Electronic Supplementary Material (ESI) for Polymer Chemistry.

Alteration of the cellulose nanocrystal surface chemistry for guided formation of polymer brush

Supporting Information

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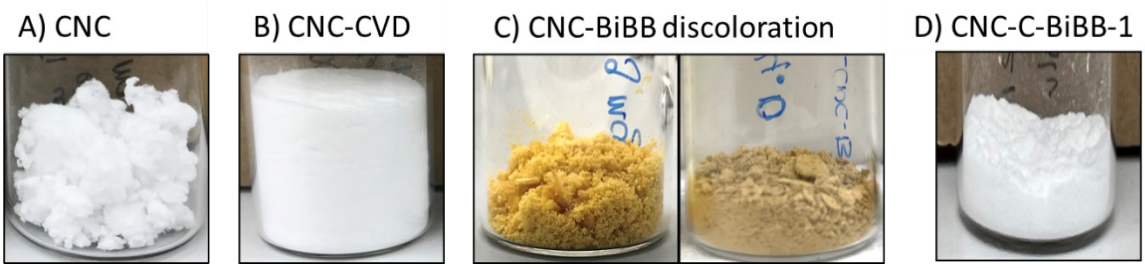

Figure S1, Samples of A) unmodified CNCs, B) CNC-CVD, C) CNC-BiBB discolored, and D) CNC-C-BiBB-1 after freeze-drying.

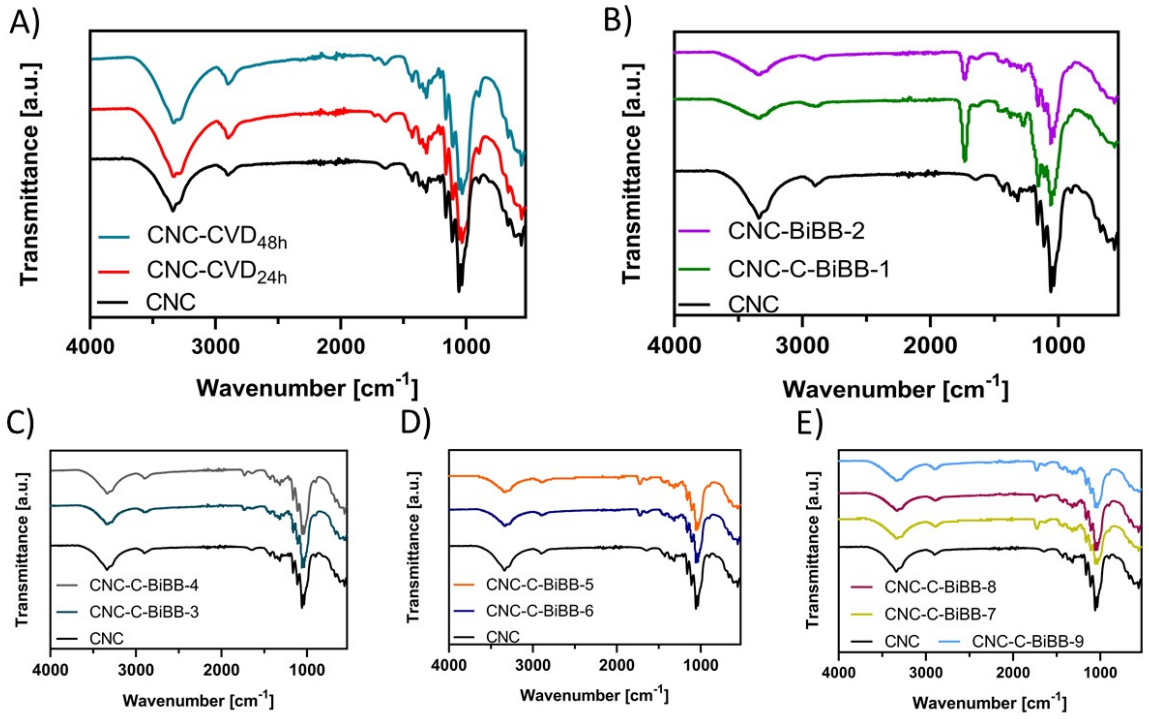

Figure S2, FT-IR spectra of CNC (Black) and ATRP initiator modified samples A) CNC-CVD 24 and 48 h. B) CNC-C-BiBB-1 and CNC-BiBB-2. C) CNC-C-BiBB-3 and -4. D) CNC-C-BiBB-5 and -6. E) CNC-C-BiBB-7, -8, and 9.

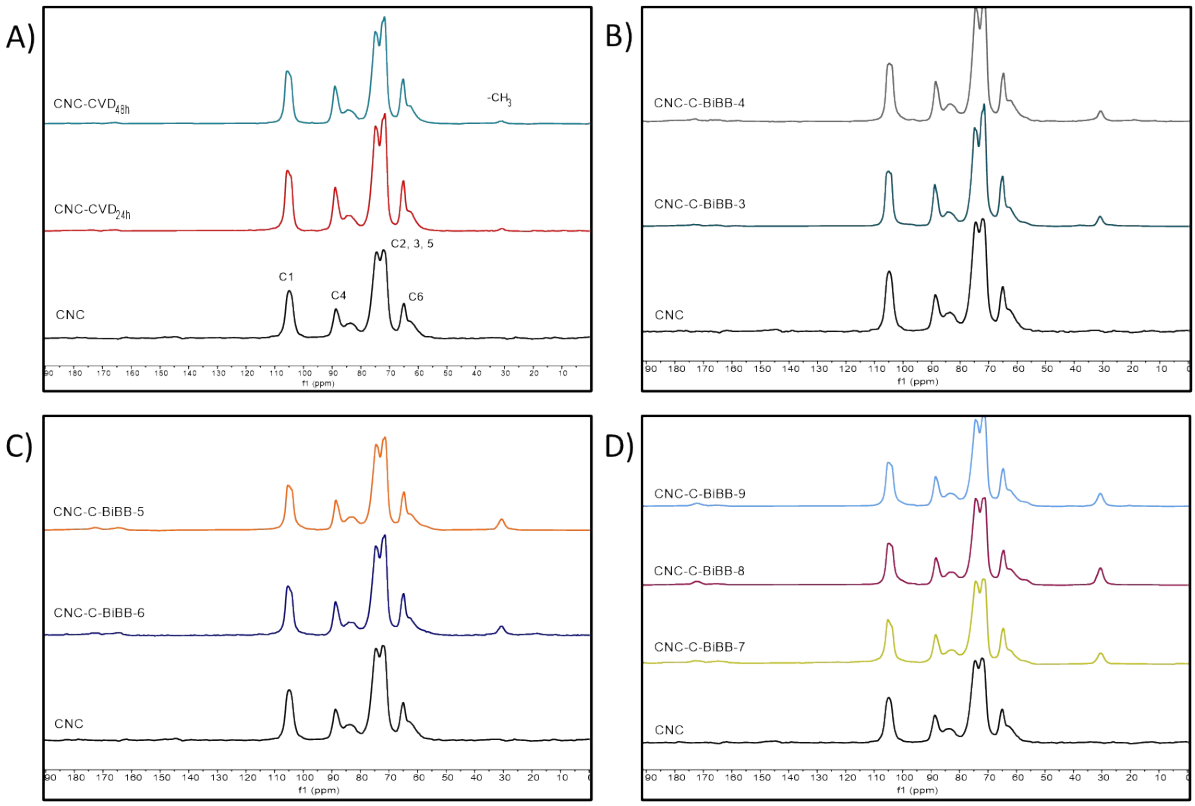

Figure S3, 13C NMR of CNC (Black) and ATRP initiator modified samples A) CNC-CVD 24 and 48 h. B) CNC-C-BiBB-3 and -4. C) CNC-C-BiBB-5 and -6. D) CNC-C-BiBB-7, -8, and 9.

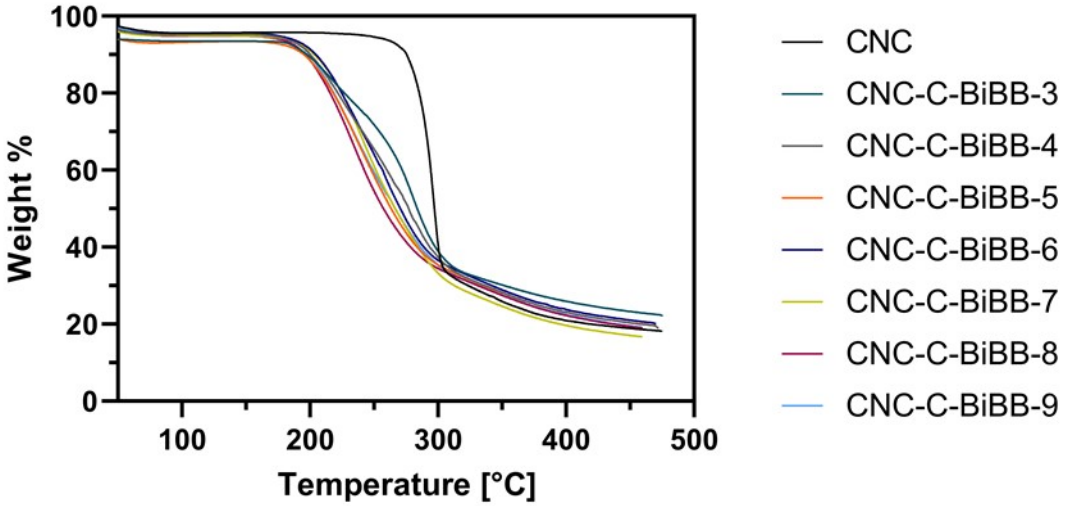

Figure S4, Thermogravimetric analysis for unmodified CNC (Black) and ATRP initiator-modified samples CNC-C-BiBB-3 to 9. Inset represents the samples decomposition area for all samples represented.

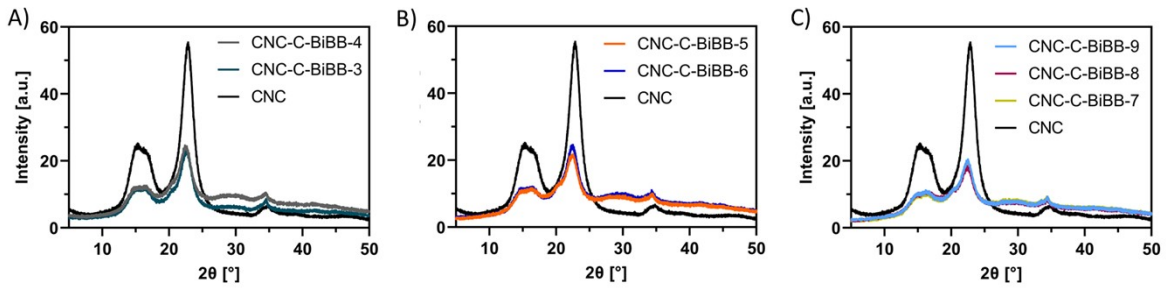

Figure S5, XRD profiles of unmodified CNC (Black) and ATRP initiator modified samples A) CNC-C-BiBB-3 and -4. B) CNC-C-BiBB-5 and -6. C) CNC-C-BiBB-7, -8, and 9. Depending on the treatment conditions, the modified CNC particles exhibit peaks consistent with cellulose I morphology.

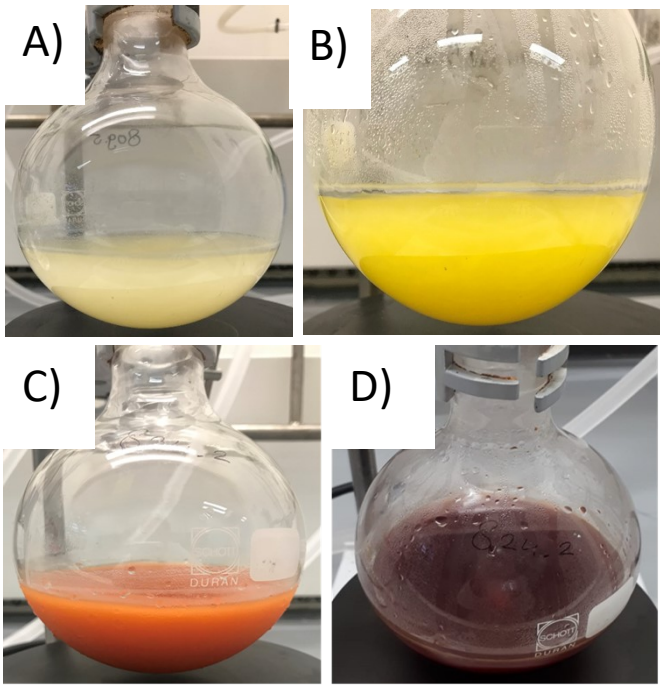

Figure S6, The discoloration reaction mixture of CNC-CVD, BiBB, and pyridine in DMF in which the amount of pyridine was changed. CNC-C-BiBB-6 A) start of the reaction, B) after 48 hours. CNC-C-BiBB-5 C) start of the reaction, D) after 48 hours.

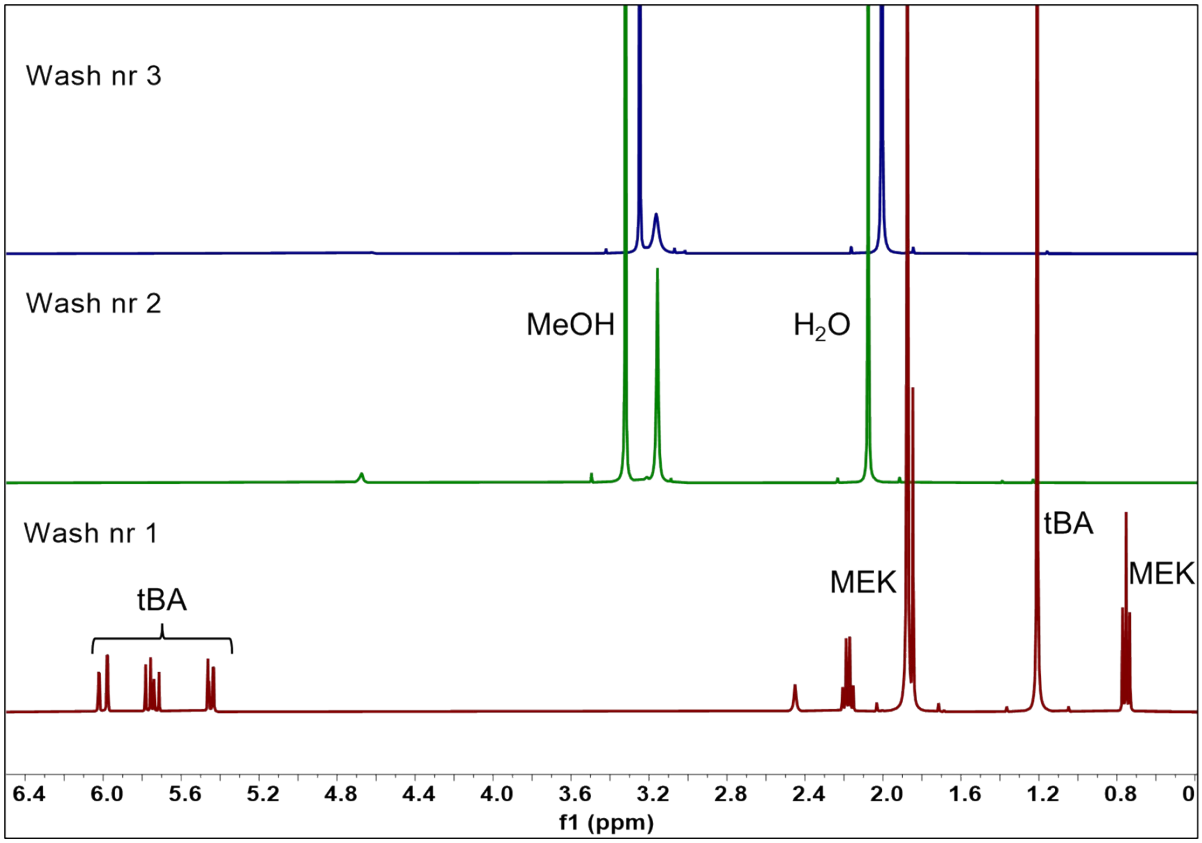

Figure S7, 1H NMR spectra of the washed layers in CDCl3 for SI-ATRP of tBA on CNC-C-BiBB-5 (CNC-PtBA1).

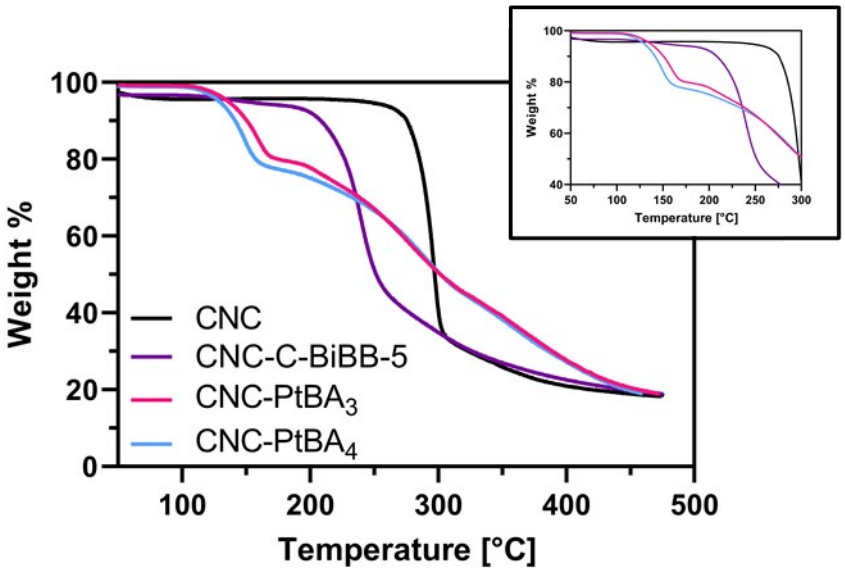

Figure S8, Thermogravimetric analysis for unmodified CNC (Black), CNC-C-BiBB-5 (Green), CNC-PtBA3 (Pink) and CNC-PtBA4 (Blue). Inset represents the samples decomposition area for all samples represented.

Table S1: Thermogravimetric analysis of decomposition temperatures

Sample	**Reaction conditions**			**Results**	
	DS	**Eq tBA**	**Time**	**T_{onset} [℃]**	**T_{max} [℃]**
CNC				260	296
CNC-C-BiBB-3				202	220
CNC-PtBA$_1$	7.0%	1000	15 h	182	200
CNC-PtBA$_2$	10%	500	6 h	176	188
CNC-PtBA$_3$	7.5%	1000	4 h	137	183
CNC-PtBA$_4$	10 %	250	2 h	129	149