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Cellulose, the most abundant biopolymer on earth, can offer environmentally sustainable materials to replace fossil-based polymers due to its availability, renewability, and biodegradability. Cellulosic nanomaterials, such as cellulose nanocrystals (CNC) and cellulose nanofibers (CNF), have outstanding properties and versatile applicability in functional fibres, films, foams, photonics, nanocomposites and biomedical devices.^{1–11} Chemical modification of the exposed functional groups (hydroxyl) on the surface of cellulose nanomaterials is, however, often a prerequisite to adapt CNCs and CNFs into composite materials or add functionality to nanocellulose-based materials.^{2,4,12} The major hurdle in chemical modification of native cellulose comes from the strong network of hydrogen bonds within and between cellulose fibrils, which hinders the dissolution and dispersion of cellulose in common solvents, and promotes nanocellulose aggregation, all of which can restrict the chemical reactivity.² Heterogeneous modification of nanocelluloses generally

requires either chemical pre-treatment with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) oxidation,^{13–15} sulfate half ester formation during hydrolysis¹⁶ or carboxymethylation¹⁷ to yield stable dispersions in solvents. On the other hand, homogeneous modification of cellulose involves dissolution into an ionic liquid^{18–20} or harsh reaction conditions,²¹ which can lead to high degrees of functionalization of the cellulose polymer, but destroys the native structure and mechanical properties of nanocelluloses. Furthermore, in both approaches, the amount of solvent is commonly 10–100-fold higher compared to the cellulosic material, leading to a large amount of waste generated.

Beyond cellulose as a practical alternative for fossil-based polymers, there is a clear demand for producing chemicals in a sustainable and environmentally friendly manner. An emerging greener route to achieve this relies on solid-state reactions, where solvent use is avoided or drastically reduced.^{22,23} Mechanochemistry in particular^{24–26} has gained importance not only in organic or (metallo)organic synthesis,^{27,28} but also in polymer science²⁹ and material chemistry.^{30,31} Mechanochemical methods for cellulose modification have the potential to avoid large-scale use of solvents,³² with reactions taking place between the solid substrate and solid (or liquid) reactants by milling, grinding or other types of mechanical mixing.³³ Previous mechanochemical reactions on cellulose have reported depolymerization of (ligno) cellulose,^{34–37} and different modifications like phosphoryl-

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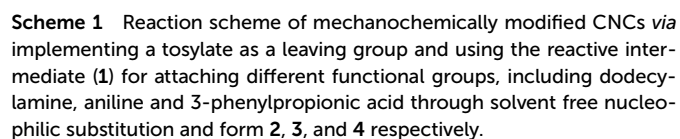
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persion of cellulose nanomaterials and generation of solvent waste, by reducing the solvent use compared to conventional modifications more than 10-fold.

Results and discussion

In the initial experiments of the mechanochemical tosylation of CNCs, we investigated the role and amount of the base (pyridine) in the formation of **1**, using different liquid-to-solid ratios (η). We opted to use η ($\mu\text{L mg}^{-1}$),⁵⁵ to allow relevant comparison to other mechanochemical, neat ($\eta = 0.0 \text{ mL mg}^{-1}$), liquid-assisted-grinding LAG ($\eta \approx 0\text{--}1 \text{ }\mu\text{L mg}^{-1}$) and slurry state ($\eta > 1 \text{ }\mu\text{L mg}^{-1}$) reactions. Indeed, the neat grinding of CNCs with TsCl without the base catalyst ($\eta = 0.0 \text{ }\mu\text{L mg}^{-1}$) did not yield **1**, showing that the base is required for the tosylation to take place (Fig. 1a). Addition of a small amount of pyridine in a liquid-assisted-grinding experiment (LAG with $\eta = 0.21 \text{ }\mu\text{L mg}^{-1}$) yielded a DS_{Tos} of 0.06 of the CNCs, which can be doubled to a DS_{Tos} of 0.12 when pyridine is introduced at $\eta = 0.36 \text{ }\mu\text{L mg}^{-1}$ (Fig. 1a). Synthesis near the slurry state with $\eta = 0.95 \text{ mL mg}^{-1}$ again almost doubles the DS_{Tos} to 0.23 (Fig. 1a),



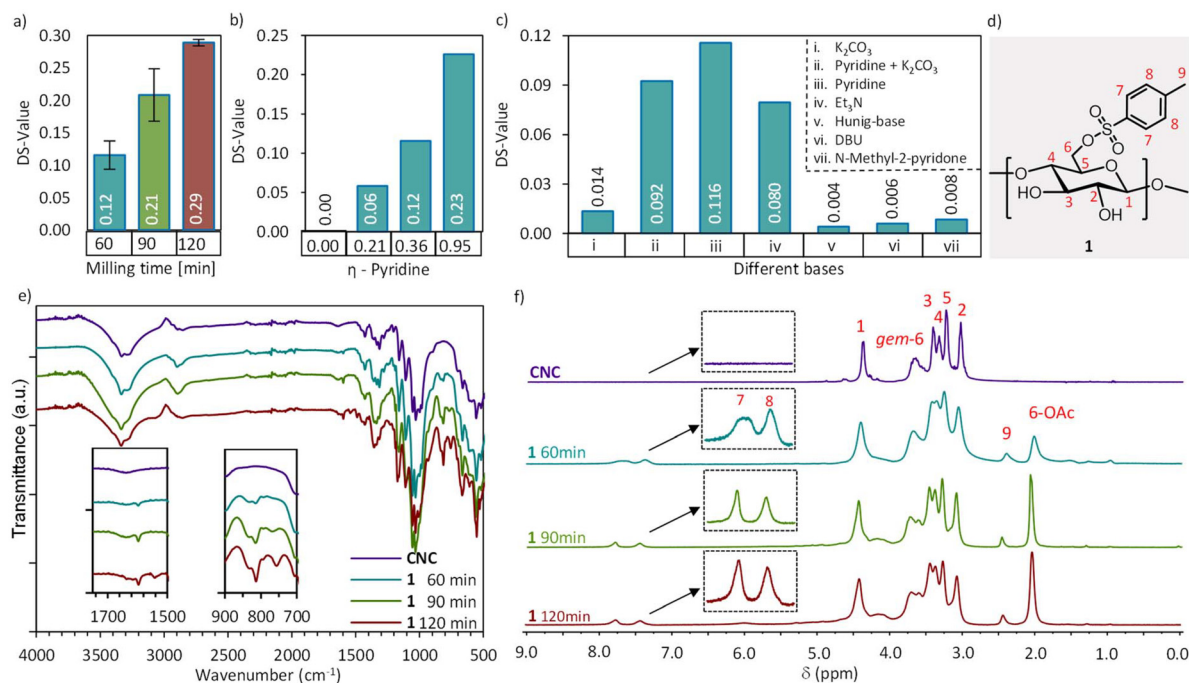


Fig. 1 Key optimisation parameters for mechanochemical tosylation reaction and characterisation: (a) Influence of $\eta = 0.0$ to $0.95 \mu\text{L mg}^{-1}$ for the synthesis of **1**. (b) Impact of different bases on the synthesis of **1**. (c) Effect of the milling time (60 min, 90 min, 120 min) on the DS value of **1**. (d) Chemical structure of product **1**. (e) ATR-IR characterization of the milling time influence on the synthesis of **1**. Insets show magnified areas of interest in the aromatic area between $1700\text{--}1500 \text{ cm}^{-1}$ and $900\text{--}700 \text{ cm}^{-1}$. (f) Partial diffusion-edited ^1H spectra of CNC, **1** 60 min, 90 min and 120 min, showing the aromatic (7, 8), aliphatic (9) and cellulosic (1–6) region used for qualitative analysis of the reaction. ^1H -NMR is displayed in Fig. S6†

however with the consequence of tripling the amount of pyridine used for the synthesis. Fig. 1b shows that triethylamine (Et_3N , $\eta = 0.95 \mu\text{L mg}^{-1}$) also delivers good DS_{Tos} 0.08 and that the total amount of pyridine can be reduced by 50% by partially substituting it with potassium carbonate (pyridine + K_2CO_3 , with pyridine $\eta = 0.116 \mu\text{L mg}^{-1}$ and 1.8 eq. of K_2CO_3) giving DS_{Tos} of 0.09. Next, we investigated the influence of milling duration on the tosylation of CNCs (Fig. 1c). As pyridine outperformed the other bases, LAG conditions with $\eta = 0.36 \mu\text{L mg}^{-1}$ were used for the further optimization. Triplicate experiments show a clear linear correlation (Fig. S5†) between the increased milling time and the increase of the DS_{Tos} , with 60, 90 and 120 minutes of milling leading to DS_{Tos} of 0.12, 0.21 and 0.29, respectively. Considering the limited amount of exposed hydroxyl groups on the surface of CNCs, these bulk DS_{Tos} values indicate that the mechanochemical approach achieves very high surface coverage of the tosylation ($>50\%$ surface modified, see ESI section 2.3†). ATR-IR measurements (Fig. 1e) show the appearance of the characteristic tosyl signals, the band at 1597 cm^{-1} (ref. 52) and out-of-plane at 812 cm^{-1} of aromatics, which are not present in the CNC starting material. The magnitude of the signals correlates well with the elemental analysis results. Evidence of covalent bond formation between cellulose and the tosyl group (Fig. 1d) is delivered by the recently reported solution state NMR for cellulose and its derivatives in the $[\text{P}_{4444}][\text{OAc}]/\text{DMSO-}d_6$ ionic liquid.^{60,61} The peaks corresponding to the cellulose backbone

appear in the region of $3.0\text{--}4.5 \text{ ppm}$ (Fig. 1f). Characteristic peaks of the tosyl group at $7.3\text{--}8.0 \text{ ppm}$ (aromatic) and at 2.4 ppm (CH_3) within the diffusion band of cellulose (Fig. 1f), for all three samples of **1** shows that tosyl groups are covalently attached to the polymeric cellulose chains. Importantly, the $[\text{P}_{4444}][\text{OAc}]/\text{DMSO-}d_6$ ionic liquid contains an acetate counterion, which we observe to largely substitute the reactive C6-tosyl group of **1** under the dissolution conditions (65°C , $16\text{--}20 \text{ h}$). The 6-OAc cellulose acetate peak is observed at 2.0 ppm . The replacement of the tosyl group with the acetate group is corroborated by a matching set of released tosylate peaks in the ^1H -NMR (Fig. S1†). The remaining aromatic tosyl signals ($7.3\text{--}8.0 \text{ ppm}$) are likely to originate from unreacted C6-tosyl and/or less reactive C2-tosyl groups. To differentiate between these, and estimate the regioselectivity of the tosylation reaction, high temperature NMR experiment was performed at 80°C , to push the acetate replacement to completion (see ESI section 2.4†). No 2-OAc or 3-OAc peaks appear in the cellulose diffusion band.⁶² Assuming that the remaining bound tosyl signals arise solely from the less reactive C2-tosyl groups, and that the C6-tosyl groups have been fully replaced by acetate (as witnessed by the single acetate peak), this experiment shows that the tosylation proceeds with very high regioselectivity (at least $50:1$) of the C6 position over C2 (ESI section 2.4, Fig. S3†).

In addition to the chemical characterization, electron microscopy imaging (TEM) and powder X-ray diffraction (PXRD) analysis of the resulting tosylated CNCs (**1**) were

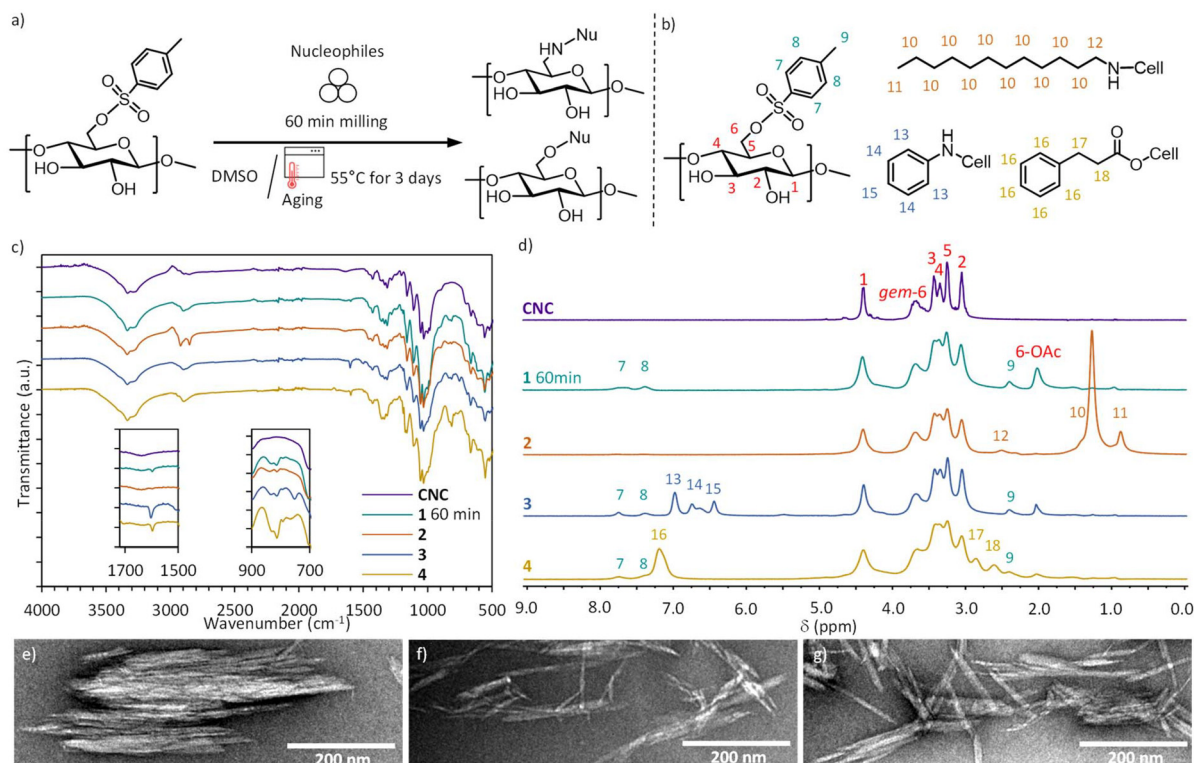


Fig. 3 Nucleophilic substitution of tosylated CNCs. (a) Reaction scheme of the nucleophilic substitution. (b) Shows the molecules and their peak assignment for the NMR in Fig. 4d. (c) ATR-IR characterization of the nucleophilic substitution of tosylated CNCs (1 60 min) with dodecylamine (2), aniline (3) and 3-phenylpropionic acid (4) and the CNC as starting material. Inserts showing areas of interest in the aromatic area between 1700–1500 cm^{-1} and 900–700 cm^{-1} . (d) Diffusion edited ^1H spectra of CNC, 1 60 min, 2, 3, and 4, showing the aromatic (7, 8, 13, 14, 15, 16), aliphatic (9, 10, 11, 17, 18) and cellulosic (1–6) region used for qualitative analysis of the reaction. (e–g) Zoomed TEM images of 2, 3, and 4 respectively. For full images see Fig. S9a–c.†

washing and drying procedure as described for the isolation of 1, to yield the product 2 as an off-white powder. Higher DS_{Nu} of 0.131 of 2 was achieved by the incorporation of the aging step (Table 2), compared to the DS_{Nu} 0.021 achieved by only ball milling for 60 min (Fig. S17; Table S8†). Similar DS_{Nu} of 0.11 was achieved when the aging step was carried out at 70 °C for 48 h (Fig. S18, Table S9†). For the amination with dodecylamine, the ATR-IR shows the characteristic CH stretching of alkanes in the region of 3000–2840 cm^{-1} and simultaneous

reduction in the characteristic aromatic bands at 1597 cm^{-1} and at 812 cm^{-1} of the tosyl group (Fig. 3c). Diffusion-edited ionic liquid ^1H NMR also demonstrates the nearly complete substitution of the covalently bound tosyl group with the aliphatic amine, which appears as three peaks in the 1.0–2.6 ppm region of the spectra (Fig. 3d). Absence of the 6-OAc peak in this sample also provides key evidence that the substitution reaction is complete before the dissolution in the ionic liquid, as otherwise the large excess of the ionic liquid would lead to substitution of unreacted C6-tosyl with the acetate. No reduction of the cellulose molecular weight was observed for 2 (DP_n 280), in comparison to the CNC starting material (DP_n 270) by gel permeation chromatography (ESI section 1.9†). The thermal properties of the starting material (HCl-CNC), the tosylated CNCs (1 60 min) and the dodecylamine-modified CNCs (2) were compared, showing that the chemical modification of cellulose reduced the thermal stability of the CNCs (Fig. S22, S23, Table S11†). The amination with aromatic aniline was also successful under these synthesis conditions, yielding product 3, albeit with a slightly lower DS_{Nu} of 0.10 compared to substitution with the dodecylamine (Table 2). Indeed, the corresponding NMR (Fig. 3d) confirms the partial conversion, as the peaks for covalently bound aniline (Fig. 3d, entry 3, peaks 13–15) coexist with residual

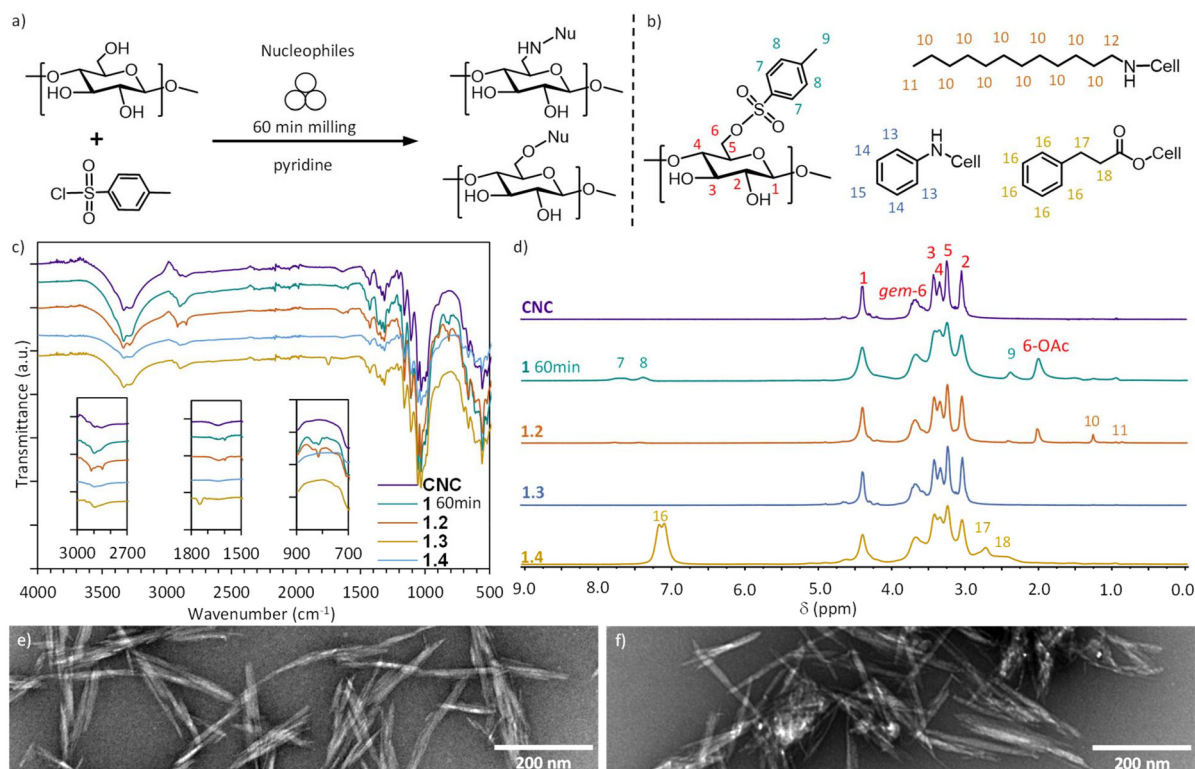
Table 2 The degree of substitution DS_{Nu} achieved through nucleophilic substitution of tosylated CNCs (Fig. 4)

Samples	Elemental analysis				DS^a	DS^b
	%H	%C	%S	%N		
2	7.10	47.75	0.45	0.98	0.02	0.13
3	6.15	45.53	0.82	0.95	0.05	0.10
4	6.04	45.79	0.17	0.00	ND ^c	ND ^c

^a DS calculated from sulphur content obtained by elemental analysis, represents unreacted tosyl groups on cellulose. ^b DS calculated from nitrogen content obtained by elemental analysis. ^c Elemental analysis could not be used to calculate the DS , as there are no S or N atoms in 3-phenylpropionic acid.



The TEM images of **2**, **3**, **4** (Fig. 3e–g) show rod-shaped objects, indicating that the morphology of CNCs is intact also after nucleophilic substitution. The product **2**, when dispersed from water, forms bundles of CNCs (Fig. 3e) most likely due to the aggregation of the long aliphatic chains attached to CNC surfaces. The samples **3** and **4** (Fig. 3g and h) show similar distribution of the rod-shaped CNCs as **1** and the starting material (Fig. 2), reflecting the poor dispersibility of the non-charged CNCs in water. Success in the optimization of the individual steps of mechanochemical tosylation and nucleophilic substitution led us to investigate the combination of both steps together as a one-step mechanochemical reaction. This reaction would eliminate the isolation steps of the reactive tosylated-CNCs, instead allowing **1** to react *in situ* with the nucleophile. Although addition of an aging step delivered higher DS_{Nu} in the nucleophilic substitution stage, aging in the presence of tosylation reactants led to degradation of cellulose, likely due to instability of cellulose in the presence of TsCl and pyridine at elevated temperatures (Fig. S14†). Therefore, only mechanochemical one-step reactions could be considered. In Fig. 4a the reaction scheme of the one-step reaction can be observed, where the CNC starting material is mixed in a stainless-steel milling jar with 1.5 eq. of TsCl and 1.5 eq. of the nucleophile in the presence of pyridine as the base and



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was transferred in a 50 mL Falcon tube and freeze dried. The parameters were varied depending on the nucleophile. First, the SN conditions for dodecylamine were optimized with investigating the aging temperature and time (55 °C for 72 h and 70 °C for 48 h; ESI section 2.10†), and the influence of milling and milling + aging (ESI section 2.9†). Next, the comparison of aniline with(out) DMSO (ESI section 2.11†), followed by the influence of K₂CO₃ on 3-phenylpropionic acid (ESI section 2.12†).

Summary of material characterisation methods

Elemental analysis (EA) was carried out to obtain the degree of substitution (DS_{Tos} and DS_{Nu}). The DS value is determined as the ratio of modified anhydroglucose units to the unmodified ones. The calculation of DS is based on the sulphur and nitrogen content (see eqn (1) and (2) in ESI section 1.6†). Solution-state NMR in [P₄₄₄₄][OAc]/DMSO-*d*₆ (w/w = 1 : 4) solvent was used for chemical characterisation and to confirm the covalent linkage between cellulose and the modifying group. Powder X-ray diffraction (PXRD) revealed relative changes (see eqn (3) in ESI†) in crystallinity upon different reaction conditions. Transmission electron microscopy (TEM) was used to observe morphological changes of the samples from milling. Thermal analysis was used to compare the thermal stability of CNCs and modified CNCs. Gel permeation chromatography (GPC) was used to compare the molecular mass of cellulose in CNCs and modified CNCs.

Author contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Data availability

The data supporting this article have been included as part of the ESI. The ESI file compiles detailed information on the materials, methods, and equipment used. It also contains the description of the equations used for calculations (eqn (1)–(3), supplementary Fig. (S1–S23) and Tables (S1–S11) referenced in the manuscript.†

Conflicts of interest

There are no conflicts to declare.

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References

- 1 R. J. Moon, A. Martini, J. Nairn, J. Simonsen and J. Youngblood, *Chem. Soc. Rev.*, 2011, **40**, 3941.
- 2 Y. Habibi, L. A. Lucia and O. J. Rojas, *Chem. Rev.*, 2010, **110**, 3479–3500.
- 3 I. Siró and D. Plackett, *Cellulose*, 2010, **17**, 459–494.
- 4 Y. Habibi, *Chem. Soc. Rev.*, 2014, **43**, 1519–1542.
- 5 T. Abitbol, A. Rivkin, Y. Cao, Y. Nevo, E. Abraham, T. Ben-Shalom, S. Lapidot and O. Shoseyov, *Curr. Opin. Biotechnol.*, 2016, **39**, 76–88.
- 6 E. Kontturi, P. Laaksonen, M. B. Linder, Nonappa, A. H. Gröschel, O. J. Rojas and O. Ikkala, *Adv. Mater.*, 2018, **30**, 1703779.
- 7 K. Oksman, Y. Aitomäki, A. P. Mathew, G. Siqueira, Q. Zhou, S. Butylina, S. Tanpichai, X. Zhou and S. Hooshmand, *Composites, Part A*, 2016, **83**, 2–18.
- 8 M. Mujtaba, A. Negi, A. W. T. King, M. Zare and J. Kuncova-Kallio, *Curr. Opin. Biomed. Eng.*, 2023, **28**, 100475.
- 9 E. Anaya-Plaza, E. van de Winckel, J. Mikkilä, J. M. Malho, O. Ikkala, O. Gulías, R. Bresolí-Obach, M. Agut, S. Nonell, T. Torres, M. A. Kostiaainen and A. de la Escosura, *Chem. – Eur. J.*, 2017, **23**, 4320–4326.
- 10 H. Rosilo, J. R. McKee, E. Kontturi, T. Koho, V. P. Hytönen, O. Ikkala and M. A. Kostiaainen, *Nanoscale*, 2014, **6**, 11871–11881.
- 11 S. Imlimthan, S. Otaru, O. Keinänen, A. Correia, K. Lintinen, H. A. Santos, A. J. Airaksinen, M. A. Kostiaainen and M. Sarparanta, *Biomacromolecules*, 2019, **20**, 674–683.
- 12 J. Gröndahl, K. Karisalmi and J. Vapaavuori, *Soft Matter*, 2021, **17**, 9842–9858.
- 13 Y. Habibi, H. Chanzy and M. R. Vignon, *Cellulose*, 2006, **13**, 679–687.
- 14 T. Saito, Y. Nishiyama, J.-L. Putaux, M. Vignon and A. Isogai, *Biomacromolecules*, 2006, **7**, 1687–1691.
- 15 A. Isogai and Y. Kato, *Cellulose*, 1998, **5**, 153–164.
- 16 S. Beck-Candanedo, M. Roman and D. G. Gray, *Biomacromolecules*, 2005, **6**, 1048–1054.
- 17 L. Wågberg, G. Decher, M. Norgren, T. Lindström, M. Ankerfors and K. Axnäs, *Langmuir*, 2008, **24**, 784–795.
- 18 M. Gericke, J. Schaller, T. Liebert, P. Fardim, F. Meister and T. Heinze, *Carbohydr. Polym.*, 2012, **89**, 526–536.
- 19 M. Granström, J. Kavakka, A. King, J. Majoinen, V. Mäkelä, J. Helaja, S. Hietala, T. Virtanen, S.-L. Maunu,



- D. S. Argyropoulos and I. Kilpeläinen, *Cellulose*, 2008, **15**, 481–488.
- 20 K. N. Onwukamike, S. Grelrier, E. Grau, H. Cramail and M. A. R. Meier, *ACS Sustainable Chem. Eng.*, 2019, **7**, 1826–1840.
- 21 S. Eyley and W. Thielemans, *Chem. Commun.*, 2011, **47**, 4177.
- 22 K. Tanaka and F. Toda, *Chem. Rev.*, 2000, **100**, 1025–1074.
- 23 G. Kaupp, in *Encyclopedia of Physical Organic Chemistry*, 5 Volume Set, ed. Z. Wang, John Wiley & Sons, Inc., Hoboken, NJ, USA, 1st edn, 2016, pp. 1–79.
- 24 V. Štrukil, M. D. Igrc, L. Fábíán, M. Eckert-Maksić, S. L. Childs, D. G. Reid, M. J. Duer, I. Halasz, C. Mottillo and T. Friščić, *Green Chem.*, 2012, **14**, 2462–2473.
- 25 S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed and D. C. Waddell, *Chem. Soc. Rev.*, 2012, **41**, 413–447.
- 26 T. Friščić, C. Mottillo and H. M. Titi, *Angew. Chem., Int. Ed.*, 2020, **59**, 1018–1029.
- 27 S. Tanaka, *Mechanochemical synthesis of MOFs*, Elsevier Inc., 2020.
- 28 S. Kaabel, R. S. Stein, M. Fomitšenko, I. Järving, T. Friščić and R. Aav, *Angew. Chem., Int. Ed.*, 2019, **58**, 6230–6234.
- 29 A. Krusenbaum, S. Grätz, G. T. Tigineh, L. Borchardt and J. G. Kim, *Chem. Soc. Rev.*, 2022, **51**, 2873–2905.
- 30 X. Li, M. Baldini, T. Wang, B. Chen, E. Xu, B. Vermilyea, V. H. Crespi, R. Hoffmann, J. J. Molaison, C. A. Tulk, M. Guthrie, S. Sinogeikin and J. V. Badding, *J. Am. Chem. Soc.*, 2017, **139**, 16343–16349.
- 31 A. P. Amrute, J. De Bellis, M. Felderhoff and F. Schüth, *Chem. – Eur. J.*, 2021, **27**, 6819–6847.
- 32 L. P. Jameson and S. V. Dzyuba, *Beilstein J. Org. Chem.*, 2013, **9**, 786–790.
- 33 J. Lease, T. Kawano and Y. Andou, *RSC Adv.*, 2023, **13**, 27558–27567.
- 34 M. Kessler and R. Rinaldi, *Front. Chem.*, 2022, **9**, 816553.
- 35 P. Dornath, H. J. Cho, A. Paulsen, P. Dauenhauer and W. Fan, *Green Chem.*, 2015, **17**, 769–775.
- 36 S. Furusato, A. Takagaki, S. Hayashi, A. Miyazato, R. Kikuchi and S. T. Oyama, *ChemSusChem*, 2018, **11**, 888–896.
- 37 F. Hammerer, L. Loots, J. Do, J. P. D. Therien, C. W. Nickels, T. Friščić and K. Auclair, *Angew. Chem., Int. Ed.*, 2018, **57**, 2621–2624.
- 38 B. G. Fiss, L. Hatherly, R. S. Stein, T. Friščić and A. Moores, *ACS Sustainable Chem. Eng.*, 2019, **7**, 7951–7959.
- 39 F. Zhang, W. Qiu, L. Yang, T. Endo and T. Hirotsu, *J. Mater. Chem.*, 2002, **12**, 24–26.
- 40 M. Beaumont, P. Jusner, N. Gierlinger, A. W. T. King, A. Potthast, O. J. Rojas and T. Rosenau, *Nat. Commun.*, 2021, **12**, 1–8.
- 41 M. Beaumont, B. L. Tardy, G. Reyes, T. V. Koso, E. Schaubmayr, P. Jusner, A. W. T. King, R. R. Dagastine, A. Potthast, O. J. Rojas and T. Rosenau, *J. Am. Chem. Soc.*, 2021, **143**, 17040–17046.
- 42 A. Lucia, H. W. G. Van Herwijnen, J. T. Oberlerchner, T. Rosenau and M. Beaumont, *ChemSusChem*, 2019, **12**, 4679–4684.
- 43 I. Solala, U. Henniges, K. F. Pirker, T. Rosenau, A. Potthast and T. Vuorinen, *Cellulose*, 2015, **22**, 3217–3224.
- 44 T. Motokawa, M. Makino, Y. Enomoto-Rogers, T. Kawaguchi, T. Ohura, T. Iwata and M. Sakaguchi, *Adv. Powder Technol.*, 2015, **26**, 1383–1390.
- 45 K. Rahn, M. Diamantoglou, D. Klemm, H. Berghmans and T. Heinze, *Angew. Makromol. Chem.*, 1996, **238**, 143–163.
- 46 L. El Hamdaoui, A. Es-said, M. El Marouani, M. El Bouchti, R. Bchitou, F. Kifani-Sahban and M. El Moussaouiti, *ChemistrySelect*, 2020, **5**, 7695–7703.
- 47 Th. Heinze, A. Koschella, L. Magdaleno-Maiza and A. S. Ulrich, *Polym. Bull.*, 2001, **46**, 7–13.
- 48 S. Schmidt, T. Liebert and T. Heinze, *Green Chem.*, 2014, **16**, 1941–1946.
- 49 T. Heinze, M. Siebert, P. Berlin and A. Koschella, *Macromol. Biosci.*, 2016, **16**, 10–42.
- 50 L. Jasmani, S. Eyley, R. Wallbridge and W. Thielemans, *Nanoscale*, 2013, **5**, 10207.
- 51 D. Joram Mendoza, L. M. M. Mouterde, C. Browne, V. Singh Raghuwanshi, G. P. Simon, G. Garnier and F. Allais, *ChemSusChem*, 2020, 6552–6561.
- 52 E. Feese, H. Sadeghifar, H. S. Gracz, D. S. Argyropoulos and R. A. Ghiladi, *Biomacromolecules*, 2011, **12**, 3528–3539.
- 53 H. Wang, J. He, M. Zhang, K. C. Tam and P. Ni, *Polym. Chem.*, 2015, **6**, 4206–4209.
- 54 G. A. Bowmaker, *Chem. Commun.*, 2013, **49**, 334–348.
- 55 T. Friščić, S. L. Childs, S. A. A. Rizvi and W. Jones, *CrystEngComm*, 2009, **11**, 418–426.
- 56 I. Huskić, C. B. Lennox and T. Friščić, *Green Chem.*, 2020, **22**, 5881–5901.
- 57 T. Pääkkönen, P. Spiliopoulos, A. Knuts, K. Nieminen, L.-S. Johansson, E. Enqvist and E. Kontturi, *React. Chem. Eng.*, 2018, **3**, 312–318.
- 58 E. Kontturi, A. Meriluoto, P. A. Penttilä, N. Baccile, J. Malho, A. Potthast, T. Rosenau, J. Ruokolainen, R. Serimaa, J. Laine and H. Sixta, *Angew. Chem., Int. Ed.*, 2016, **55**, 14455–14458.
- 59 R. S. Tipson, *J. Org. Chem.*, 1944, **09**, 235–241.
- 60 L. Fliri, K. Heise, T. Koso, A. R. Todorov, D. R. Del Cerro, S. Hietala, J. Fiskari, I. Kilpeläinen, M. Hummel and A. W. T. King, *Nat. Protoc.*, 2023, **18**, 2084–2123.
- 61 A. W. T. King, V. Mäkelä, S. A. Kedzior, T. Laaksonen, G. J. Partl, S. Heikkinen, H. Koskela, H. A. Heikkinen, A. J. Holding, E. D. Cranston and I. Kilpeläinen, *Biomacromolecules*, 2018, **19**, 2708–2720.
- 62 T. Koso, M. Beaumont, B. L. Tardy, D. Rico Del Cerro, S. Eyley, W. Thielemans, O. J. Rojas, I. Kilpeläinen and A. W. T. King, *Green Chem.*, 2022, **24**, 5604–5613.
- 63 B. Stefanovic, K. F. Pirker, T. Rosenau and A. Potthast, *Carbohydr. Polym.*, 2014, **111**, 688–699.
- 64 M. Ago, T. Endo and T. Hirotsu, *Cellulose*, 2004, **11**, 163–167.



- 65 P. Ahvenainen, I. Kontro and K. Svedström, *Cellulose*, 2016, **23**, 1073–1086.
- 66 O. M. Vanderfleet and E. D. Cranston, *Nat. Rev. Mater.*, 2020, **6**, 124–144.
- 67 D. Tan and F. García, *Chem. Soc. Rev.*, 2019, **48**, 2274–2292.
- 68 T. Heinze, A. Pfeifer, A. Koschella, J. Schaller and F. Meister, *J. Appl. Polym. Sci.*, 2016, **133**, 43987.

