Continuous production of cellulose mixed esters via homogeneous reactive twin-screw extrusion catalyzed by ionic liquid

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This file includes Figures S1 to S9 and Tables S1 to S3. Table of Contents is summarized in the next page.

Table of Contents | Page

Scheme of Reactive Twin-screw Extruder

Fig. S1 Schematic representation of the twin screw extruder as a flow reactor for continuous production of CAP via REX of cellulose with a pre-mixed acyl reagents (IPAc/VPr, 2.5:0.5 molar equiv./AGU) in the EmimOAc/DMSO mixed solvents

    The screw configuration used in this study comprised of conveying and kneading elements. L, N, and R represent the left-hand, neutral, and right-hand kneading elements, respectively. The stagger angles for each kneading element are 45° (L), 90° (N), and −45° (R).

Identification of Regenerated Cellulose after Solubility Tests by ATR-mode FT-IR
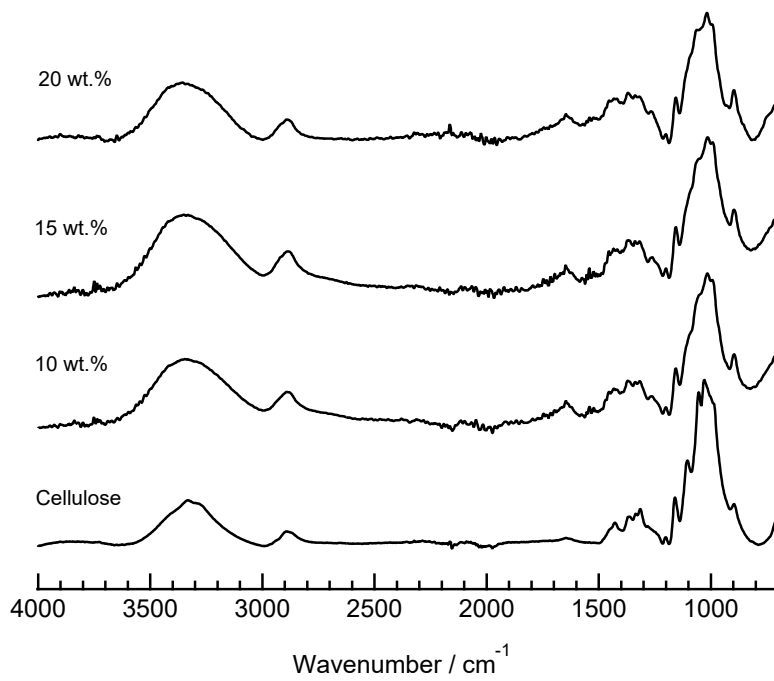
Fig. S2 ATR-mode FT-IR spectra of pristine cellulose and regenerated cellulose obtained after the solubility tests in EmimOAc/DMSO using a twin-screw extruder

Identification of CAPs Synthesized via Continuous REX by ATR-mode FT-IR
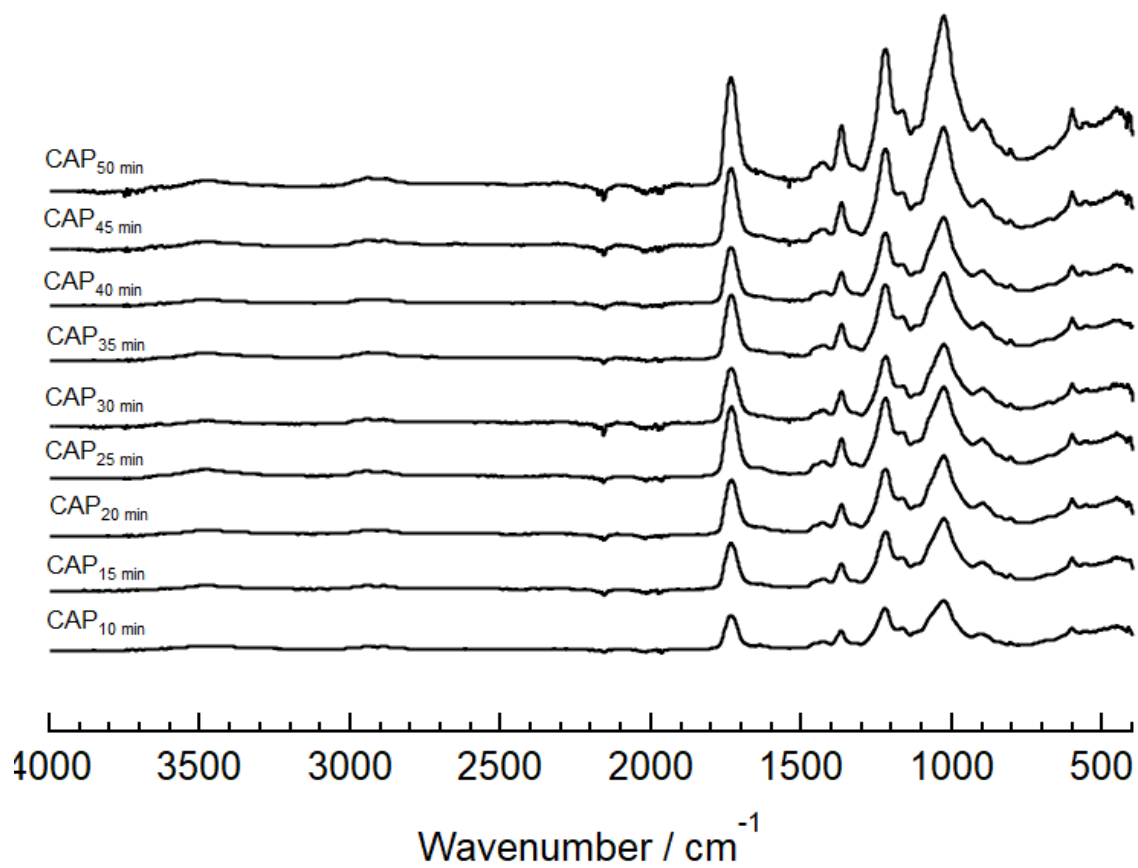
Fig. S3 ATR-mode FT-IR spectra of CAPs collected at every 5 min during continuous REX for total 50 min operation

Identification of CAPs Synthesized via Continuous REX by ^{1}H NMR
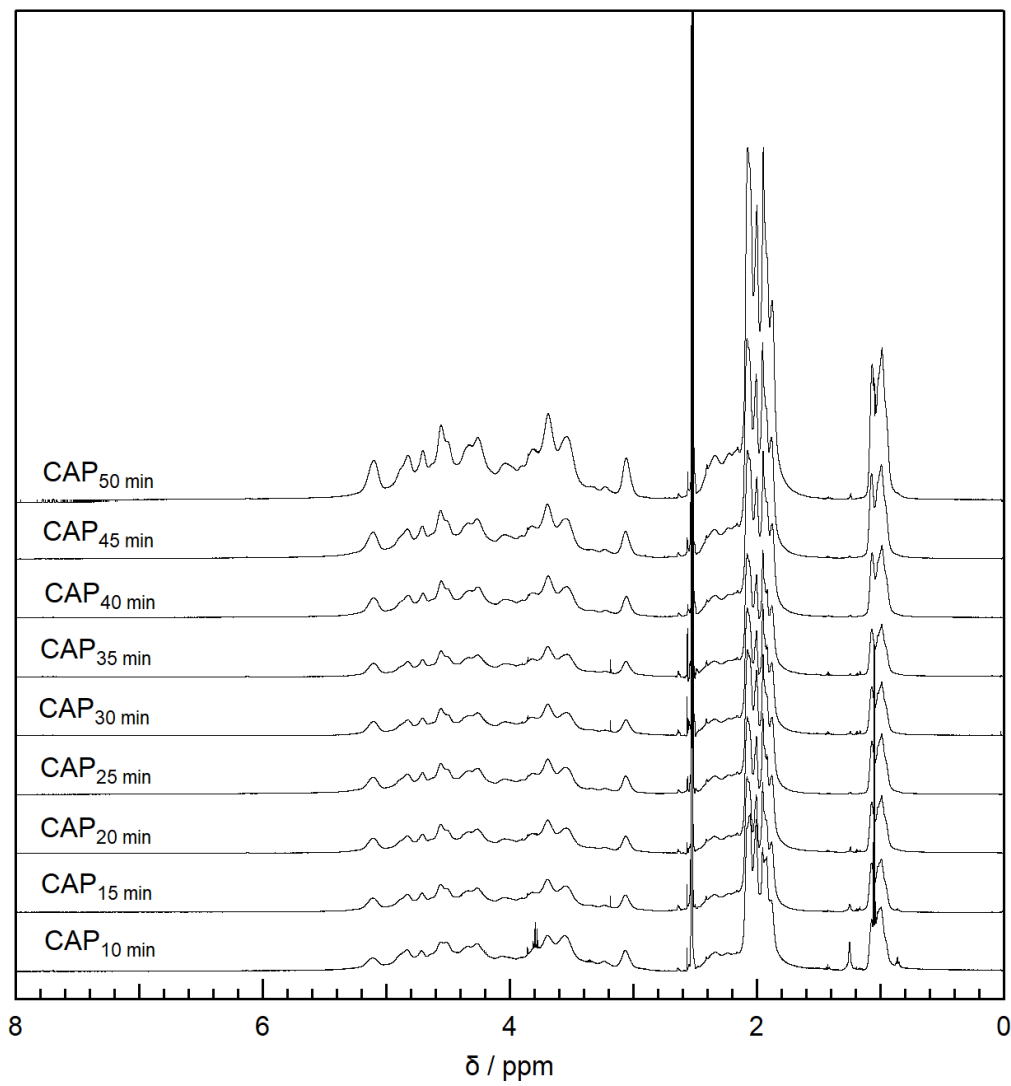
Fig. S4 ^{1}H NMR spectra of CAPs collected at every 5 min during continuous REX for total 50 min operation, measured in DMSO-d_6

Identification of CAP$_{15\ min}$ Synthesized via Continuous REX by ^{13}C NMR

A portion of CAP$_{15\ min}$ (60 mg) was dissolved in deuterated DMSO (DMSO-d_6, 0.8 mL). ^{13}C nuclear magnetic resonance (NMR) of the CAP$_{15\ min}$ solution was measured at 25 °C for 10,000 scans using a JNM-ECZ R 600Hz spectrometer (JEOL Ltd., Tokyo, Japan) at the Advanced Research Center in Kanazawa University. The NMR spectrum was analyzed using Delta NMR (JEOL Ltd., Tokyo, Japan), and the chemical shifts (δ, ppm) were referenced to tetramethylsilane (TMS, δ = 0 ppm) as an internal standard.
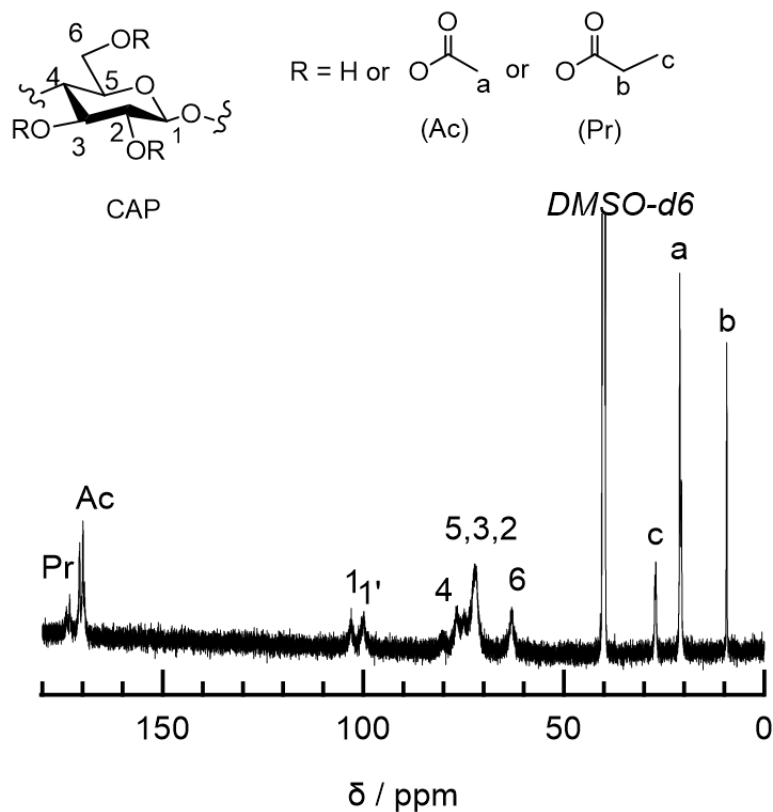
Fig. S5 ^{13}C NMR spectrum of CAP$_{15\ min}$ collected at 15 min during continuous REX for total 50 min operation, measured in DMSO-d_6

For the additional confirmation of the chemical structure of CAP,^{13}C NMR analysis was performed (**Fig. S5**). There were characteristic signals of the cellulose backbone (labeled 1−6) from 62 to 101 ppm (Iwata et al. 1992). The chemical shift at 98 ppm is assigned to 1′ due to the resonance of the C1 position of cellulose, that has shown to increase as the DS increases (Kono et al. 2015). Furthermore, two chemical shifts corresponding to the carbonyl carbons (C=O) in Ac groups at 170 ppm and Pr groups at 173 ppm were detected. These results suggest the successful substitution of cellulose-OH groups with both the Ac and Pr groups via continuous REX.

DSs of Ac and Pr Groups and Isolated Yields of CAPs Synthesized via Continuous REX

Table S1 Degrees of substitutions (DSs) of Ac and Pr groups and isolated yields of CAPs synthesized via continuous REX from 15 wt.% cellulose in EmimOAc/DMSO (1:3, g/g)

Collection time of CAP	DS			Isolated yield[a] / %
	Ac	Pr	Total	
10 min	1.72	0.45	2.17	79
15 min	1.80	0.45	2.25	72
20 min	1.80	0.46	2.26	81
25 min	1.81	0.51	2.31	78
30 min	1.74	0.50	2.24	78
35 min	1.72	0.51	2.23	77
40 min	1.77	0.52	2.30	74
45 min	1.79	0.53	2.32	73
50 min	1.79	0.53	2.32	77
Ave. (n = 9)	1.77 ± 0.04	0.50 ± 0.03	2.27 ± 0.07	77 ± 2

[a] Isolated yield (%) = the actual yield / theoretical yield of CAPs. The theoretical yield is based on the measured DSs.

Distributions of Ac and Pr Groups in CAP$_{15\ min}$ Synthesized via Continuous REX
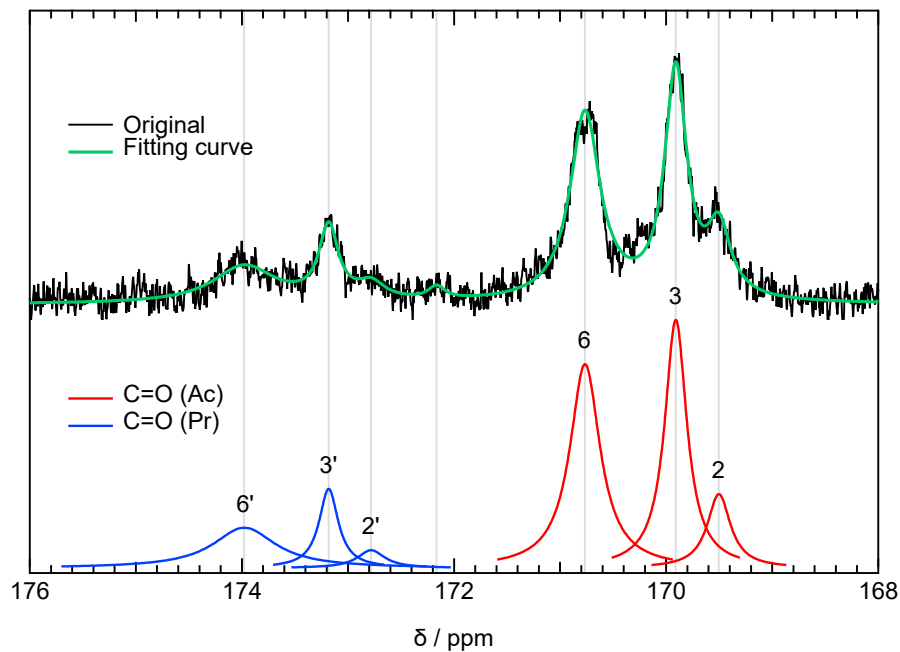
Fig. S6 The magnification of ^{13}C NMR signals due to the carbonyl carbons of Ac and Pr groups in CAP$_{15\ min}$ (**Fig. S5**) and the peak-fitting curves

Table S2 Estimated distributions of Ac and Pr groups in CAP$_{15\ min}$

Substituent	DS for each position of cellulose-OH groups			
	C6-OH	C3-OH	C2-OH	Total
Ac	0.80	0.71	0.23	1.74
Pr	0.28	0.17	0.05	0.50

Identification of B-CAPs Synthesized in Batch by ATR-mode FT-IR

Fig. S7 ATR-mode FT-IR spectra of pristine cellulose and B-CAP$_{1–240\ min}$ synthesized in batch from 5 wt.% cellulose solutions

Identification of B-CAPs Synthesized in Batch by ^{1}H NMR
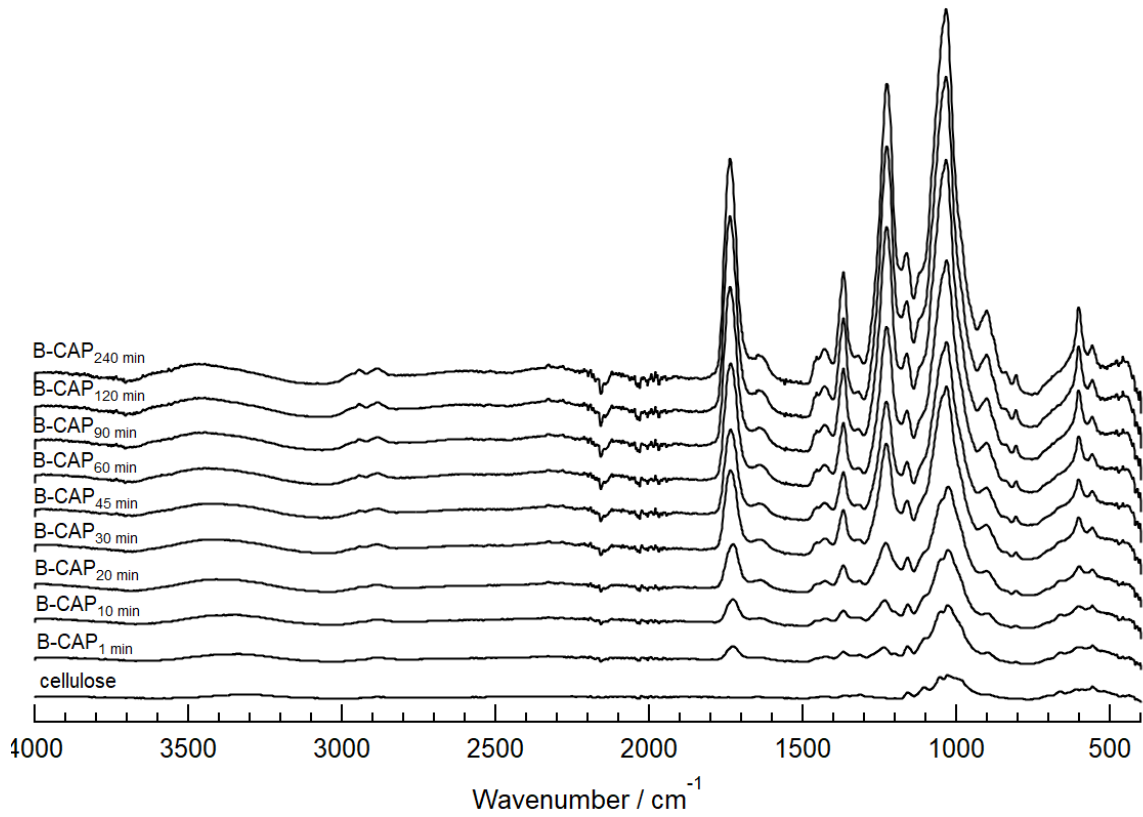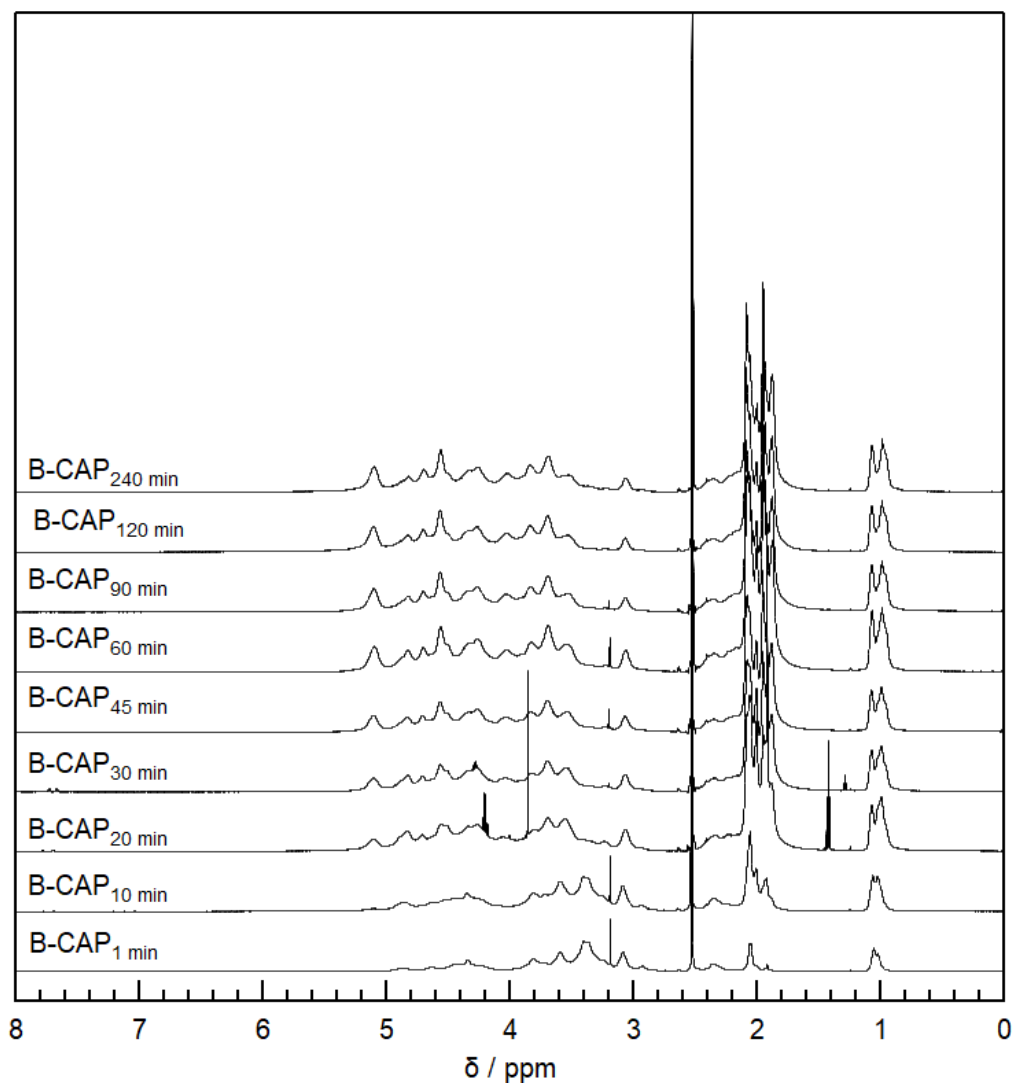

Fig. S8 ^{1}H NMR spectra of B-CAP$_{1-240\ \text{min}}$ synthesized in batch from 5 wt.% cellulose solutions, measured in DMSO-d_6

DSs of Ac and Pr Groups and Isolated Yields of B-CAPs Synthesized in Batch

Table S3 Average DSs of Ac and Pr groups and average isolated yields of B-CAPs (n = 3) synthesized in batch from 5 wt.% cellulose in EmimOAc/DMSO (1:3, g/g)

Collection time of B-CAP	DS			Isolated yield [a] / %
	Ac	Pr	Total	
1 min	0.40 ± 0.15	0.33 ± 0.06	0.73 ± 0.21	83 ± 2
10 min	1.62 ± 0.19	0.48 ± 0.02	2.11 ± 0.21	53 ± 2
20 min	1.83 ± 0.08	0.46 ± 0.01	2.29 ± 0.09	73 ± 5
30 min	1.92 ± 0.13	0.47 ± 0.02	2.40 ± 0.15	73 ± 6
45 min	2.11 ± 0.06	0.48 ± 0.01	2.59 ± 0.07	75 ± 1
60 min	2.08 ± 0.02	0.47 ± 0.02	2.54 ± 0.04	76 ± 1
90 min	2.10 ± 0.01	0.49 ± 0.01	2.59 ± 0.02	75 ± 4
120 min	2.14 ± 0.03	0.47 ± 0.00	2.61 ± 0.03	76 ± 3
240 min	2.09 ± 0.03	0.46 ± 0.01	2.56 ± 0.04	75 ± 2

[a] Isolated yield (%) = the actual yield / theoretical yield of B-CAPs. The theoretical yield is based on the measured DSs.

Molar Mass Distribution of CAPs Synthesized via Continuous REX and Batch Processes

The molar mass of CAPs was determined by a size exclusion chromatography (SEC, Prominence UFLC system, Shimadzu Co., Tokyo, Japan) based on polystyrene standards. The SEC measurements were performed at 40 °C using TSK gel α-M (Tosoh Co., Tokyo, Japan), and 0.01 mol L^{-1} lithium bromide (LiBr) in dimethylformamide (DMF) was used as an eluent at a flow rate of 0.5 mL min^{-1}.
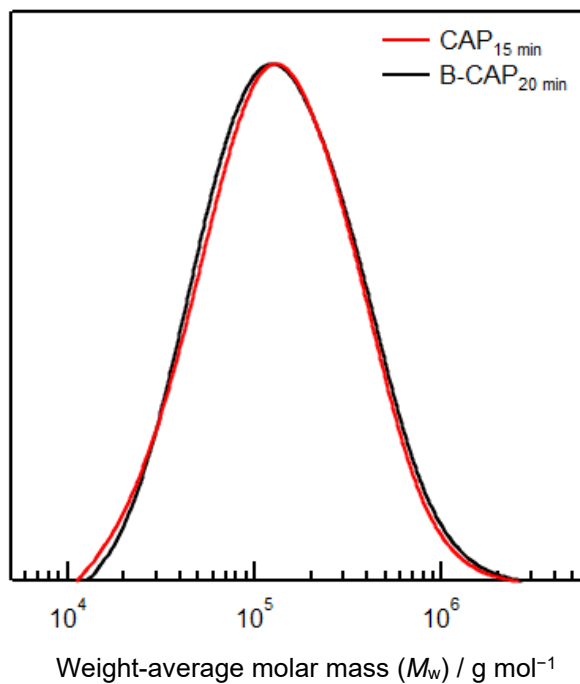

Fig. S9 Molar mass distribution of $CAP_{15\ min}$ and B-$CAP_{20\ min}$ synthesized via continuous REX and batch processes, respectively

References in Supporting Information

Iwata, T., Azuma, J. I., Okamura, K., Muramoto, M. & Chun, B. Preparation and n.m.r. assignments of cellulose mixed esters regioselectively substituted by acetyl and propanoyl groups. *Carbohydr Res* **224**, 277–283 (1992).

Kono, H., Hashimoto, H. & Shimizu, Y. NMR characterization of cellulose acetate: Chemical shift assignments, substituent effects, and chemical shift additivity. *Carbohydr Polym* **118**, 91–100 (2015).