn-based fibres as well. Those peaks are attributed to the stretch vibration of the ester and carbonyl carboxyl groups that were produced by the esterification reaction between carbonyl in citric acid and hydroxyl in starch-based fibres [18, 19]. The renewed peak of cross-linked fibres primly confirmed the chemical linkages between starch-based fibres and citric acid.

4. Conclusion: In this Letter, we demonstrate that citric acid can be an efficient cross-linker for improving the water stability of centrifugally spun starch-based fibres. The citric acid concentration has significant effect on the fibre morphology and water stability of starch-based fibres. Under the optimal concentration, cross-linked fibres can maintain fibrous structure for 24 h in water, which are greatly improved in comparison with non-cross-linked fibres. In conclusion, this Letter provides an insight to harm-less production system for preparing starch-based fibres, and is helpful for developing applications of starch-based fibres in food packaging, wound dressing, tissue engineering and so on.

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6 References

- [1] Avella M., De Vlieger J.J., Errico M.E., *ET AL.*: 'Biodegradable starch/clay nanocomposite films for food packaging applications', *Food Chem.*, 2005, **93**, (3), pp. 467–474
- [2] Arvanitoyannis I., Biliaderis C.G., Ogawa H., *ET AL.*: 'Biodegradable films made from low-density polyethylene (LDPE), rice starch and potato starch for food packaging applications: part 1', *Carbohydr. Polym.*, 1998, **36**, (2-3), pp. 89–104
- [3] López O.V., Lecot C.J., Zaritzky N.E., *ET AL.*: 'Biodegradable packages development from starch based heat sealable films', *J. Food Eng.*, 2011, **105**, (2), pp. 254–263
- [4] Prachayawarakorn J., Hwansanoet W.: 'Effect of silk protein fibers on properties of thermoplastic rice starch', *Fiber Polym.*, 2012, **13**, (5), pp. 606–612
- [5] Ahmed J., Auras R.: 'Effect of acid hydrolysis on rheological and thermal characteristics of lentil starch slurry', *LWT-Food Sci. Technol.*, 2011, **44**, (4), pp. 976–983
- [6] Goehring L.: 'Drying and cracking mechanisms in a starch slurry', *Phys. Rev. E*, 2009, **80**, (3), p. 036116
- [7] Mundargi R.C., Shelke N.B., Rokhade A.P., *ET AL.*: 'Formulation and in-vitro evaluation of novel starch-based tableted microspheres for controlled release of ampicillin', *Carbohydr. Polym.*, 2008, **71**, (1), pp. 42–53
- [8] Alves V.D., Mali S., Beléia A., *ET AL.*: 'Effect of glycerol and amylose enrichment on cassava starch film properties', *J. Food Eng.*, 2007, **78**, (3), pp. 941–946
- [9] Bertuzzi M.A., Vidaurre E.C., Armada M., *ET AL.*: 'Water vapor permeability of edible starch based films', *J. Food Eng.*, 2007, **80**, (3), pp. 972–978
- [10] Ghosh Dastidar T., Netravali A.: 'Cross-linked waxy maize starch-based 'green' composites', *ACS Sustain. Chem. Eng.*, 2013, **1**, (12), pp. 1537–1544
- [11] Kong L., Ziegler R.G.: 'Patents on fiber spinning from starches', *Recent Pat. Food Nutr. Agric.*, 2012, **4**, (3), pp. 210–219
- [12] Kong L., Ziegler G.R.: 'Role of molecular entanglements in starch fiber formation by electrospinning', *Biomacromolecules*, 2012, **13**, (8), pp. 2247–2253
- [13] Kong L., Ziegler G.R.: 'Fabrication of pure starch fibers by electrospinning', *Food Hydrocoll.*, 2014, **36**, pp. 20–25
- [14] Wang W., Jin X., Zhu Y., *ET AL.*: 'Effect of vapor-phase glutaraldehyde crosslinking on electrospun starch fibers', *Carbohydr. Polym.*, 2016, **140**, pp. 356–361
- [15] Quellmalz A., Mhranyan A.: 'Citric acid cross-linked nanocellulose-based paper for size-exclusion nanofiltration', *ACS Biomater. Sci. Eng.*, 2015, **1**, (4), pp. 271–276
- [16] Aoki H., Taguchi T., Saito H., *ET AL.*: 'Rheological evaluation of gelatin gels prepared with a citric acid derivative as a novel cross-linker', *Mater. Sci. Eng. C*, 2004, **24**, (6), pp. 787–790
- [17] Ma X., Jian R., Chang P.R., *ET AL.*: 'Fabrication and characterization of citric acid-modified starch nanoparticles/plasticized-starch composites', *Biomacromolecules*, 2008, **9**, (11), pp. 3314–3320
- [18] Reddy N., Yang Y.: 'Citric acid cross-linking of starch films', *Food Chem.*, 2010, **118**, (3), pp. 702–711
- [19] Menzel C., Olsson E., Plivelic T.S., *ET AL.*: 'Molecular structure of citric acid cross-linked starch films', *Carbohydr. Polym.*, 2013, **96**, (1), pp. 270–276
- [20] Li X., Chen H., Yang B.: 'Centrifugally spun starch-based fibers from amylopectin rich starches', *Carbohydr. Polym.*, 2016, **137**, pp. 459–465
- [21] Bertoft E., Piyachomkwan K., Chatakanonda P., *ET AL.*: 'Internal unit chain composition in amylopectins', *Carbohydr. Polym.*, 2008, **74**, (3), pp. 527–543
- [22] Hizukuri S., Kaneko T., Takeda Y.: 'Measurement of the chain length of amylopectin and its relevance to the origin of crystalline polymorphism of starch granules', *BBA-Gen. Subjects*, 1983, **760**, (1), pp. 188–191