Supporting Information

Ethyl Cellulose-*block*-Poly(benzyl glutamate) Block Copolymer Compatibilizers for Ethyl Cellulose/Poly(ethylene terephthalate) Blends

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Materials and Methods

Materials

All reagents and solvents were obtained from commercial vendors and used as received unless otherwise stated. Potassium ethyl xanthate was purchased from Thermo-Fisher. Ethyl cellulose (ECel) (48.0 - 49.5 % wt./wt. ethoxyl basis) was purchased from Sigma Aldrich, and polyethylene terephthalate (PET) was supplied by Eastman Chemical Company and vacuum dried at 100 °C before use. Finally, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was purchased from Sigma Aldrich.

^{1}H NMR and ^{13}C NMR Spectroscopy

Most spectra were recorded at room temperature on a Bruker Avance NMR spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C spectra. ^{1}H NMR and ^{13}C NMR spectra for ECel and its derivatives were recorded at room temperature using a Bruker Avance 500 NMR spectrometer (500 MHz and 125 MHz, respectively). DMSO-d_6 and $CDCl_3$ were used as NMR solvents and chemical shifts are reported in ppm relative to internal solvent resonances.

Size Exclusion Chromatography with Multi-Angle Light Scattering (SEC-MALS)

Size exclusion chromatography with multi-angle light scattering (SEC-MALS) was performed on two different systems: 1) In some cases, SEC-MALS was performed in a mobile phase of tetrahydrofuran (THF) at 1 mL min^{-1} at 30 ^{o}C on two Agilent PLgel 10 um MIXED-B columns connected in series with a Wyatt Dawn Heleos 2 light scattering detector and a Wyatt Optilab Rex refractive index detector. 2) In other cases, SEC-MALS was performed in a mobile phase consisting of *N,N*-dimethylacetamide (DMAc) with 50 mM LiCl at a rate of 1.0 mL/min at 40 °C on two Agilent Technologies PL gel 10 μm MIXED-B LS 300 x 7.5 mm columns connected in series with a Wyatt Technologies TRIOS II light scattering detector and an Optilab T-REX differential refractive index (dRI) detector.

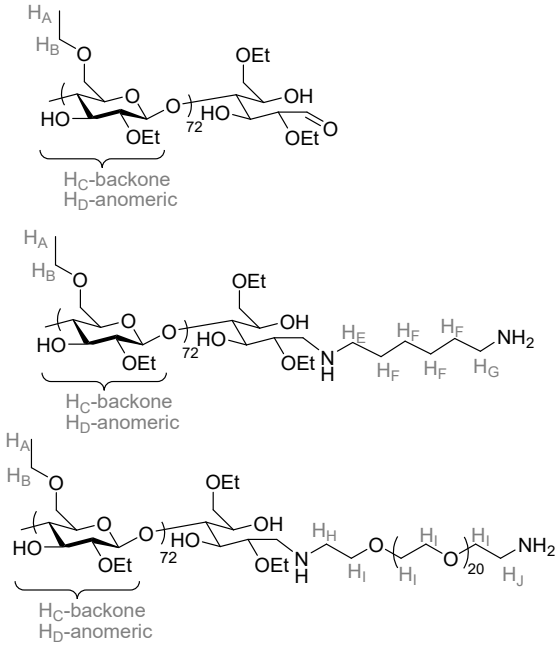
In order to estimate the d*n*/d*c* values for each of the BCPs, we first measured the d*n*/d*c* ECel in both THF and DMAc/LiCl using an offline method for each of the constituent blocks [ECel and poly(BG)]. In brief, we prepared samples of as -received ECel at 1, 2, 4, 5, and 10 mg/mL for THF and 2, 4, 6, 8, and 10 mg/mL in DMAc/LiCl and recorded the dRI signal for each. The slope of the plot of dRI signal intensity versus concentration afforded d*n*/d*c* values of 0.060 mL/g for ECel in THF and 0.039 mL/g for ECel in DMAc/LiCl. The d*n*/d*c* for poly(BG) in DMAc/LiCl was measured in our previous work and was found to be 0.109 mL/g.[1] The d*n*/d*c* for poly(BG) in THF was previously measured and reported in the literature to be 0.150 mL/g.[2] To estimate the d*n*/d*c* of each BCP sample, we first used ^{1}H NMR spectroscopy to estimate the M_n of poly(BG) by determining the poly(BG)/ECel ratio and using the ECel M_n = 17,200 measured on our SEC-MALS system in THF. Based upon this ratio, we calculated weight percentages of ECel and poly(BG), then estimated the copolymer d*n*/d*c* values using these weight percentages and the d*n*/d*c* values for each homopolymer in the respective solvent according to the equation discussed in a published report.[3]

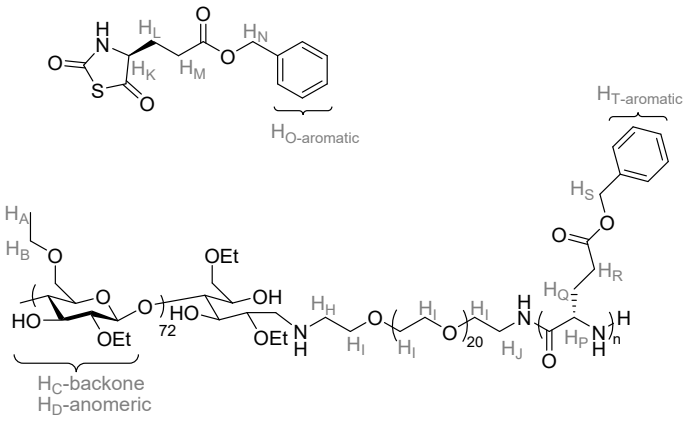
DOSY NMR Spectroscopy

DOSY experiments were performed at 21.25 °C on a Bruker Avance III 400 MHz High Power Diffusion NMR system with a Diff50 probe. Diffusion experiments were performed using Topspin 3.7.0 using the diff-5.8 diffusion module. To compensate for convection, data was acquired using a double stimulated echo sequence (diffDste) with a gradient pulse length (δ) of 1ms, a diffusion delay (Δ) of 30ms, an eddy current delay (T_e) of 20 ms, and a gradient recovery delay (t_g) of 1us with a 300 g/cm maximum gradient strength. All experiments were recorded using 8 scans and 16 linear gradient steps. The acquisition time was 0.6s with a relaxation delay of 3s using 7424 data points in the F 2 dimension covering 6188 Hz. DOSY plots were created by the Bruker Dynamics' Center software package.

Synthesis

The chemical structures below show the labeling scheme for the ^{1}H NMR spectra discussed below.

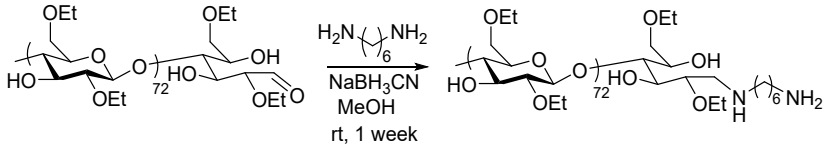




Synthesis of BG-NTA

Synthesis of BG-NTA was performed using previously reported methods and the spectra matched reported values.[1]

Synthesis of ECel-NH_2 (ECel-NH_2) macroinitiator.



Scheme S1: Synthesis of ECel-NH_2.

Synthesis of ECel-NH_2 was done similarly to a previously published procedure.[1] ECel (5.0 g, 0.3 mmol, 1 equiv) was dissolved in 100 mL MeOH at rt. Next, hexamethylenediamine (0.99 g, 8.8 mmol, 30 equiv) and sodium cyanoborohydride (0.93 g, 14.7 mmol, 50 equiv) were added while stirring. The reaction mixture was allowed to stir at rt for 7 d and subsequently, the solvent was removed under vacuum. The crude product was then dialyzed against acetone (3 x 1000 mL, MWCO 6-8 kg/mol), concentrated, and dried to afford a light brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.17 (H_A, m, 573 H, CH_3), 1.83 (H_E, m, 2 H, CH_2), 2.14 (H_G, m, 2 H, CH_2), 2.85-4.77 (m, 836 H, CH and CH_2).

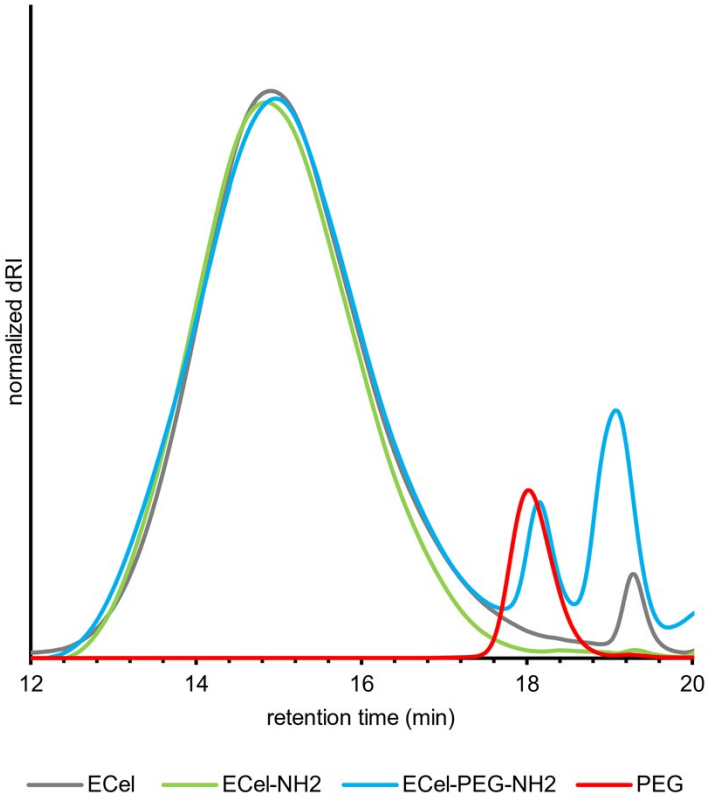


Figure S1: SEC-MALS traces of ECel, ECel-NH_2, ECel-PEG-NH_2, and PEG in THF. M_n was estimated using d*n*/d*c* of 0.060 mL/g for ECel derivatives and 0.067 mL/g for PEG. M_n of ECel, ECel-NH_2, ECel-PEG-NH_2, and PEG were estimated to be 17.2 kg/mol, 20.3 kg/mol, 18.2 kg/mol, 2.9 kg/mol respectively ($Đ$= 1.9, 1.7, 1.7, and 6.1, respectively). (We suspect column interactions are an issue with the PEG sample, causing inaccurate M_n and M_w measurements.)

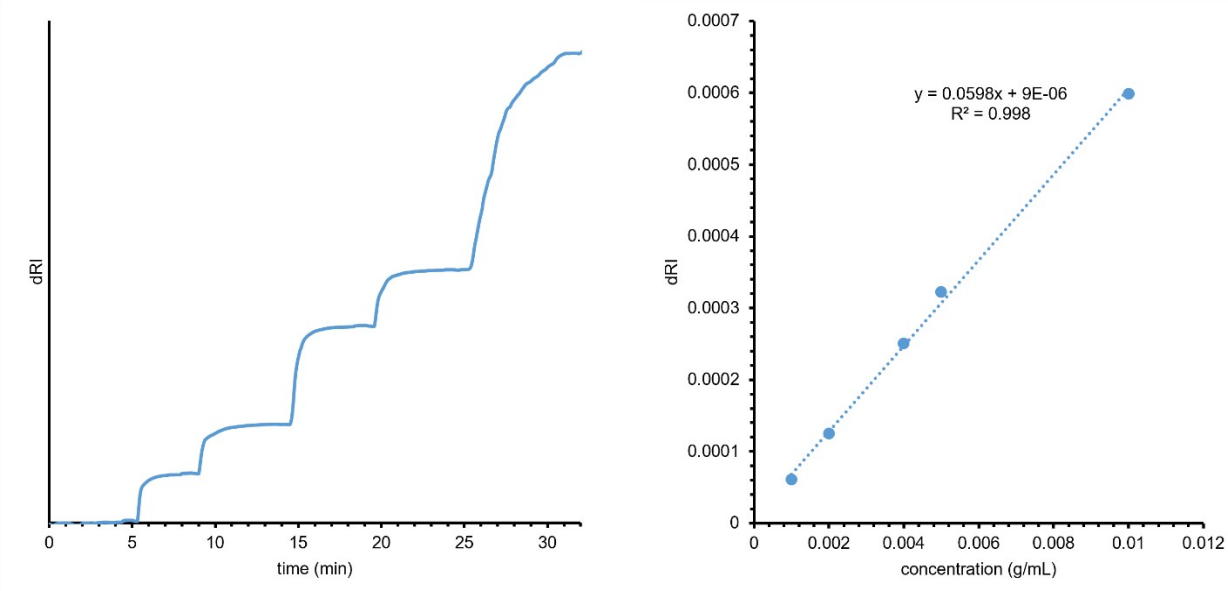


Figure S2: Raw output data from the dRI detector (left) and d*n*/d*c* estimate for as-received ethyl cellulose (right) based on the slope of the graph of the dRI versus concentration (eluent is THF). d*n*/d*c* measured to be 0.060 mL/g.

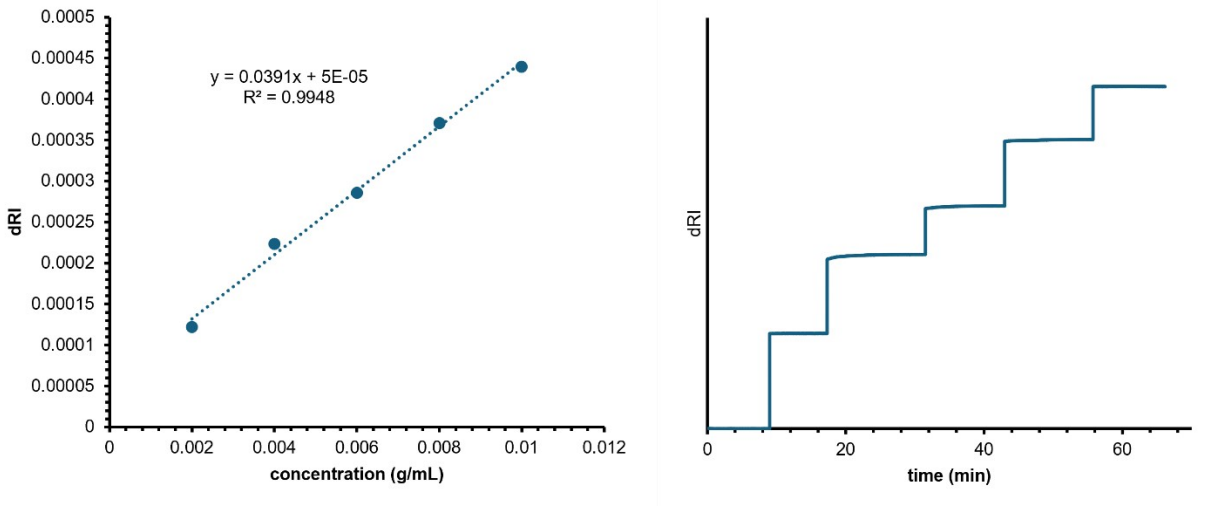


Figure S3: Raw output data from the dRI detector (left) and d*n*/d*c* estimate for as-received ethyl cellulose (right) based on the slope of the graph of the dRI versus concentration (eluent is DMAc/LiCl). d*n*/d*c* measured to be 0.039 mL/g.

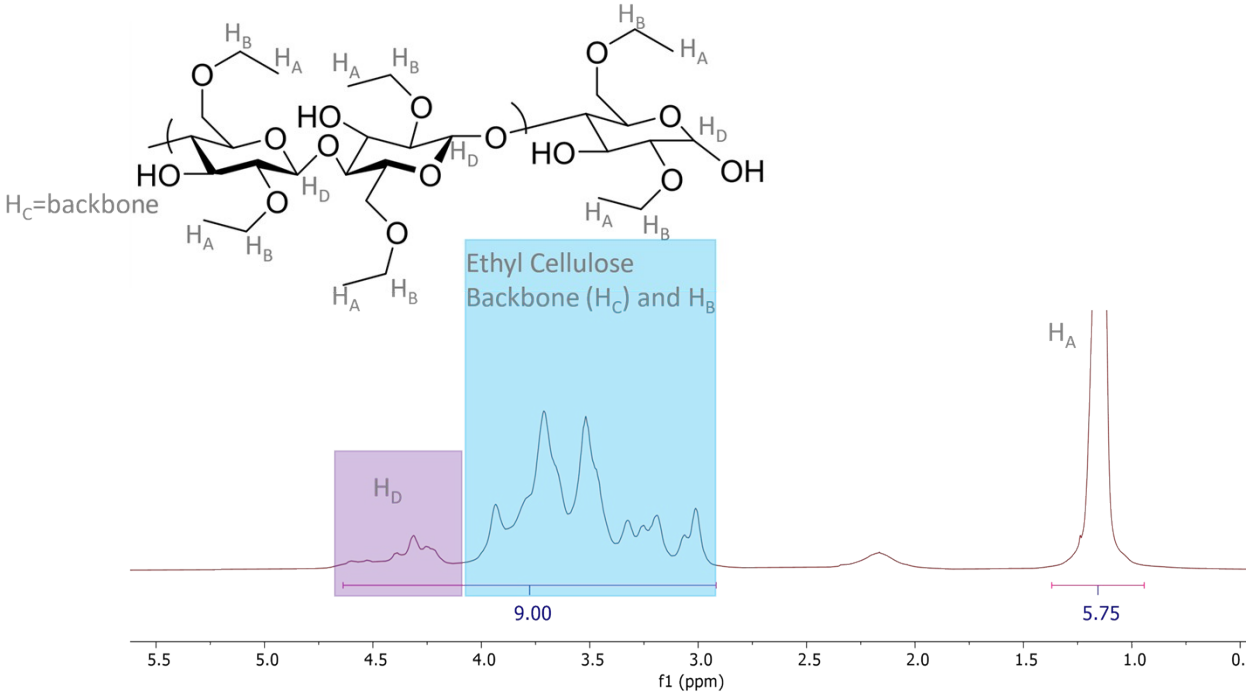


Figure S4: ^{1}H NMR spectrum of ECel in $CDCl_3$. The ethyl groups are placed at specific positions for sake of clarity in drawing; this is not meant to imply regioselectivity. To find DS, H_C, H_B, H_D and backbone were set to 9. DS was found by a ratio of number of ethyl groups (H_A/3) to number of repeat units for that number of ethyl groups [(9-(2/3)*H_A))/7]. DS was found to be 2.6 and the average repeat unit molecular weight for ECel was then calculated to be

235 g/mol. M_n by SEC-MALS in THF was found to be 17,200 g/mol using a d*n*/d*c* value of 0.060, giving DP of ECel to be 72. H_A was then calculated to be 565 protons for one ECel polymer chain (DS 2.6, DP 72). H_A integral (565) was used as a standard for the following ^{1}H NMR spectra.

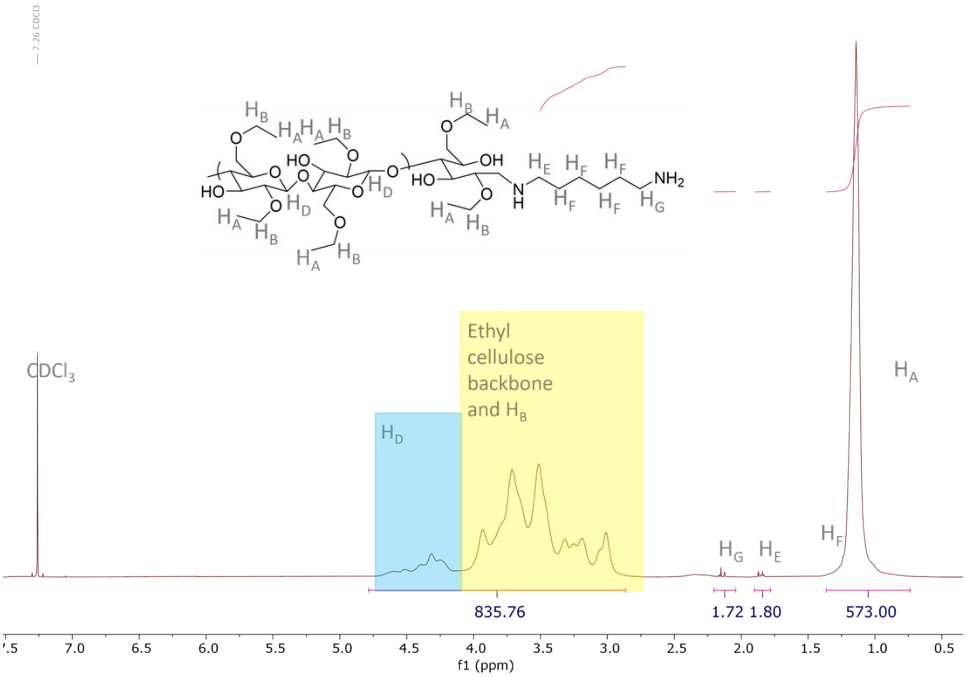
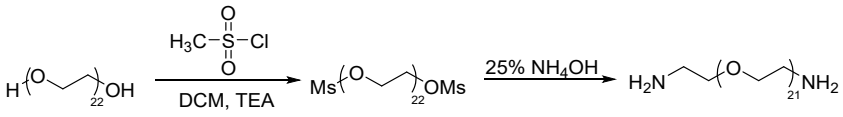


Figure S5: ^{1}H NMR spectrum of ECel-NH_2 in $CDCl_3$. Upon coupling, H_E shifts upfield from H_G. To confirm successful reductive amination and removal of unreacted diamine, the H_A + H_F peak integration was set to 573 (565 for H_A + 8 for H_F). In the case of full functionalization of the end group, H_E and H_G would each integrate to 2.00; the actual integral values indicate 88% functionalization. The H_G:H_E ratio close to 1.00 suggests near-quantitative removal of residual diamine.

Synthesis of H_2N-PEG-NH_2 (PEG diamine) macroinitiator precursor.



Scheme S2: Synthesis of $_2$HN-PEG-NH_2

PEG diamine (H_2N-PEG-NH_2) was synthesized using a similar method to those previously reported.[4] A 250 mL roundbottom flask was charged with HO-PEG-OH (M_n ~1,000 g/mol) (10.0 g, 10 mmol, 1 equiv) and 100 mL toluene, and the solution was azeotropically distilled under nitrogen to remove approximately 30 mL of the solvent. The reaction mixture was then cooled to 0 °C, and 40 mL of anhydrous dichloromethane was added. Triethylamine (4.2 mL, 0.03 mol, 3 equiv) was added dropwise while stirring. Then, methane sulfonyl chloride (2.4 mL, 0.03 mol, 3 equiv) was added dropwise while stirring. The reaction mixture was allowed to warm to rt

overnight, and then the reaction mixture was subsequently filtered to remove the triethylammonium-HCl salt. The supernatant was then precipitated into ether, isolated, and dried under vacuum to afford an off-white solid. The product was directly used in the next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.07 (H_U, s, 6 H, CH_3), 3.62-3.69 (H_I, m, 91 H, CH_2), 3.76 (H_W, m, 4 H, CH_2), 4.38 (H_J, m, 4 H, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$): δ 70.52, 69.19, 68.90, 45.73.

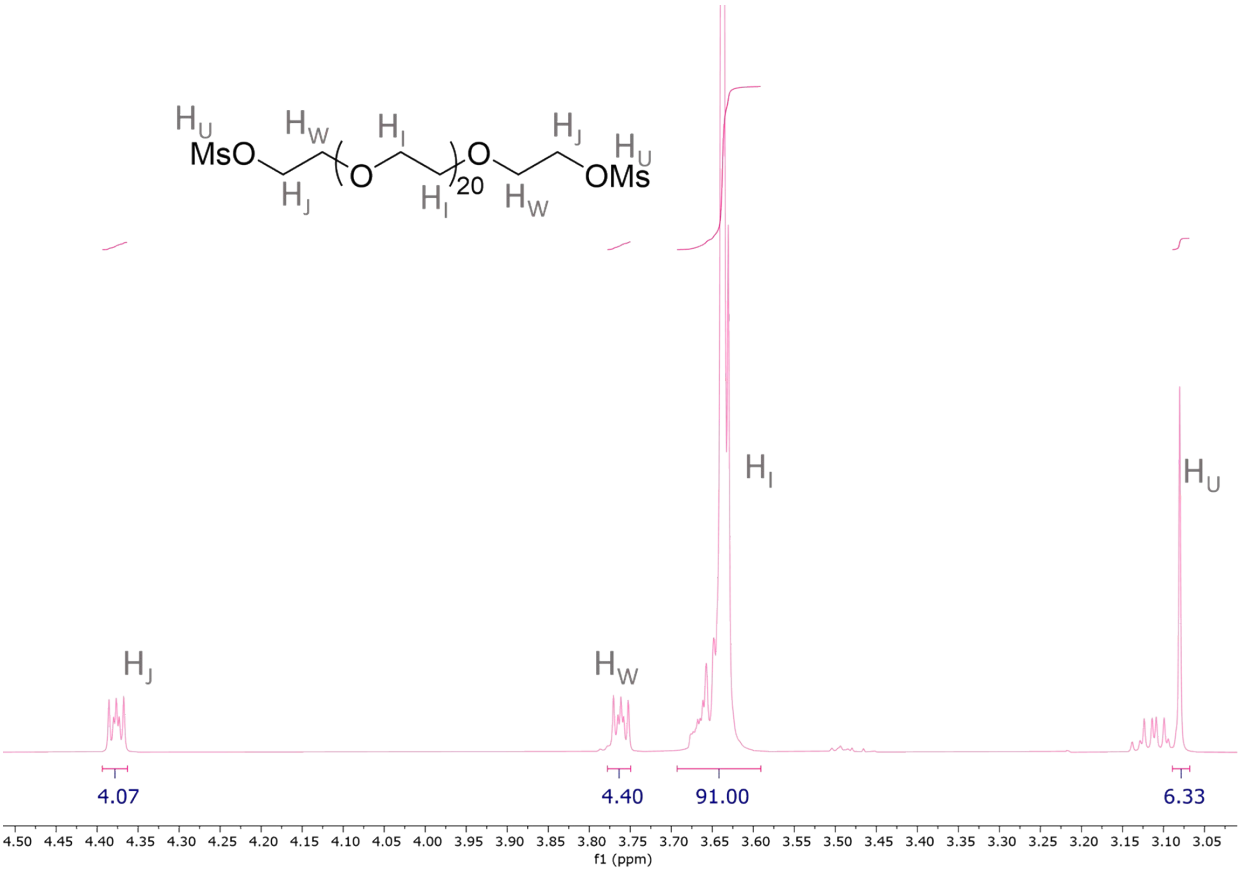


Figure S6: ^{1}H NMR spectrum of MsO-PEG-OMs in $CDCl_3$.

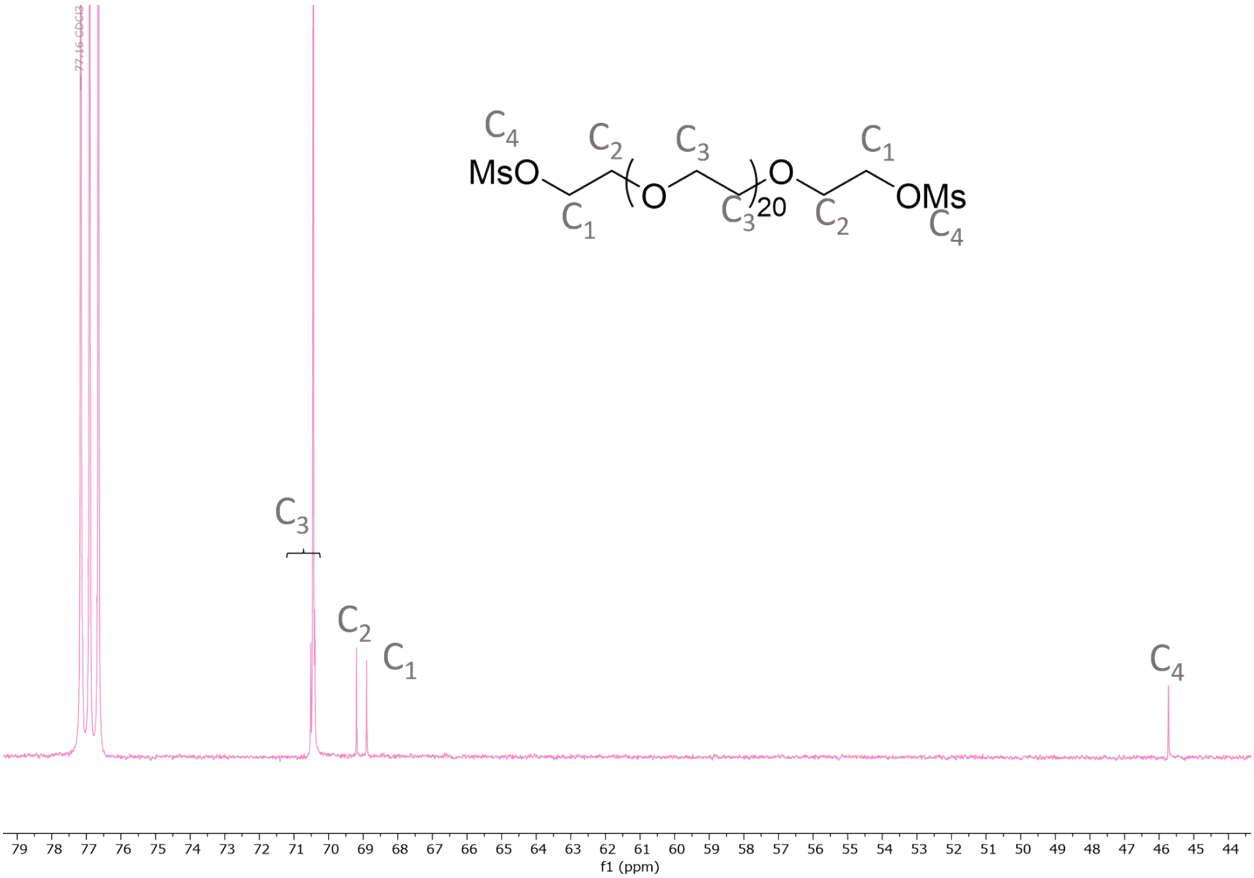


Figure S7: ^{13}C NMR spectrum of MsO-PEG-OMs in $CDCl_3$.

MsO-PEG-OMs was dissolved in 25% NH_4OH solution (300 mL) in a 500 mL roundbottom flask. The reaction mixture was sealed with a septum and stirred at rt for 4 d. After 4 d, the reaction flask was opened, and ammonia was allowed to evaporate for 1 d. NaOH (5 M in water) was added dropwise until the solution had a pH of ~13. The product was then extracted with dichloromethane (3 x 75 mL), washed with brine (1 x 50 mL), dried, and concentrated via rotary evaporation. The crude product was precipitated into ether, isolated, and dried to afford an off-white solid (4.45 g yield, 45%). ^1H NMR (400 MHz, $CDCl_3$): δ 3.65 (H_I, m, 91 H, CH_2), 3.50 (H_W, t, J = 5.2 Hz, 4 H, CH_2), 2.85 (H_J, t, J = 5.2 Hz, 4 H, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$): δ 73.35, 70.55, 70.34, 41.75.

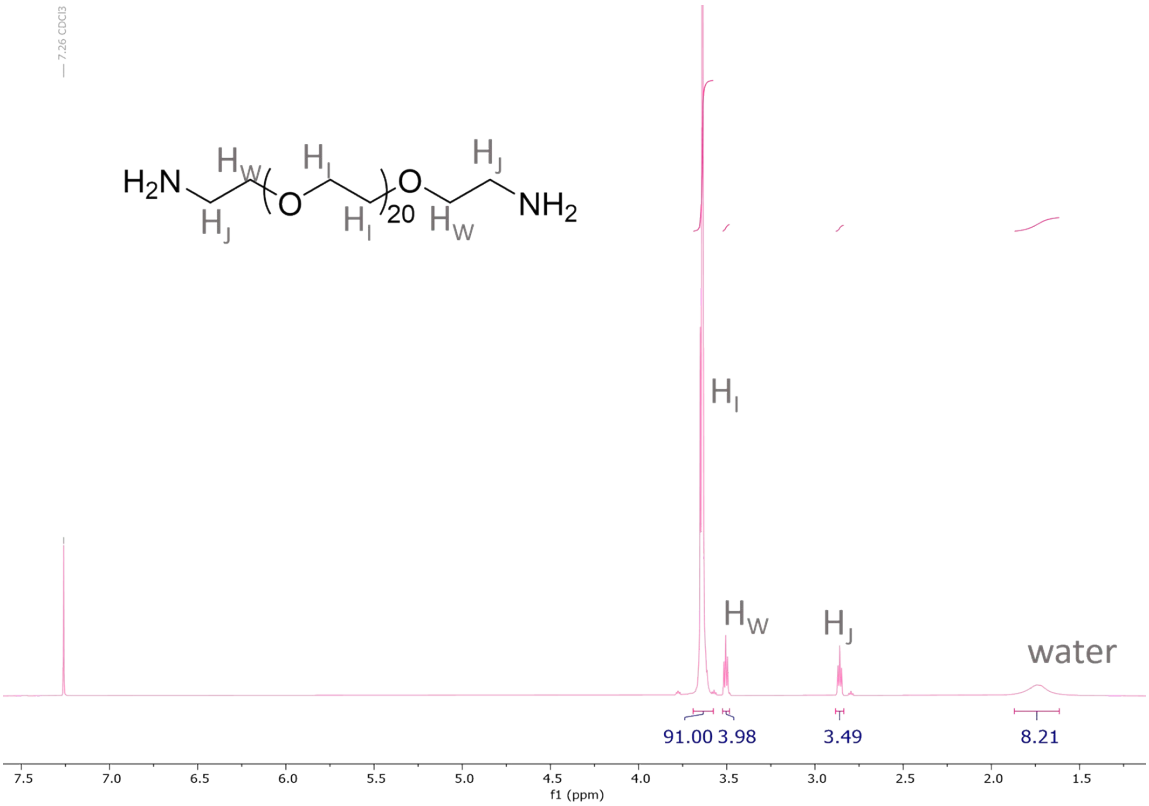
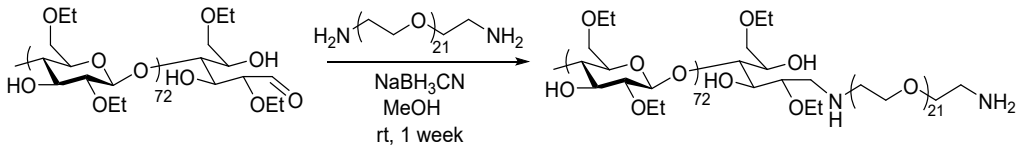


Figure S8: ^{1}H NMR spectrum of $_{2}$HN-PEG-NH_2 in $CDCl_3$.

Figure S9**:** ^{13}C NMR spectrum of H_2N-PEG-NH_2 in $CDCl_3$.

Synthesis of ECel-PEG-NH_2 macroinitiator.



Scheme S3: Synthesis of ECel-PEG-NH_2.

Synthesis of ECel-PEG-NH_2 was done similarly to a previously published procedure.[1] ECel (1.6 g, 0.09 mmol, 1 equiv) was dissolved in 50 mL MeOH at rt in a 250 mL roundbottom flask. Then, H_2N-PEG-NH_2 (0.97 g, 0.9 mmol, 10 equiv) and sodium cyanoborohydride (0.306 g, 4.5 mmol, 50 equiv) were added while stirring. The reaction mixture was allowed to stir at rt for 7 d, and subsequently the solvent was removed under vacuum. The crude product was then dialyzed against acetone (3 x 1000 mL, MWCO 6-8 kg/mol), concentrated via rotary evaporation, and dried. The product was isolated as a brown solid (yield 0.526 g, 31%). The low yield was likely due to acetone affecting the pore size in the dialysis tubing, allowing some of the product to escape. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.17 (H_A, m, 565 H, CH_3), 2.82 (H_H, m, 2 H, CH_2), 2.88 (H_J, m, 2 H, CH_2), 2.95-4.11 ($H_{C,B,I}$, m, 951 H, CH and CH_2), 4.14-4.76 (H_D, m, 82, CH).

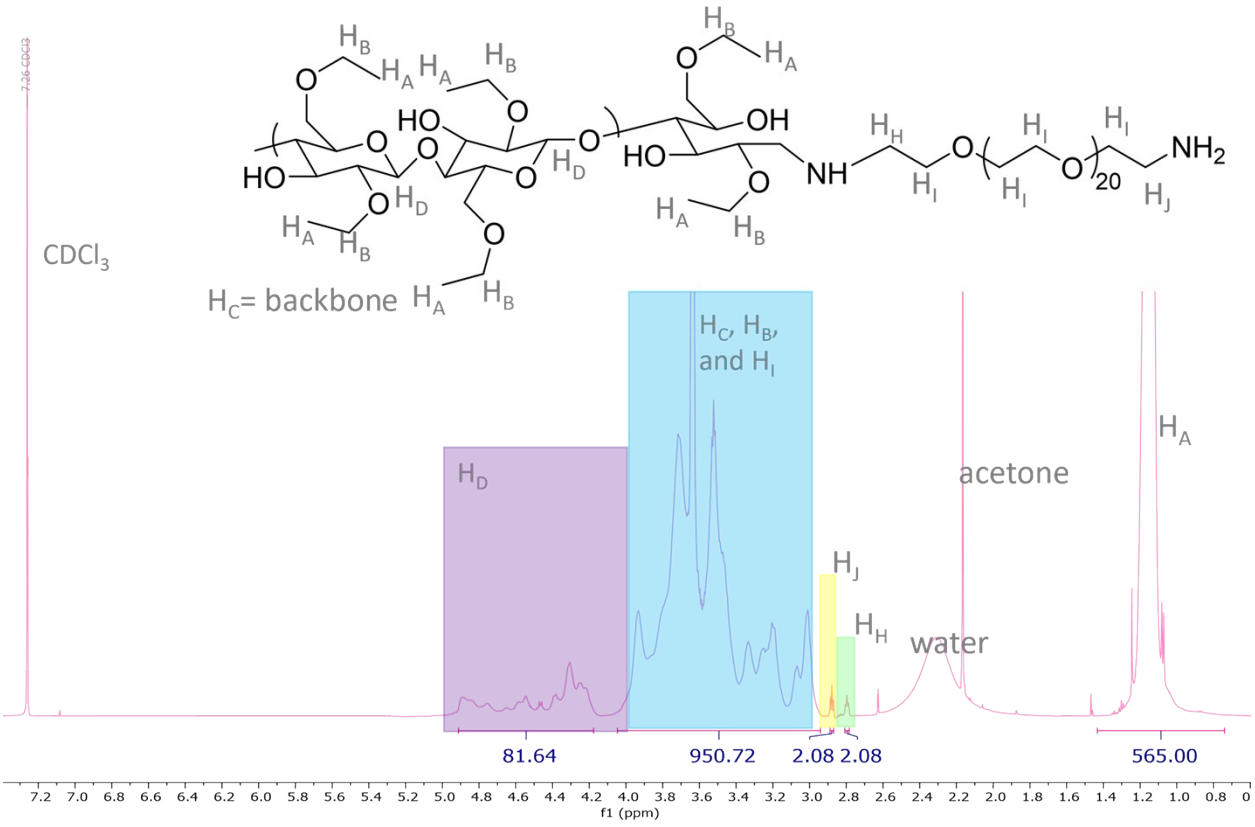
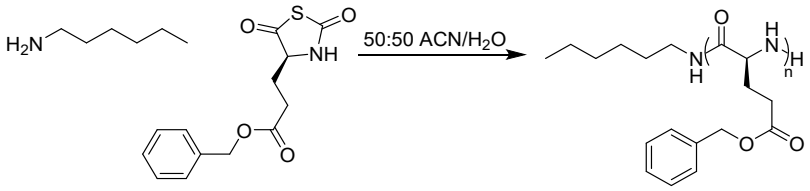


Figure S10: ^{1}H NMR spectrum of ECel-PEG-NH_2 in $CDCl_3$. Upon coupling, H_H shifts upfield from H_J. To confirm successful reductive amination and removal of unreacted diamine, the ratios of H_H:H_A and H_J:H_H were used, respectively. H_H:H_A allows us to calculate functionality since H_H

should be 2 if fully functionalized. H_H is slightly higher than 2 due to trace not fully reaching baseline and overlapping with ECel backbone peaks. H_J:H_H should be 1 if no unreacted diamine remains, and the actual ratio is 1.04, indicating successful removal of unreacted diamine.

Polymerization and Characterization

Polymerization of BG-NTA to synthesize poly(BG) homopolymer in CH_3CN/H_2O.



Scheme S4: Polymerization of BG-NTA to synthesize poly(BG) homopolymer in CH_3CN/H_2O.

Monomer BG-NTA (15 mg, 0.054 mmol, 100 equiv) was dissolved in 4 mL 50:50 CH_3CN/H_2O in a scintillation vial. Subsequently, hexylamine initiator (4.3 µL of 126 mM stock solution in CH_3CN, 0.0005 mmol, 1 equiv) was added while stirring. The reaction mixture was allowed to stir at rt for 24 h. The reaction mixture was subsequently concentrated via rotary evaporation, and the crude product was recovered as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (H_U, m, 0.1 H, CH_3), 1.27 (H_V, m, 0.21 H, CH_2), 1.79-2.79 ($H_{R,Q,M,L}$, m, 4 H, CH_2), 3.73-4.47 ($H_{K,P}$, m, 0.83 H, CH_2), 4.79-5.12 (H_S, m, 1.86 H, CH_2), 5.12-5.19 (H_N, 0.14 H, CH_2), 7.25 ($H_{T,O}$ and $CDCl_3$, m, 5.51 H, CH aromatic).

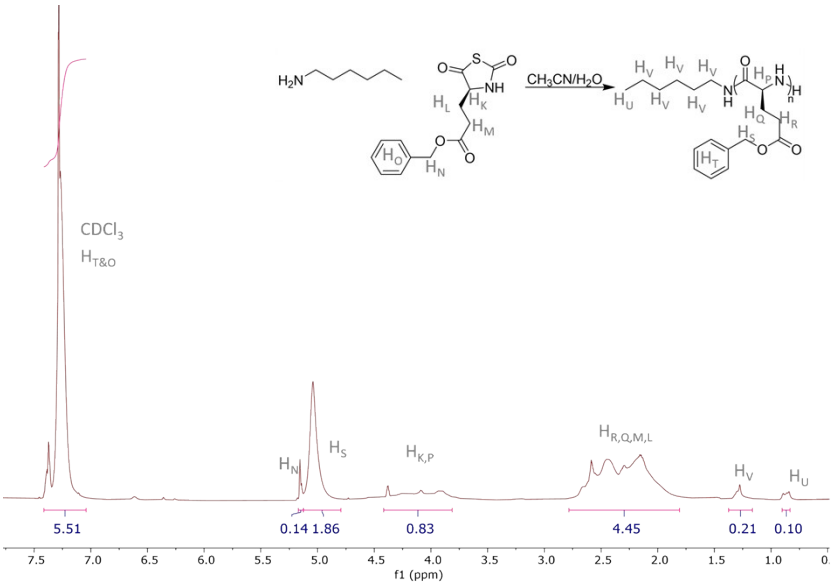
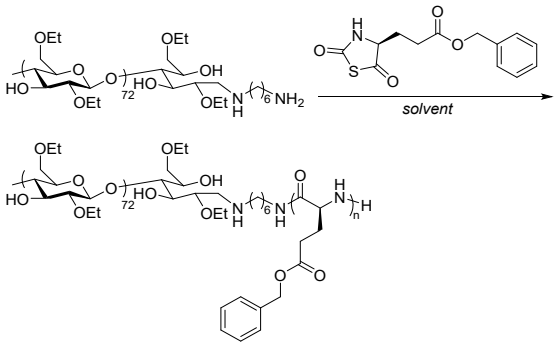


Figure S11: ^{1}H NMR spectrum of crude poly(BG) in $CDCl_3$. ^{1}H NMR spectrum shows conversion of 93% using conversion from H_N to H_S.

Representative polymerization of BG-NTA to synthesize ECel-*block*-poly(BG) block copolymer in various solvents.



Scheme S5: Representative polymerization of BG-NTA to synthesize ECel-*block*-poly(BG) block copolymer in various solvents.

Macroinitiator Ecel-NH_2 (10 mg, 0.00059 mmol, 1 equiv) was dissolved in 50:50 CH_3CN/H_2O (2 mL) in scintillation vial. Subsequently, monomer BG-NTA (15 mg, 0.059 mmol, 100 equiv) was added to the reaction mixture, and it was allowed to stir at rt for 24 h. The reaction mixture was concentrated under vacuum, and a ^1H NMR spectrum was taken in $CDCl_3$. Monomer % conversion was measured using the method described in **Fig. S14**. Polymerizations were done using [M]:[I] of 90:1 except for the polymerizations including acetone or CH_3CN, which had a ratio of 100:1.

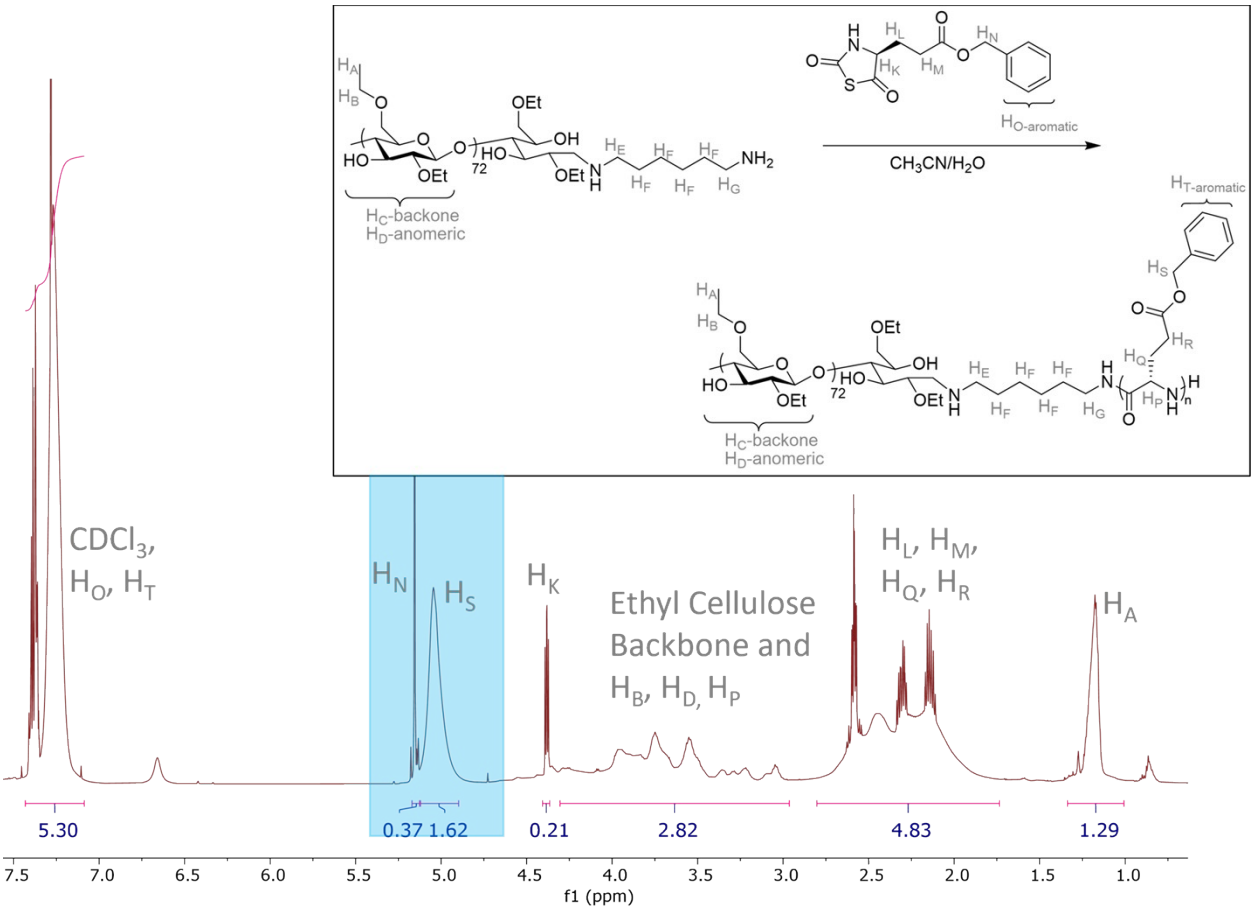
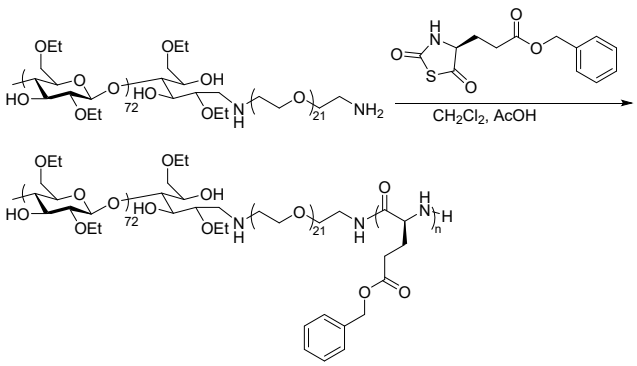


Figure S12: ^{1}H NMR spectrum ($CDCl_3$) of ECel-*block*-poly(BG), synthesized in CH_3CN/H_2O. ^{1}H NMR spectrum shows conversion of 81% using conversion from H_N to H_S.

Representative polymerization of BG-NTA to synthesize ECel-PEG-*block*-poly(BG) block copolymer in CH_2Cl_2.



Scheme S6: Polymerization of BG-NTA to synthesize ECel-PEG-*block*-poly(BG) block copolymer in CH_2Cl_2.

Macroinitiator ECel-PEG-NH_2 (600 mg, 0.033 mmol, 1 equiv) was dissolved in CH_2Cl_2 (130 mL) in a 500 mL roundbottom flask. Subsequently, glacial AcOH (19 µL, 0.00033 mol, 10

equiv) and monomer BG-NTA (700 mg, 0.0025 mol, 75 equiv) were added with stirring. The reaction mixture was allowed to stir for 24 h at rt, at which point another 5 equiv of AcOH (10 µL, 0.00017 mol, 5 equiv) were added. The reaction mixture was allowed to stir for another 24 h at rt. The solvent was removed by rotary evaporation, and a crude ^{1}H NMR spectrum in $CDCl_3$ was taken, which showed 95% monomer conversion. The crude product was dialyzed against acetone (3 x 1000 mL, MWCO 6-8 kg/mol) to remove unreacted monomer, and the contents of the dialysis tube were concentrated by rotary evaporation and dried under vacuum to afford the final product as a brown solid (yield 950 mg, 83%). M_n NMR = 37 kg/mol based on macroinitiator:poly(BG) ratio using H_S to calculate DP of poly(BG).

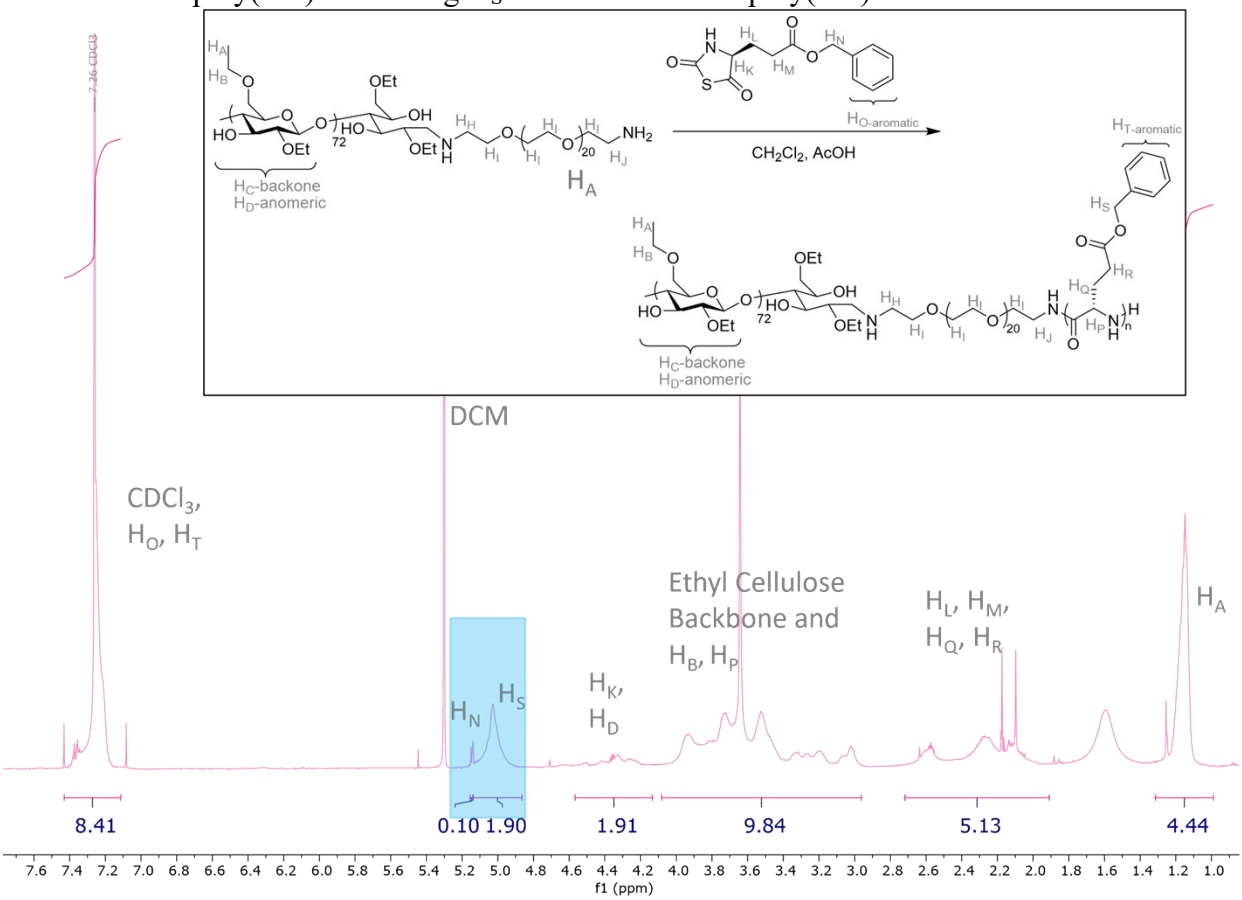


Figure S13: ^{1}H NMR spectrum of crude ECel-PEG-*block*-poly(BG) in $CDCl_3$. ^{1}H NMR spectrum shows conversion of 95% using conversion from H_N to H_S.

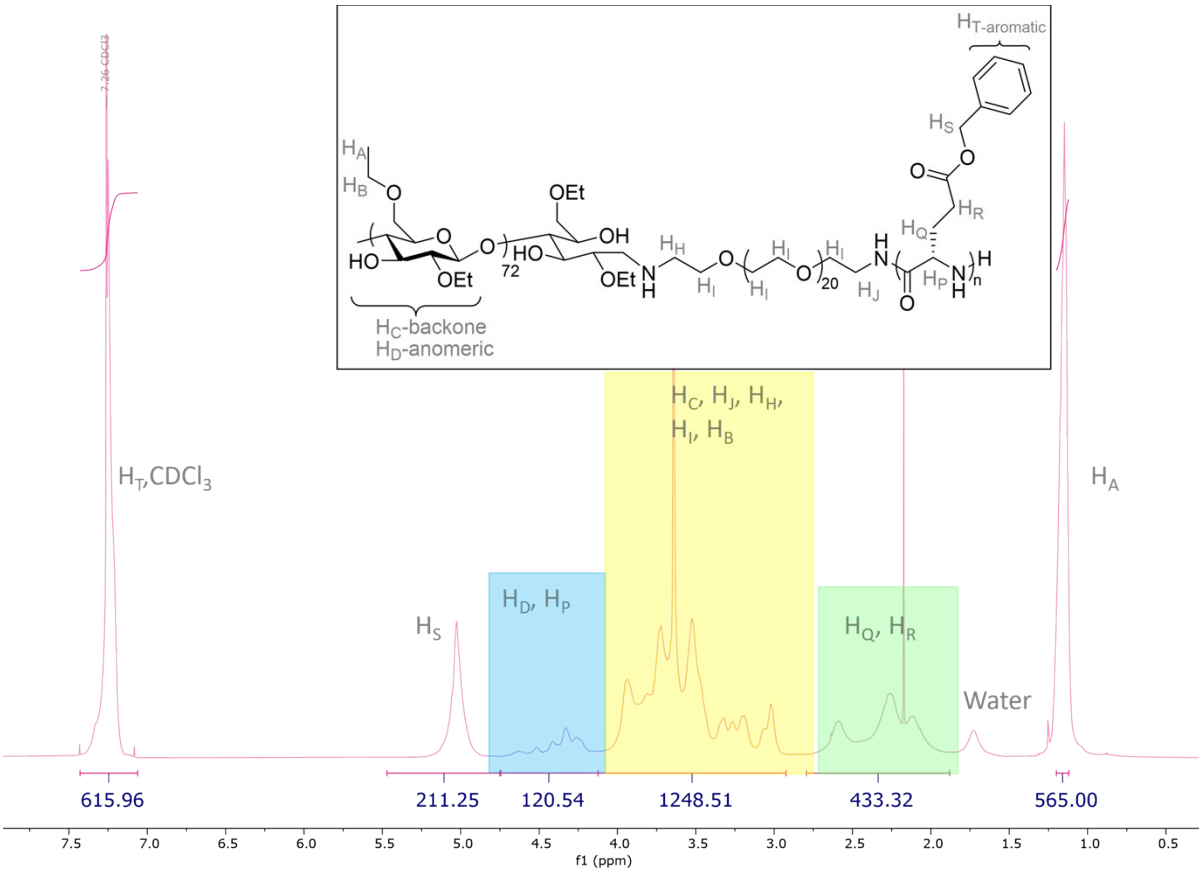
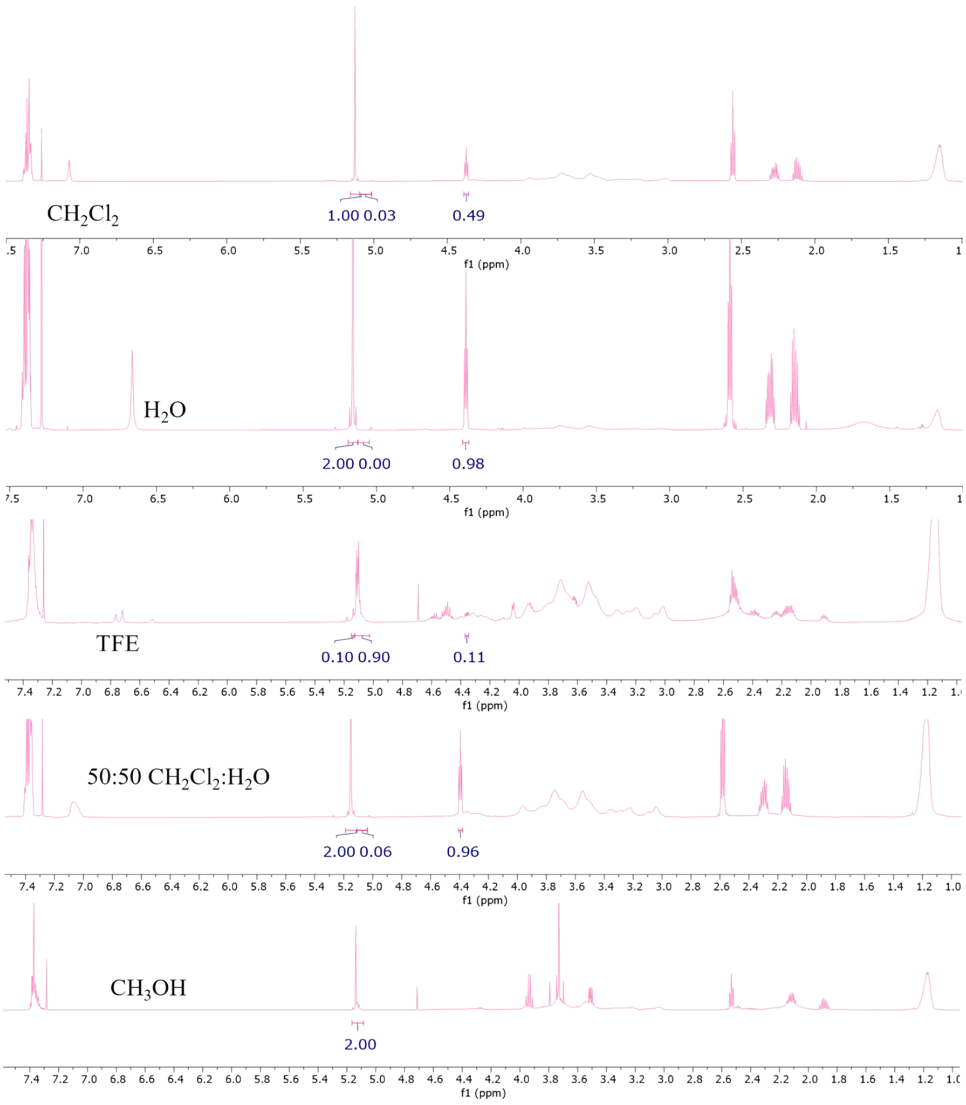


Figure S14: ^{1}H NMR spectrum of dialyzed ECel-PEG-*block*-poly(BG) in $CDCl_3$. NMR M_n was estimated using H_A set to 565 and measuring H_S:H_A to afford the polypeptide/polysaccharide molar ratio. Conversion to a weight ratio afforded NMR M_n = 40.4 kg/mol (23.4 kg/mol poly(BG) block).


CH2Cl2
1.00 0.03
0.49
f1 (ppm)
H2O
2.00 0.00
0.98
f1 (ppm)
TFE
0.10 0.90
0.11
f1 (ppm)
50:50 CH2Cl2:H2O
2.00 0.06
0.96
f1 (ppm)
CH3OH
2.00
f1 (ppm)

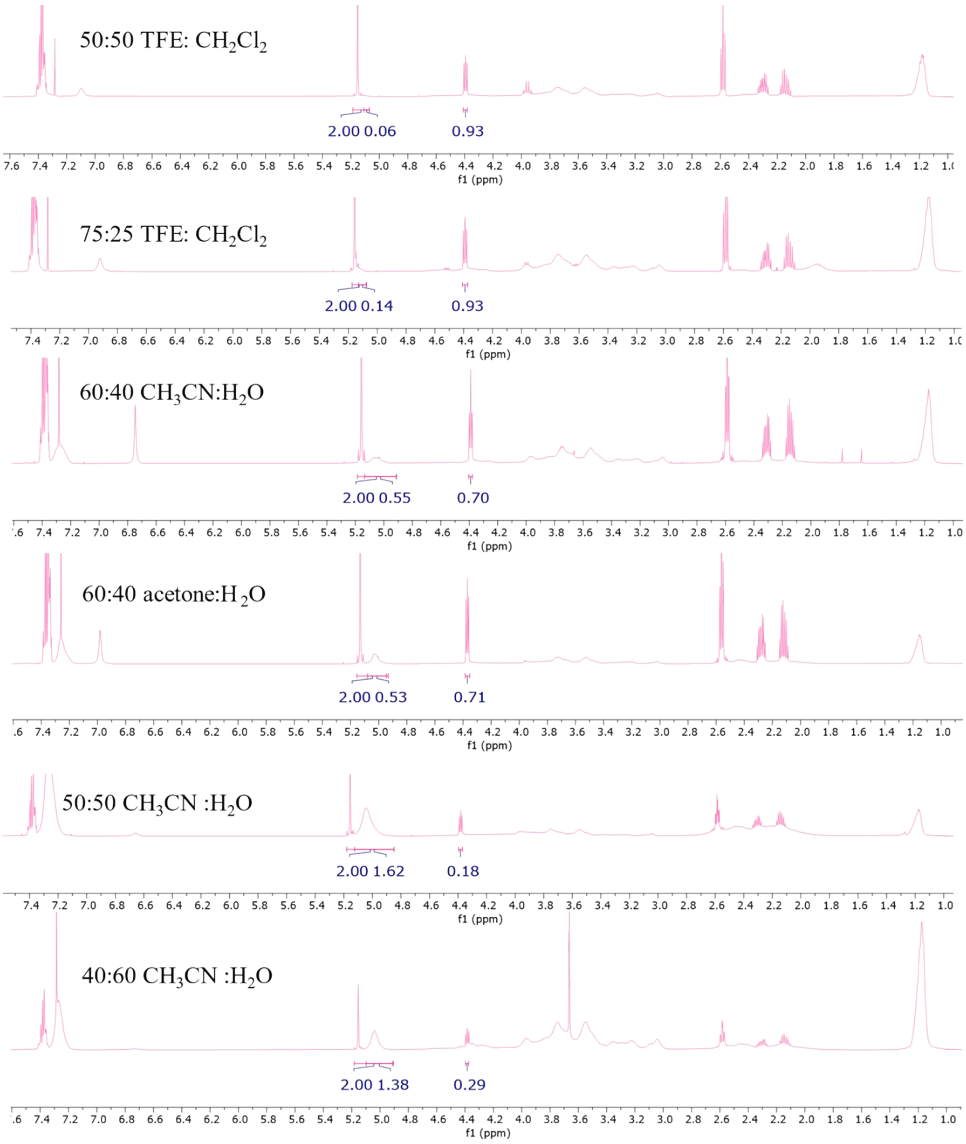
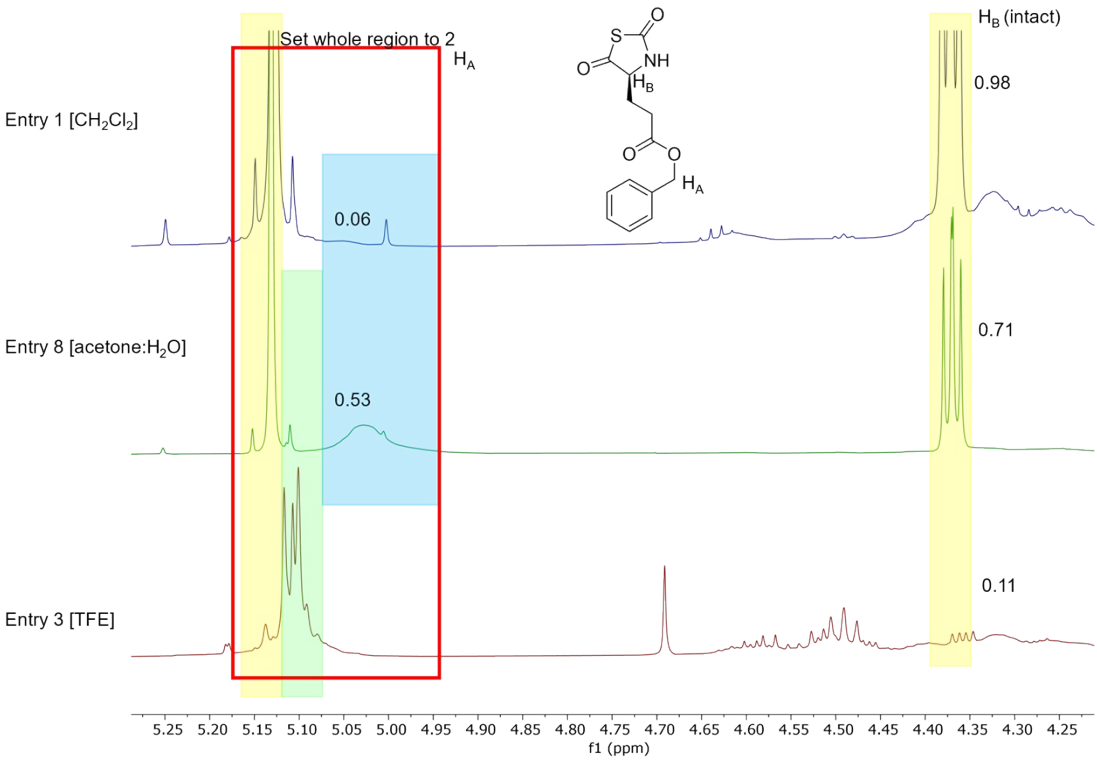
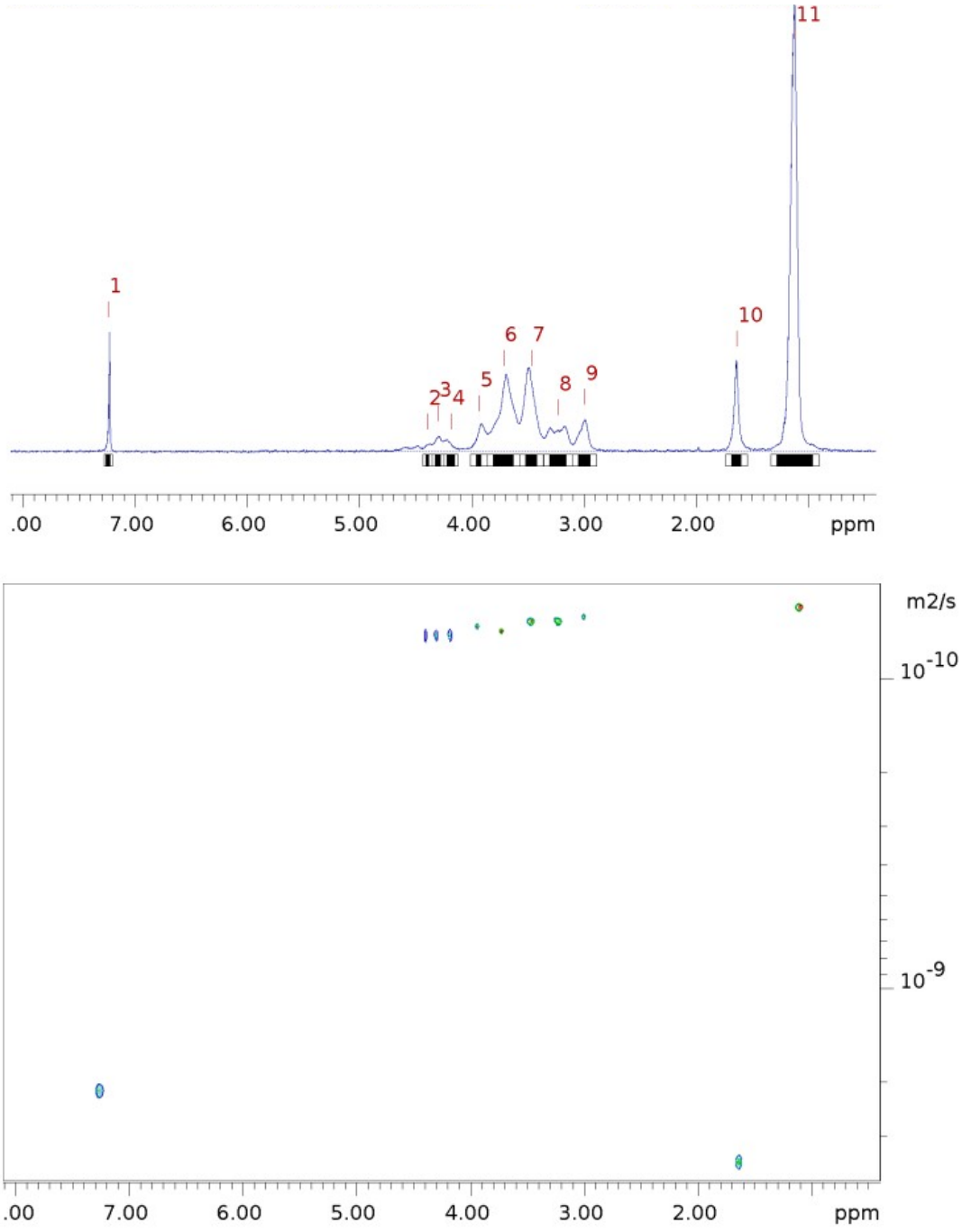


Figure S15: ^{1}H NMR spectra ($CDCl_3$) of polymerizations of BG-NTA using ECel-NH_2 under various reaction conditions demonstrating BG-NTA conversion. Values for % conversion, % hydrolyzed, and % NTA remaining were calculated using method described in Fig. S14.



Red region includes NTA (intact), NTA (hydrolyzed), and poly(BG)

Figure S16: ^{1}H NMR spectra of polymerizations of BG-NTA using ECel-NH_2 using various conditions demonstrating conversion in $CDCl_3$. The region in the red box was set as a standard to 2 to represent H_A. % NTA remaining was measured using H_B (highlighted in yellow around 4.4 ppm). % conversion to poly(BG) was calculated by measuring the region highlighted in blue and dividing it by 2. % hydrolyzed was calculated by subtracting the % NTA remaining and % conversion to polymer from 1.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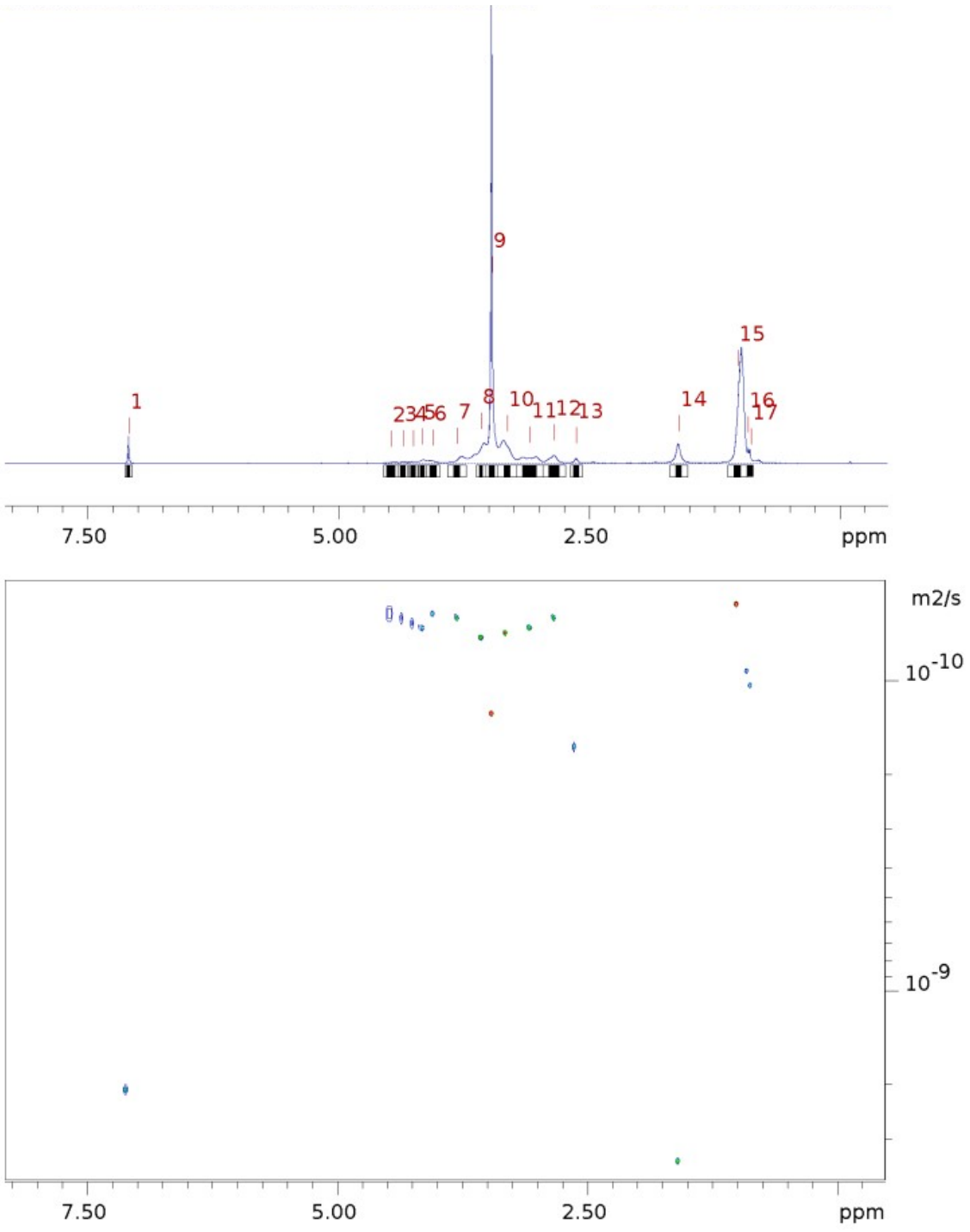
Peak name	F2 [ppm]	Io	error	D [m2/s]	error	fitInfo
1	7.239	4.09e+09	1.750e+07	2.12e-09	1.763e-11	Done
2	4.395	1.08e+09	6.393e+06	7.19e-11	9.786e-13	Done
3	4.300	2.55e+09	7.103e+06	7.20e-11	4.600e-13	Done
4	4.183	1.99e+09	7.893e+06	7.15e-11	6.515e-13	Done
5	3.935	5.36e+09	8.354e+06	6.72e-11	2.432e-13	Done
6	3.717	2.59e+10	1.173e+07	7.05e-11	7.338e-14	Done
7	3.468	2.15e+10	9.815e+06	6.54e-11	6.955e-14	Done
8	3.229	1.06e+10	1.094e+07	6.59e-11	1.583e-13	Done
9	2.994	6.80e+09	9.849e+06	6.28e-11	2.138e-13	Done
10	1.637	1.42e+10	3.935e+07	3.60e-09	1.902e-11	Done
11	1.118	7.21e+10	1.373e+07	5.90e-11	2.679e-14	Done

Figure S17: DOSY data for as-received ECel, including the 1D ^{1}H NMR spectrum, the DOSY spectrum, and the table of peaks and diffusion coefficients. The average diffusion coefficient (ignoring solvent signals) was found to be $6.7 \pm 0.5 * 10^{-11}$ m^2/s.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2.50
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Peak name	F2 [ppm]	Io	error	D [m2/s]	error	fitInfo
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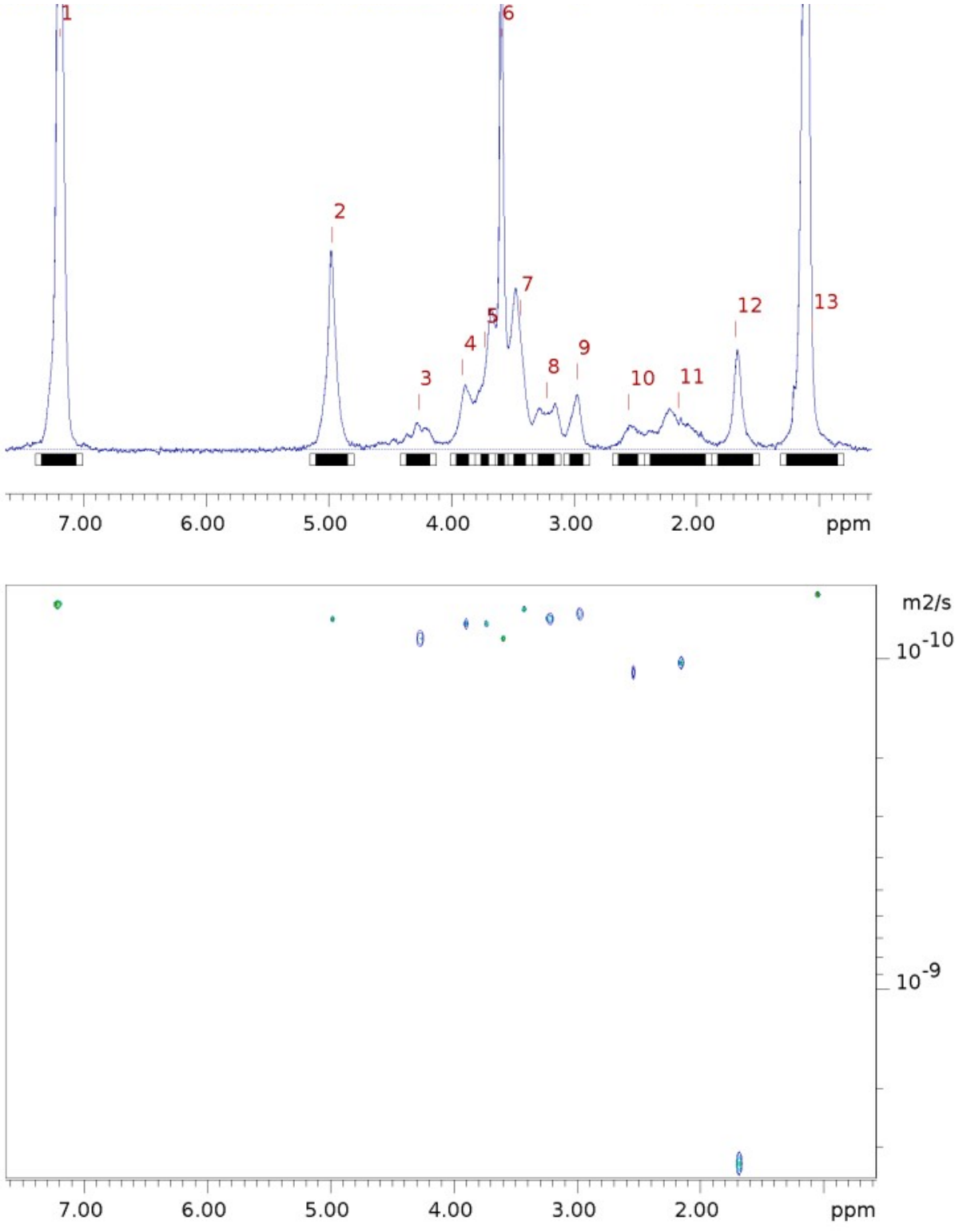
2	4.478	2.22e+08	1.271e+06	6.04e-11	1.042e-12	Done
3	4.359	2.24e+08	1.016e+06	6.38e-11	8.498e-13	Done
4	4.255	2.90e+08	9.988e+05	6.45e-11	6.505e-13	Done
5	4.165	5.02e+08	9.843e+05	6.65e-11	3.759e-13	Done
6	4.057	5.34e+08	1.212e+06	6.14e-11	4.172e-13	Done
7	3.819	1.38e+09	1.446e+06	6.30e-11	1.952e-13	Done
8	3.578	3.03e+09	1.073e+06	7.20e-11	7.119e-14	Done
9	3.470	1.75e+10	1.315e+06	1.27e-10	2.272e-14	Done
10	3.317	5.24e+09	1.463e+06	6.88e-11	5.457e-14	Done
11	3.093	2.51e+09	1.723e+06	6.64e-11	1.317e-13	Done
12	2.851	1.57e+09	1.581e+06	6.26e-11	1.869e-13	Done
13	2.630	4.50e+08	1.417e+06	1.62e-10	1.186e-12	Done
14	1.608	2.90e+09	4.681e+06	3.51e-09	1.103e-11	Done
15	1.023	1.58e+10	1.424e+06	5.68e-11	1.591e-14	Done
16	0.918	4.19e+08	4.716e+05	9.35e-11	2.678e-13	Done
17	0.886	5.48e+08	7.838e+05	1.01e-10	3.613e-13	Done

Figure S18: DOSY for ECel-PEG-NH_2 macroinitiator including the 1D ^1H NMR spectrum, the DOSY spectrum, and the table of peaks and diffusion coefficients. The average diffusion coefficient (ignoring solvent signals) was found to be $8 \pm 3 * 10^{-11}$ m^2/s.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Peak name	F2 [ppm]	Io	error	D [m2/s]	error	fitInfo
1	7.199	4.79e+10	1.238e+07	6.84e-11	5.016e-14	Done
2	4.973	1.56e+10	1.220e+07	7.57e-11	1.608e-13	Done
3	4.270	4.00e+09	1.122e+07	8.64e-11	6.233e-13	Done
4	3.907	6.57e+09	9.106e+06	7.89e-11	2.912e-13	Done
5	3.725	1.25e+10	8.261e+06	7.83e-11	1.383e-13	Done
6	3.590	2.36e+10	6.743e+06	8.68e-11	6.375e-14	Done
7	3.439	1.62e+10	8.962e+06	7.18e-11	1.105e-13	Done
8	3.221	7.23e+09	9.796e+06	7.50e-11	2.766e-13	Done
9	2.976	4.73e+09	9.227e+06	7.25e-11	3.903e-13	Done
10	2.554	3.19e+09	1.102e+07	1.09e-10	9.021e-13	Done
11	2.150	9.88e+09	1.591e+07	1.03e-10	4.031e-13	Done
12	1.681	9.80e+09	3.813e+07	3.33e-09	2.638e-11	Done
13	1.054	5.15e+10	1.417e+07	6.46e-11	5.181e-14	Done

Figure S19: DOSY for ECel-PEG-*block*-poly(BG) BCP including the 1D ^{1}H NMR spectrum, the DOSY spectrum, and the table of peaks and diffusion coefficients. The average diffusion coefficient (ignoring solvent signals) was found to be $8 \pm 1 * 10^{-11}$ m^2/s. Blue highlights in the table represent peaks corresponding to poly(BG), red highlights represent peaks corresponding to ECel, and green highlights represent peaks corresponding to PEG.

Blends and Other Characterization
Preparation of ECel/PET blends

Thin films (<10 μm thick) of the ECel/PET 70/30 blends, suitable for phase contrast optical microscopy and small angle laser light scattering, were prepared through solution casting. Blend solutions in HFIP (1% wt/vol) were prepared by dissolving the polymers and compatibilizer in the desired compositions at rt for 48 h under stirring. Then, 0.03 mL of the solution was cast onto microscope slides and covered with an inverted 25 mL Erlenmeyer to control evaporation at rt over a period of about 15 min. After this period, the samples were kept uncovered for 24 h before analysis to allow for evaporation of any residual solvent. The blends were labeled as ECel/PET-C, where ECel is the wt.% of ECel, PET is the wt.% of polyethylene terephthalate and C is the wt.% of the compatibilizer ECel-PEG-*block*-poly(BG). Control samples of ECel/ECel-PEG and PET/Poly(BG) in a 70/30 composition were also prepared following the same method.

Phase contrast optical microscopy (PCOM)

The morphology of the blends was characterized by phase contrast optical microscopy (PCOM) using a Nikon Eclipse LV100 microscope equipped with an AmScope digital camera (MU503B) for image acquisition. The optical microscope was used in phase contrast mode with a 20x Ph1 objective. Due to irregular shapes of the phase-separated domains, the average dimensions of the phase-separated domains were quantified using ImageJ by measuring the individual areas of the domains, which were then used to calculate a representative circular diameter. Statistical analysis was performed using JMP software. The data is presented as the mean ± standard deviation. One-way analysis of variance (ANOVA) approach was used, and the means were compared though Tukey's analysis. **Table 1** and **Table 2** present the p values of all the comparisons of the Tukey's analysis. Results were considered statistically different if $p < 0.05$.

Table 1: Pair wise p values from Tukey's analysis of the large domains observed in PCOM images.

Compatibilizer Level (wt%)	Compatibilizer Level (wt%)	p value
0	20	<.0001
0	10	<.0001
5	20	<.0001
5	10	<.0001
0	5	<.0001
10	20	<.0001

Table 2: Pair wise p values from Tukey's analysis of the small domains observed in PCOM images.

Compatibilizer Level (wt%)	Compatibilizer Level (wt%)	p value
5	20	<.0001
5	10	<.0001
0	20	<.0001
5	0	<.0001
10	20	<.0001
0	10	<.0001

Small angle laser light scattering (SALLS)

The interdomains distances of the blends were measured using small angle laser light scattering (SALLS). In this analysis, the laser font was a 3 mW He-Ne laser (λ = 632.8 nm) and a AmScope digital camera (MU503B) was used to acquire the scattering patterns. All scattering patterns were obtained in transmission with parallel polarizers (V_v mode). The sample-to-detector distance was 24 cm and the scattering vector (q) range was calibrated using a 300 grooves/mm diffraction grating. The data was analyzed by SAXSGUI software to obtain radially integrated scattering intensity as a function of the scattering vector (q). The interdomain distance (d) at the maximum intensity was calculated by equation 1:

$$d = \frac{2\pi}{q} \qquad \text{Equation 1}$$

The interdomain distance mean was obtained from measurements of 5 different samples. The statistical analysis followed the same methodology as described for the phase contrast optical microscopy analysis. Table 3 presents the p values of all the comparisons of the Tukey's analysis.

Table 3: Pair wise p values from Tukey's analysis of the SALLS interdomain distances.

Compatibilizer Level (wt%)	Compatibilizer Level (wt%)	p value
20	30	<.0001
10	30	<.0001
20	10	0.7705

Control samples

In order to be an effective compatibilizer, each block of the BCP needs to have specific interactions or miscibility with one of the polymers in the blend.[5, 6] To assess the miscibility of the homopolymers that composes each block of our BCP with the polymers of the blend, mixtures of ECel/ECel-PEG-NH_2 and PET/Poly(BG) at a 70/30 ratio were prepared. The films obtained were transparent and, as can be observed in the PCOM images displayed in **Figure S21**, the morphology of both combinations is homogeneous, with no evident phase separation. The miscibility of the studied compositions is further confirmed by the absence of scattering halos characteristic of phase separated morphologies in the SALLS profiles (**Figure S21** insets). Thus, it is possible to conclude that ECel and PET are miscible with ECL-PEG-NH_2 and poly(BG).

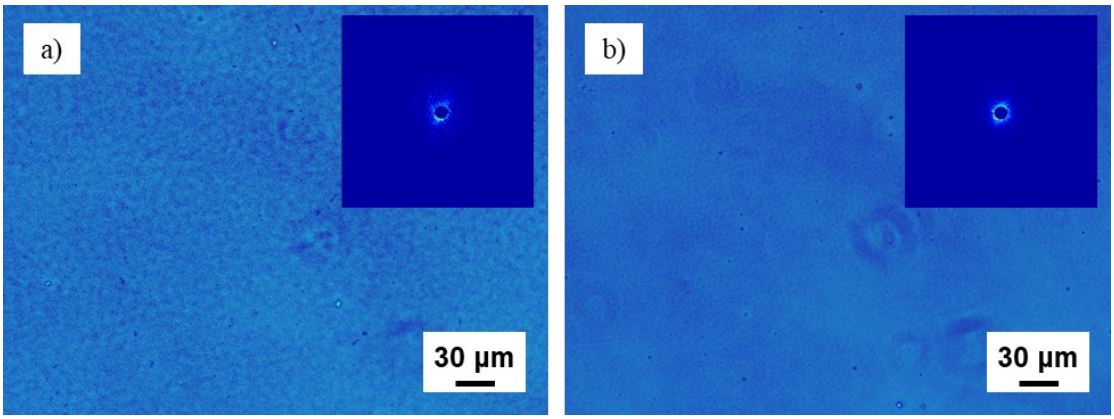

Figure S20: Phase contrast optical microscopy (PCOM) images and small angle laser light scattering (SALLS) patterns of a) ECel/ECel-PEG 70/30 and b) PET/Poly(BG) 70/30.

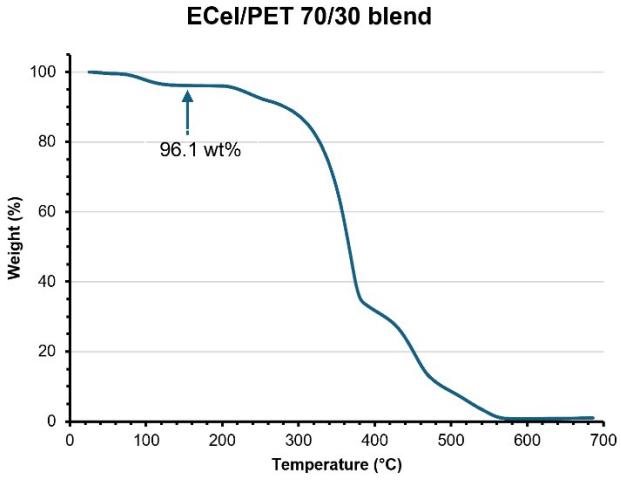

Figure S21: Thermogravimetric analysis (TGA) of ECel/PET 70/30 blend after casting and sitting 24 h. The mass loss just before 100 °C corresponds to loss of HFIP.

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