

Supplementary Information

**Studying catalytic activity of DBU and TBD upon water-initiated ROP
of ϵ -caprolactone at different thermodynamic conditions.**

Andrzej Dzieńia^{1,2*}, Paulina Maksym^{2,3}, Barbara Hachuła¹, Magdalena Tarnacka^{2,3}, Tadeusz Biela⁴,
Sylwia Golba⁵, Andrzej Zięba⁶, Mirosław Chorażewski^{1*}, Kamil Kaminski^{2,3*}, Marian Paluch^{2,3}

¹ *Institute of Chemistry, University of Silesia, ul. Szkolna 9, 40-007 Katowice, Poland*

² *Silesian Center of Education and Interdisciplinary Research, University of Silesia, ul. 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland*

³ *Institute of Physics, University of Silesia, ul. 75 Pulku Piechoty 1, 41-500 Chorzow, Poland*

⁴ *Department of Polymer Chemistry, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363, Lodz, Poland*

⁵ *Institute of Materials Science, University of Silesia, 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland*

⁶ *Department of Organic Chemistry, Faculty of Pharmaceutical Sciences in Sosnowiec, Medical University of Silesia in Katowice, Jagiellonska 4, 41-200 Sosnowiec, Poland*

*Corresponding author: e-mail adzienia@us.edu.pl; kamil.kaminski@smcebi.edu.pl phone number +48323497610;

miroslaw.chorazewski@us.edu.pl

MATERIALS AND METHODS

Materials

All chemicals used were purchased from Sigma-Aldrich. ϵ -Caprolactone (CAS: 502-44-3, 97%) and 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) (CAS: 6674-22-2, 98%) was purified by distillation from CaH₂ under high vacuum and stored with freshly activated 4A molecular sieves. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) (CAS: 5807-14-7, 98%) was dried on Schlenk line prior to use. Deionized water (CAS: 7732-18-5) and benzoic acid (CAS: 65-85-0, 99.5%) was used as received.

Procedures

Ring-opening polymerization at atmospheric pressure

To ϵ -caprolactone in a round bottom flask with a magnetic stirring bar, the proper amount of initiator (H_2O), DBU or TBD was added, the reaction mixture was purified from residual moisture by three freeze-pump-thaw cycles and degassed by inert gas flow (Argon) following by capped with a septum. For example, no. 12, ϵCL (8 ml, 70.1 mmol) was mixed with water (10.5 μl , 0.58 mmol) and TBD (101.6 mg, 0.73 mmol). The flask was immersed in an oil bath thermostated at 293 – 393 K to start the reaction. After the desired time, benzoic acid was added, and the mixture was dissolved in a small portion of chloroform, and then the polymer was isolated by precipitation into cold methanol or methanol/water mixture (50/50 v/v) for lower molar mass polymers, filtered, and then dried under vacuum to a constant mass.

Ring-opening polymerization at elevated pressure

High-pressure syntheses were performed by using the high-pressure chamber. Hydrostatic pressure was generated by displacing the piston by means of a hydraulic press. The pressure was measured by a Nova Swiss tensometric meter, which had an accuracy of 10 MPa^{54,55}. The temperature was controlled within 0.1 K by means of liquid flow from a thermostatic bath. Polymerizations were carried out in 2 or 4 mL Teflon ampoules in a high-pressure microreactor purchased from the UniPress. The reactor includes a hydraulic press model LCP20 and a pressure reaction vessel equipped with a temperature controller. The reaction mixture was prepared identically as at ring-opening polymerization at atmospheric pressure in Schlenk flask and then moved to glovebox filled with argon. Inert gas (Argon 5.0) was pumped through Drierite™ gas-drying unit. Prior to the experiment, the pressure reactor and PTFE tubes were heated at the 80°C for 30 minutes and then moved to glovebox to cool down. At inert and dry conditions, the reaction mixture was transferred to PTFE ampoule, closed with a metal cap, and then installed in pressure reactor (LC10T, manufactured by Unipress - Institute of High Pressure Physics, Warsaw). Then pressure reactor was assembled, removed from

glovebox, connected to the thermostat (Huber KISS K6s), and compressed by hydraulic press (LCP20, Unipress) to chosen thermodynamic conditions for the proper time. Sealed Teflon ampoule was installed in a preheated reactor and compressed at chosen pressure value for the proper time. After the desired amount of time, pressure was released, benzoic acid was added, and the mixture was dissolved in a small portion of chloroform, and then the polymer was isolated by precipitation into cold methanol or methanol/water mixture (50/50 v/v) for lower molecular mass polymers, filtered, and then dried under vacuum to a constant mass.

Instruments

Nuclear Magnetic Resonance

Proton nuclear magnetic resonance of polymers (^1H NMR) spectra were recorded using a Bruker Ascend 600 spectrometer operating at 600 MHz in CDCl_3 as a solvent. TMS was used as an internal standard, and its chemical shift, δ , was set at zero. Standard experimental conditions and standard Bruker program were used.

Matrix-Assisted Laser Desorption/Ionization-Time of Flight Spectroscopy

MALDI-TOF-MS experiments were performed on an Axima-Performance TOF spectrometer (Shimadzu Biotech, Manchester, UK), equipped with a nitrogen laser (337 nm). The pulsed extraction ion source accelerated the ions to the kinetic energy of 20 keV. All data have been obtained in a positive-ion linear mode, applying the accumulation of 200 scans per spectrum. The calibration of the linear-mode analysis was done using polyethylene glycol (PEG) in mass range up to 8000 g/mol. The samples were dissolved in dichloromethane at a concentration of 6 mg/mL. The sample solutions were mixed with a 7-mg/mL solution of the matrix in the same solvent. Dithranol (1,8-dihydroxy-9,10-dihydroanthracen-9-one) was used as the matrix. KCl were dissolved in THF at a concentration of 6 mg/mL. The sample and matrix and KCl were then combined at ratios of 20:10:1 v/v. Data were

acquired in continuum mode until acceptable averaged data were obtained and were analyzed using a Shimadzu Biotech Launchpad program.

Gel Permeation Chromatography

Molecular weights and dispersities were determined by size exclusion chromatography (SEC) with Viscotek GPC Max VE 2001 and a Viscotek TDA 305 triple detection (refractometer, viscosimeter, and low angle laser light scattering) used for data collecting and OmniSec 5.12 for processing. Two T6000M general mixed columns were used for separation. The measurements were carried out in THF HPLC purity, as the solvent at 308 K with a flow rate of 1 mL/min. The apparatus was used in a triple detection mode, and absolute molar mass (M_n and M_w) and dispersity (D) were determined with a triple detection calibrated with a narrow polystyrene standard.

FTIR measurements.

The FT-IR spectra were recorded for the functional group detection in the frequency range of 4000–400 cm^{-1} on a Thermo Scientific Nicolet iS50 FT-IR spectrometer equipped with a diamond iS50-ATR accessory. All spectra were collected at a spectral resolution of 4 cm^{-1} , and 100 scans were taken.

Table S1. Synthesis and characteristic of PCL obtained at 353K.

εCL polymerization with [M/I] = 120/1 and T = 353 K catalyzed via:																	
DBU 120/1/6 at p = 0.1 MPa						Pressure p = 500 MPa						Pressure and DBU 120/1/0.5 at p = 500 MPa					
No.	Time [h]	Conv. ^a [%]	M _n [kg/mol]	M _n theoretical	M _w /M _n	No.	Time [h]	Conv. ^a [%]	M _n [kg/mol]	M _n theoretical	M _w /M _n	No.	Time [h]	Conv. ^a [%]	M _n [kg/mol]	M _n theoretical	M _w /M _n
1a	1	5.8	-	0.8	-	2a	8	3.6	-	0.5		3a	24	8.8	1.1	1.2	1.08
1b	3	10.0	-	1.4	-	2b	24	8.3	1.5	1.2	1.07	3b	72	31.3	3.8	4.3	1.08
1c	6	15.4	-	2.1	-	2c	72	46.3	4.6	6.4	1.07	3c	96	38.2	4.4	5.2	1.11
1d	9	21.9	1.2	3.0	1.11	2d	96	69.0	7.0	9.5	1.06	Pressure and DBU 120/1/6 at p = 500 MPa					
1e	20	40.5	1.5	5.6	1.06	2e	168	99.0	8.2	13.6	1.27	4a	3	38.5	2.8	5.3	1.12
1f	25	47.1	2.4	6.5	1.05	-	-	-	-	-	-	4b	6	68.1	3.4	9.3	1.12
-	-	-	-	-	-	-	-	-	-	-	-	4c	9	95.1	4.2	13.0	1.04
-	-	-	-	-	-	-	-	-	-	-	-	4d	24	99.0	6.2	13.6	1.27

Table S2. Synthesis and characteristic of PCL polymers at 393K.

εCL polymerization with [M/I] = 120/1 and T = 393 K catalyzed via:																	
DBU - decomposition						Pressure p = 500 MPa						Pressure and DBU 120/1/0.5 at p = 500 MPa					
No.	Time [h]	Conv. ^a [%]	M _n [kg/mol]	M _n theoretical	M _w /M _n	No.	Time [h]	Conv. ^a [%]	M _n [kg/mol]	M _n theoretical	M _w /M _n	No.	Time [h]	Conv. ^a [%]	M _n [kg/mol]	M _n theoretical	M _w /M _n
5	-	-	-	-	-	6a	6	2.0	-	0.3	-	7a	6	23.8	1.7	3.3	1.07
-	-	-	-	-	-	6b	12	13.6	-	1.9	-	7b	12	38.4	5.9	5.3	1.14
-	-	-	-	-	-	6c	24	66.7	5.9	9.1	1.13	7c	18	61.3	9.1	8.4	1.18
-	-	-	-	-	-	6d	48	99.0	13.0	13.6	1.41	7d	24	68.3	10.7	9.4	1.28
-	-	-	-	-	-	-	-	-	-	-	-	7e	36	89.0	10.9	12.2	1.5

Table S3. Synthesis and characteristic of PCL polymers with lower monomer/initiator molar ratios.

εCL polymerization with [M/I] = 960/1 and T = 353 or 393 K catalyzed via:																	
DBU 960/1/46 at 353 K and $p = 500$ MPa						DBU 960/1/4.6 at 393 K and $p = 500$ MPa						DBU 960/1/46 at 393 K and $p = 500$ MPa					
No.	Time [h]	Conv. ^a [%]	M_n [kg/mol]	M_n theoretical [kg/mol]	M_w/M_n	No.	Time [h]	Conv. ^a [%]	M_n [kg/mol]	M_n theoretical [kg/mol]	M_w/M_n	No.	Time [h]	Conv. ^a [%]	M_n [kg/mol]	M_n theoretical [kg/mol]	M_w/M_n
8a	6	10.3	-	11.3	-	9a	6	8.7	-	9.5	-	10a	1	15.6	3.6	17.1	1.03
8b	12	25.6	8.4	28.1	1.34	9b	12	29.1	9.8	31.9	1.16	10b	2	30.3	7.9	33.2	1.25
8c	24	74.6	12.5	81.8	1.54	9c	36	94.6	14.0	103.7	1.4	10c	3	46.1	13.1	50.5	1.32
8d	72	99.0	13.1	108.0	1.49	-	-	-	-	-	-	10d	4.5	69.2	16.7	75.8	1.56
-	-	-	-	-	-	-	-	-	-	-	-	Pressure $p = 500$ MPa and 393 K Non-catalyzed 960/1					
-	-	-	-	-	-	-	-	-	-	-	-	11a	24	10.3	4.9	11.3	1.03
-	-	-	-	-	-	-	-	-	-	-	-	11b	72	17.8	9.3	19.6	1.25
-	-	-	-	-	-	-	-	-	-	-	-	11c	120	28.5	14.0	31.2	1.32
-	-	-	-	-	-	-	-	-	-	-	-	11d	168	99.9	20.3	108.5	1.56

Table. S4. Synthesis and characteristics of PCL polymers with the application of TBD.

εCL polymerization with [M/I] = 960/1 and T = 393 K catalyzed via:																	
TBD at ambient pressure, the effect of monomer to initiator ratio						TBD at $p = 0.1$ or 150 MPa, the effect of monomer to initiator ratio						TBD at ambient pressure, the effect of reaction temperature					
No.	Time [h]	Conv. ^a [%]	M_n [kg/mol]	M_n theoretical [kg/mol]	M_w/M_n	No.	Time [h]	Conv. ^a [%]	M_n [kg/mol]	M_n theoretical [kg/mol]	M_w/M_n	No.	Time [h]	Conv. ^a [%]	M_n [kg/mol]	M_n theoretical [kg/mol]	M_w/M_n
TBD 120/1/1.25 at $T = 323$ K						TBD 120/1/1.25 $T = 293$ K and $p = 150$ MPa						TBD 120/1/1.25 at $T = 293$ K					
12	2	30	10.8	4.2	1.11	16	3	64.5	8.2	8.8	1.20	19	4	23	10.0	3.2	1.12
TBD 480/1/1.25 at $T = 293$ K						TBD 480/1/1.25 at $T = 293$ K and $p = 150$ MPa						TBD 120/1/1.25 at $T = 323$ K					
13	6	22	12.0	12.1	1.11	17	3	8.2	-	4.5	-	20	2	30	10.8	4.1	1.11
TBD 480/1/1.25 at $T = 323$ K						TBD 960/1/1.25 at $T = 293$ K and $p = 150$ MPa						TBD 120/1/1.25 at $T = 353$ K					
14	6	31	10.2	17.0	1.25	18	16	3.1	-	3.4	-	21	2	64.1	-	8.8	-
-	-	-	-	-	-	-	-	-	-	-	-	22	6	68.1	8.0	9.3	1.41
TBD 960/1/1.25 at $T = 393$ K						TBD 120/1/2 $T = 353$ K and $p = 0.1$ MPa						TBD 120/1/1.25 at $T = 393$ K					
15	72	8.9	2.0	9.8	1.1	27	1	99.0	12.0	13.6	1.39	23	2	99.0	7.2	13.6	1.44

Table. S5. Synthesis and characteristics of PCL polymers with the application of TBD.

εCL polymerization with [M/I] = 960/1 and T = 393 K catalyzed via:					
TBD effect of pressure at a higher temperature					
No.	Time [h]	Conv. ^a [%]	M _n [kg/mol]	M _n theoretical [kg/mol]	M _w /M _n
TBD 120/1/0.5 at T = 353 K					
24	72	6	-	0.9	-
TBD 120/1/0.5 at T = 353 K and p = 500 MPa					
25	72	18.0	1.2	2.5	1.33
TBD 120/1/1.25 at T = 353 K					
22	6	68.1	8.0	9.3	1.41
TBD 120/1/1.25 at T = 353 K and p = 500 MPa					
26	0.5	99.0	11.0	13.6	1.68

^aestimated by ¹H NMR, CDCl₃, 600 MHz Conv(%)=I_d/(I_d+I_E)×100, where I_d and I_E are the integrations from the methylene protons of polymer (4.03 ppm [-CH₂O-]) and monomer (4.24 ppm [-CH₂O-]), respectively; M_n theoretical calculated according to the following equation

$$M_{n \text{ theor}} = ([M]/[I] * 114,14 * \text{conversion}) + \text{mass of end groups}$$

Table. S6. Comparison of experimental and calculated molecular weights from MALDI-TOF experiments.

* $M_{n \text{ calc}}$ values were calculated according to the following equation:

Sample Name	Architecture	n = 19		n = 20		n = 21		n = 22	
		$M_{n \text{ calc}}^*$	$M_{n \text{ exp}}$						
6c	■ HO-εCL-H+K ⁺	2225.63	2225.6	2339.77	2339.6	2453.91	2453.9	2568.05	2568.1
	* KO-εCL-H +K ⁺	2263.59	2263.2	2377.73	2377.3	2491.87	2492.0	2606.01	2605.8
	▲ Cyclic + K ⁺ or	2207.62	2208.3	2321.76	2321.6	2435.90	2436.1	2550.04	2550.1
	● HO-εCL-H+Na ⁺	2209.66		2323.8		2437.94		2552.08	
4c	■ HO-εCL-H +K ⁺	2225.63	2226.5	2339.77	2340.6	2453.91	2454.8	2568.05	2569.1
	* KO-εCL-H +K ⁺	2263.59	2264.7	2377.73	2378.8	2491.87	2493.6	2606.01	2607.3
	▲ Cyclic + K ⁺ or	2207.62	2208.0	2321.76	2323.3	2435.90	2435.9	2550.04	2551.6
	● HO-εCL-H+Na ⁺	2209.66		2323.8		2437.94		2552.08	
27	■ HO-εCL-H +K ⁺	2225.63	2226.8	2339.77	2340.8	2453.91	2455.2	2568.05	2569.0
	* KO-εCL-H +K ⁺	2263.59	2263.7	2377.73	2378.4	2491.87	2492.6	2606.01	2607.7
	▲ Cyclic + K ⁺ or	2207.62	2208.4	2321.76	2322.8	2435.90	2437.0	2550.04	2551.2
	● HO-εCL-H+Na ⁺	2209.66		2323.8		2437.94		2552.08	
7a	■ HO-εCL-H +K ⁺	2225.63	2224.4	2339.77	2338.7	2453.91	2452.7	2568.05	2566.8
	* KO-εCL-H +K ⁺	2263.59	2262.7	2377.73	2376.9	2491.87	2491.0	2606.01	2605.5
7b	■ HO-εCL-H +K ⁺	2225.63	2226.7	2339.77	2340.7	2453.91	2454.7	2568.05	2569.0
	* KO-εCL-H +K ⁺	2263.59	2265.2	2377.73	2379.3	2491.87	2493.4	2606.01	2607.4
	▲ Cyclic + K ⁺ or	2207.62	2208.4	2321.76	2323.2	2435.90	2436.1	2550.04	2551.9
	● HO-εCL-H+Na ⁺	2209.66		2323.8		2437.94		2552.08	
26	■ HO-εCL-H +K ⁺	2225.63	2225.4	2339.77	2339.4	2453.91	2453.3	2568.05	2567.6
	* KO-εCL-H +K ⁺	2263.59	2263.2	2377.73	2377.5	2491.87	2491.3	2606.01	2605.6
	▲ Cyclic + K ⁺ or	2207.62	2207.3	2321.76	2322.3	2435.90	2435.2	2550.04	2549.5
	● HO-εCL-H+Na ⁺	2209.66		2323.8		2437.94		2552.08	

$$M_{n \text{ calc}} = (n * 114.14) + \text{end groups}; M_{\text{Na}^+} = 22.98; M_{\text{K}^+} = 38.96; M_{\text{H}^+} = 1.00;$$

$$M_{\text{theoretical}} (\text{HOOC-eCL-H} + \text{K}^+) = M_{\text{K}} + M_{\text{O}} + (n \cdot M_{\text{mer } \epsilon\text{CL}}) + M_{\text{H}} + M_{\text{H}}$$

$$M_{\text{theoretical}} (\text{KOOc-eCL-H} + \text{K}^+) = M_{\text{K}} + M_{\text{O}} + (n \cdot M_{\text{mer } \epsilon\text{CL}}) + M_{\text{H}} + M_{\text{K}}$$

$$M_{\text{theoretical}} (\text{cyclic} + \text{K}^+) = (n \cdot M_{\text{mer } \epsilon\text{CL}}) + M_{\text{H}}$$

$$M_{\text{theoretical}} (\text{HOOC-eCL-H} + \text{Na}^+) = M_{\text{Na}} + M_{\text{O}} + (n \cdot M_{\text{mer } \epsilon\text{CL}}) + M_{\text{H}} + M_{\text{H}}$$

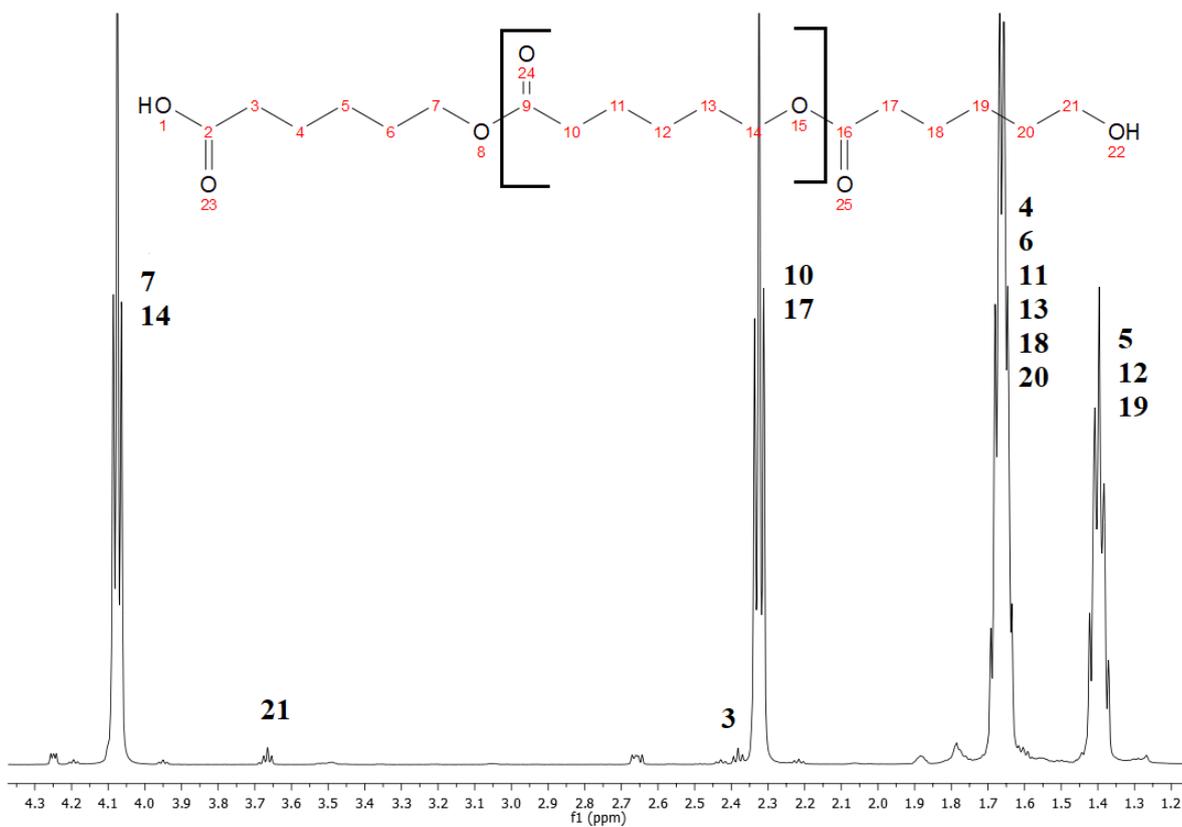


Fig. S1. ¹H NMR analysis of polymer synthesized with DBU as organocatalyst – No 7b.

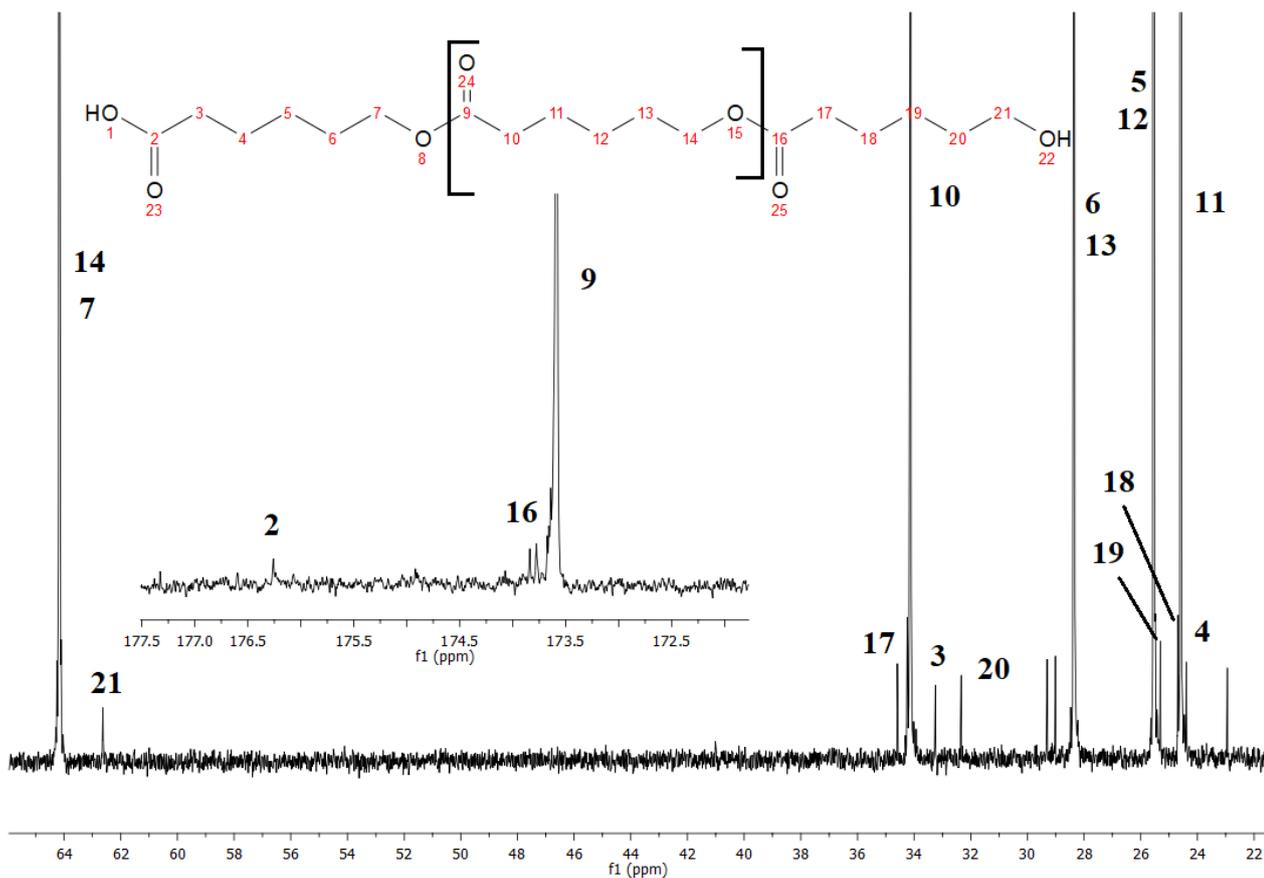


Fig. S2. ¹³C NMR analysis of polymer synthesized with DBU as organocatalyst – No 7b.

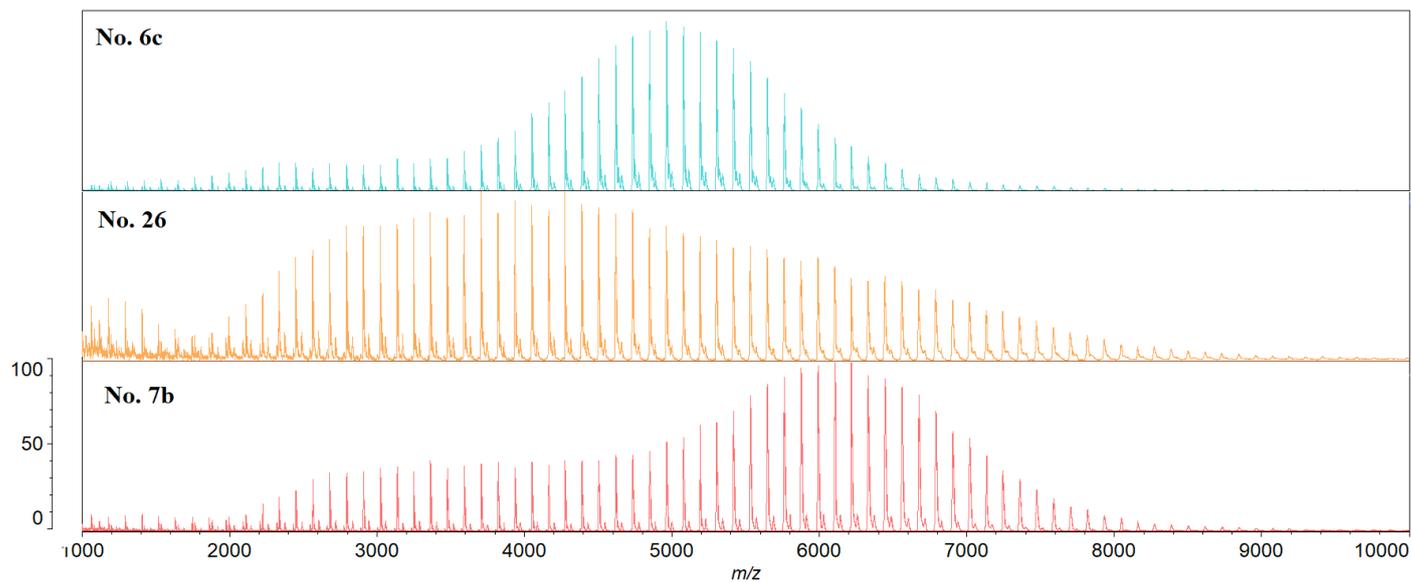


Figure S3. Full range MALDI-TOF spectra of the produced polymers: No. 6c, 26 and 7b.

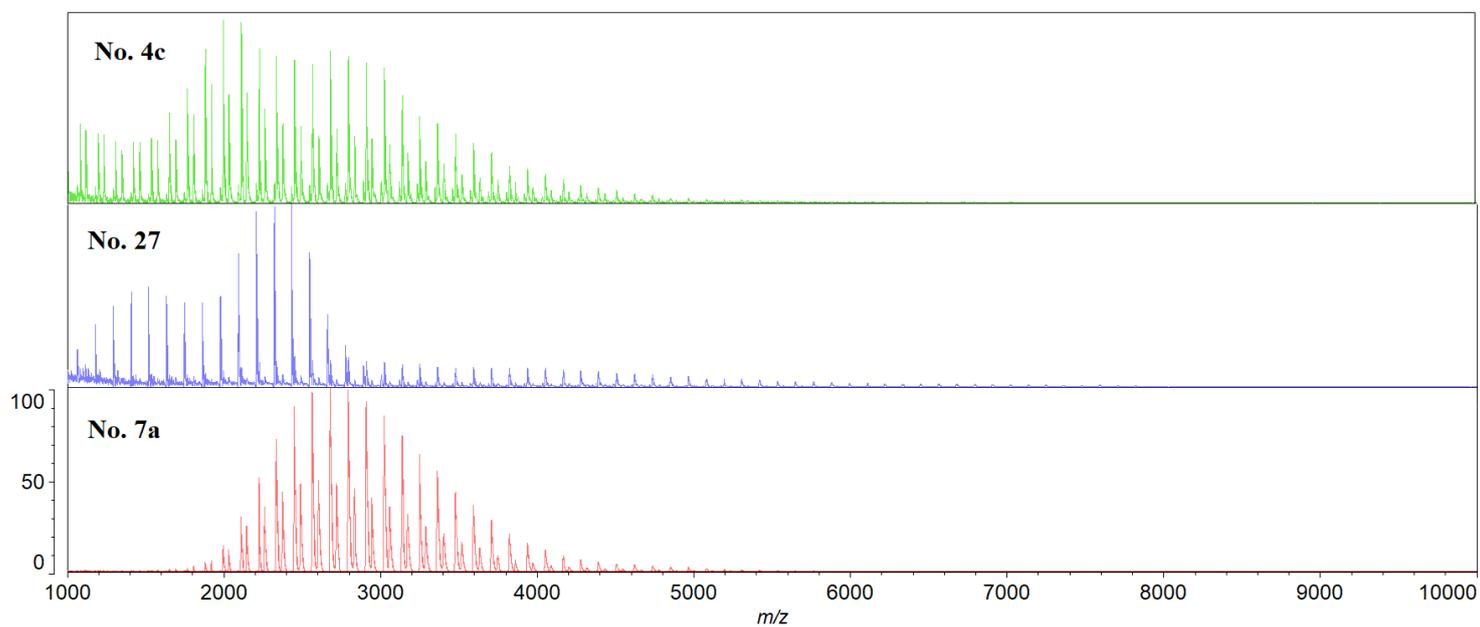


Figure S4. Full range MALDI-TOF spectra of the produced polymers: No. 4c, 27 and 7a.

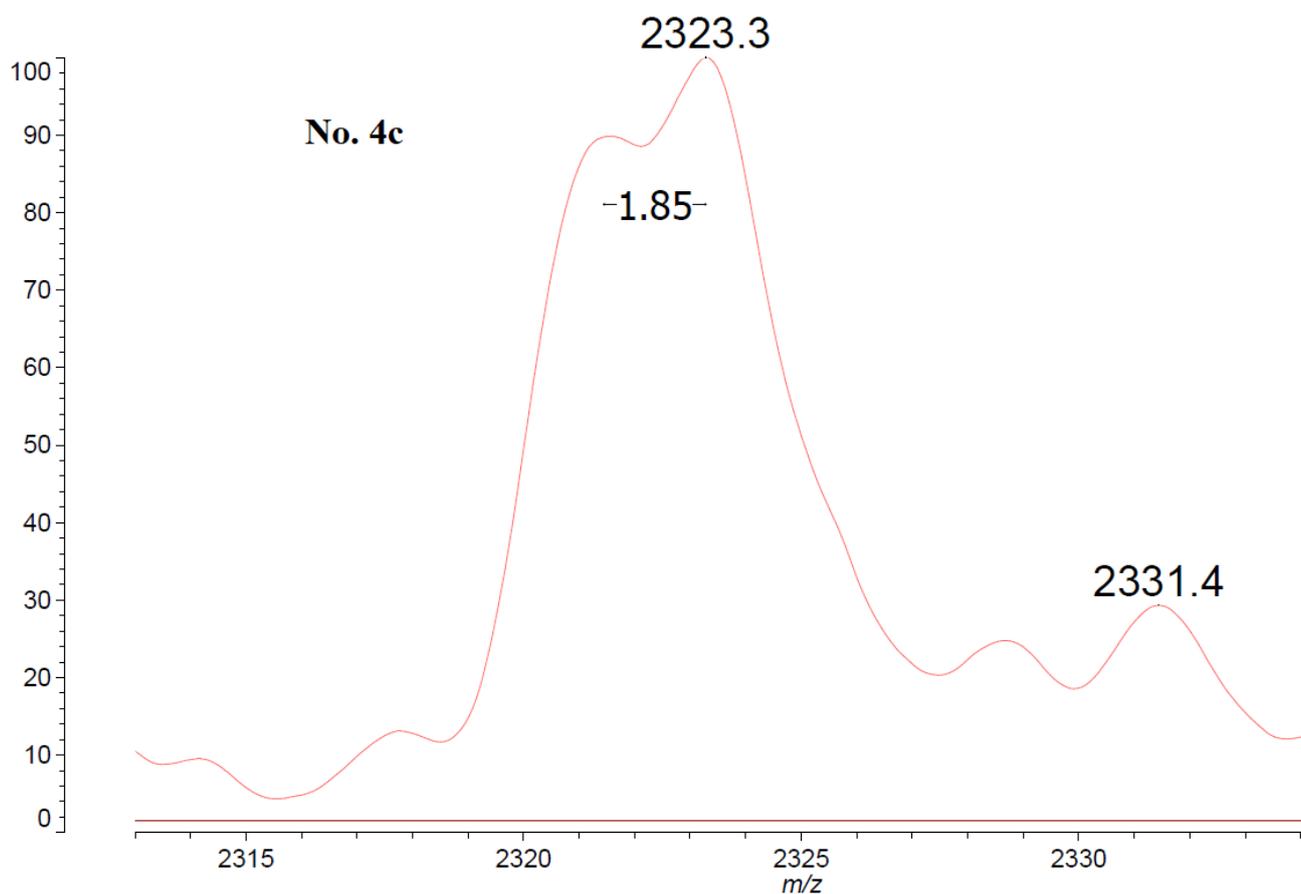


Figure S5. Amplification of peak corresponding to sodium carboxylate salt of linear polymer with proton adduct and potassium adducts of the cyclic structure. The difference in calculated molar weights of both architectures for the same polymerization degree is less than 2 units.

Analysis of FTIR measurements.

In the case of pure TBD (red line at Fig. S6(a) and S7(a)), one can observe a broad IR absorption band at the higher frequency range (3260, 3178, 3116 and 3030 cm^{-1}) mostly ascribed to the stretching vibration of the associated N-H group. The free N-H stretch in acetonitrile solution of TBD was observed by Ng et al. as a sharp peak at 3410 cm^{-1} ³. Because of hydrogen bond interactions in the solid-state of TBD, this absorption band is not visible at our spectroscopic studies. The bands assigned to the stretching vibrations of C-H groups were observed at 2924 and 2850 cm^{-1} (dotted lines at Fig S6(a)). The Bohlmann bands, i.e., a decrease of the stretching frequency of a C-H bond antiperiplanar to the lone pair of electrons on the nitrogen atom, appeared in the 3000-2800 cm^{-1} frequency region

(2880 and 2813 cm^{-1}). The vibration frequency at 1635 cm^{-1} region was attributed to the antisymmetric stretching modes of C–N bonds of two rings with the dominant contribution in the vibrational form of the internal stretching vibrational coordinate of C=N bond ⁴ (a dotted line at Fig. S6(a)). The peak located at 1517 cm^{-1} was principally attributable to the bending mode of the N-H bond. The 1400-1270 cm^{-1} region represented stretching modes of C-C and C-N bonds mixed with the C-H bending modes of methylene group ⁴.

After interpretation of interactions present in the pure catalyst, we proceed further to analyze FTIR spectra of the reference system, TBD mixtures with BnOH, as a function of the BnOH:TBD ratio (data showed at Fig. S6(a) and Fig. S7(a)). The dissolution effects suggest the existence of the hydrogen bonding interactions between TBD and BnOH molecules. For the 1:0.5, 1:0.75 and 1:1 BnOH:TBD mixtures, a broad band in the 3600-3000 cm^{-1} frequency range, originated from the stretching vibration of the hydrogen-bonded OH groups, was noticed. The free N-H stretch of TBD was also found at 3420 cm^{-1} , which can be caused by the breaking of associated catalyst molecules. Additionally, a weak IR peak about 3650 cm^{-1} , observed in the OH stretching region of the 1:0.5, 1:0.75 and 1:1 BnOH:TBD mixtures, may be assigned to the free OH groups. After dissolving TBD in excess of BnOH, the $\nu(\text{C}=\text{N})$ band was red-shifted (from 1635 cm^{-1} in pure TBD to 1611 cm^{-1} in the 1:0.5 BnOH:TBD mixture) demonstrating the existence of hydrogen bonding between TBD and BnOH (Fig. S6(a) and S7(a)). The observed perturbation of the OH and C=N group vibrations indicates that the BnOH molecules probably act as proton donors forming hydrogen-bonded complexes with TBD. That is consistent with the mechanism processing through H-bonds discussed in details at Ref.⁵.

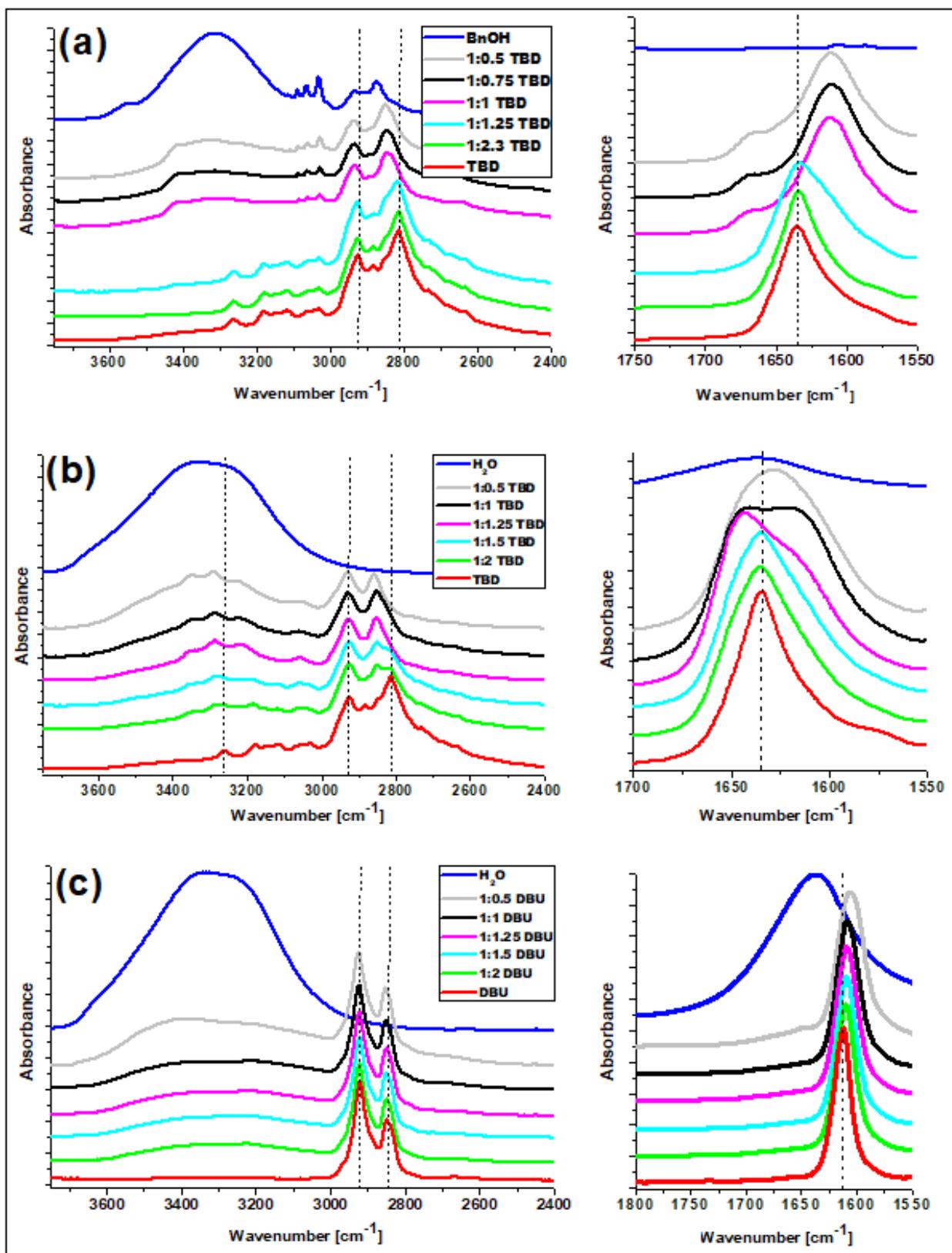


Fig. S6. FT-IR spectra of (a) BnOH:TBD, (b) H₂O:TBD and (c) H₂O:DBU mixtures in the (left) 3750-2400 cm⁻¹ and (right) the C=N stretching frequency ranges.

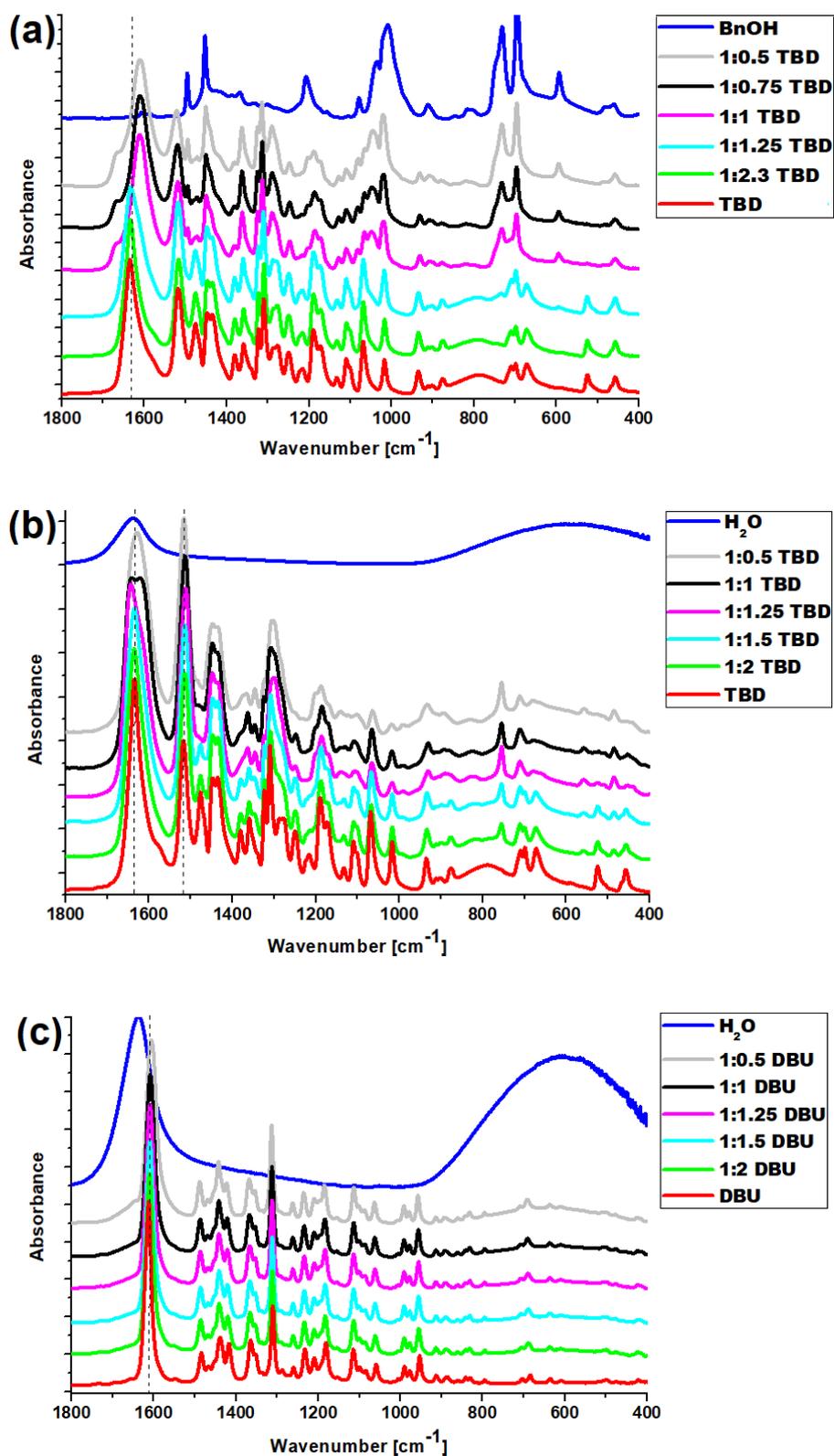


Fig. S7. FT-IR spectra of (a) BnOH:TBD, (b) H_2O :TBD and (c) H_2O :DBU mixtures in the 1800-400 cm^{-1} frequency range.

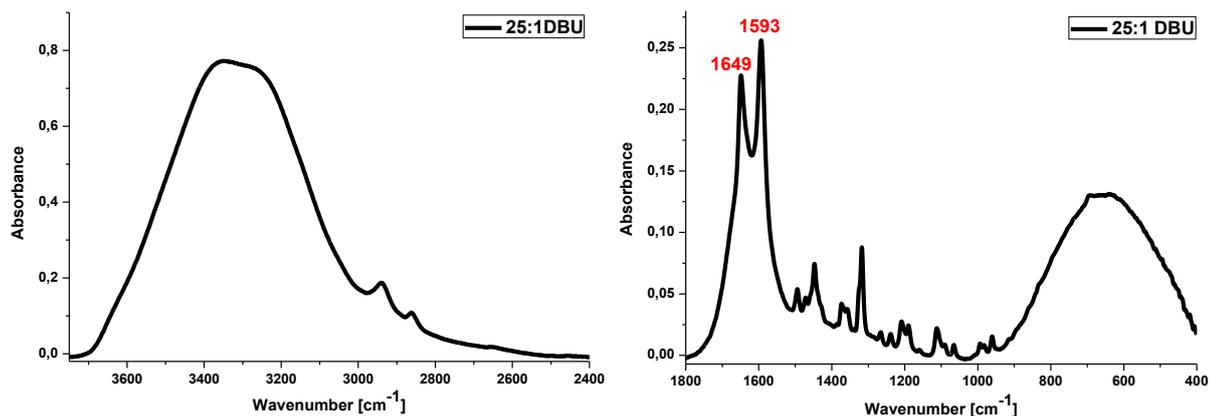


Fig. S8. FT-IR spectra of the 25:1 H₂O:DBU mixture in the (left) 3750-2400 cm⁻¹ and (right) 1800-400 cm⁻¹ frequency ranges.

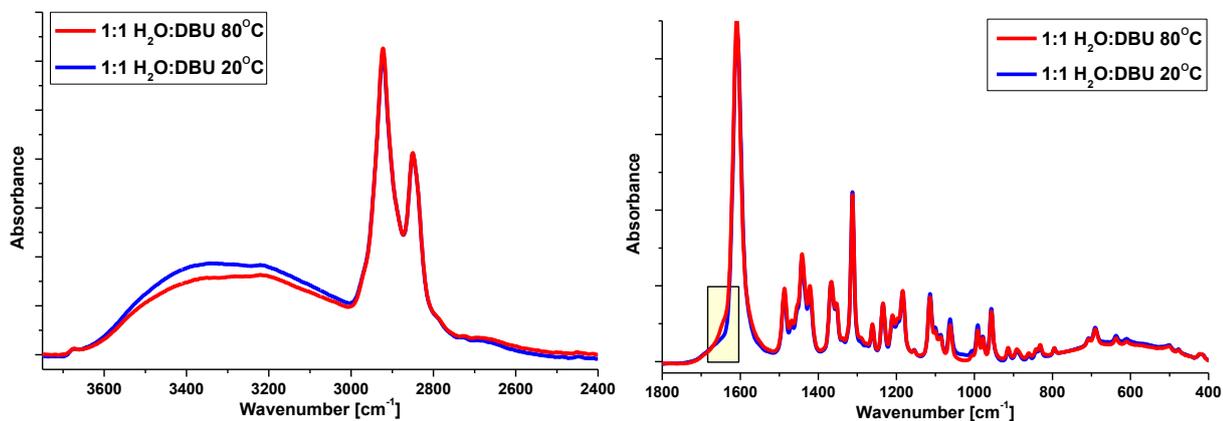


Fig. S9. FT-IR spectra of the 1:1 H₂O:DBU mixture in the (left) 3750-2400 cm⁻¹ and (right) 1800-400 cm⁻¹ frequency ranges.

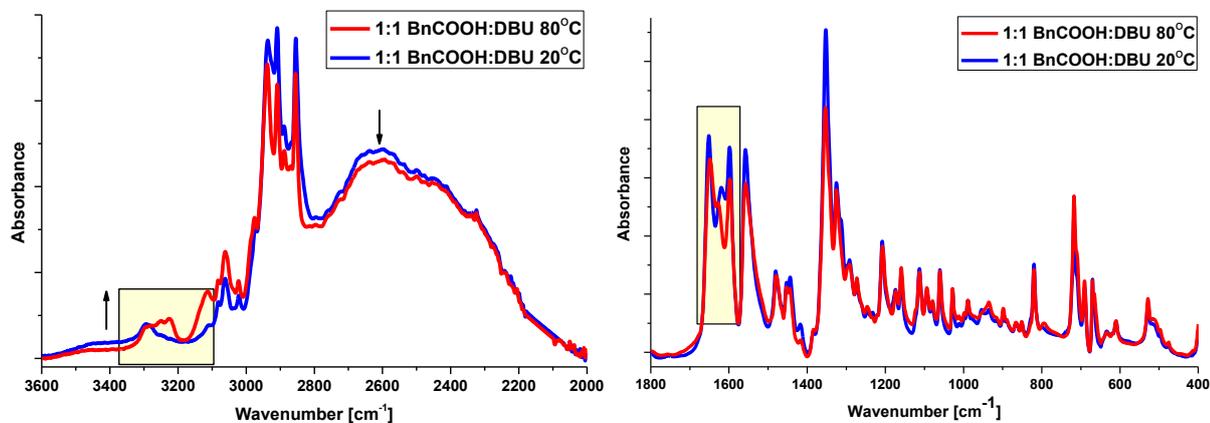


Fig. S10. FT-IR spectra of the 1:1 BnCOOH:DBU mixture in the (left) 3600-2000 cm⁻¹ and (right) 1800-400 cm⁻¹ frequency ranges.

References:

- 1 G. P. Johari and E. Whalley, *Faraday Symp. Chem. Soc.*, 1972, **6**, 23–41.
- 2 C. M. Roland, S. Hensel-Bielowka, M. Paluch and R. Casalini, *Reports Prog. Phys.*, 2005, **68**, 1405–1478.
- 3 S. W. Ng, P. Naumov, S. Chantrapromma, S. S. S. Raj, H. K. Fun, A. R. Ibrahim, G. Wojciechowski and B. Brzezinski, *J. Mol. Struct.*, 2001, **569**, 139–145.
- 4 B. Brzezinski, G. Schroeder, V. I. Rybachenko, L. I. Kozhevina and V. V. Kovalenko, *J. Mol. Struct.*, 2000, **516**, 123–130.
- 5 A. Chuma, H. W. Horn, W. C. Swope, R. C. Pratt, L. Zhang, B. G. G. Lohmeijer, C. G. Wade, R. M. Waymouth, J. L. Hedrick and J. E. Rice, *J. Am. Chem. Soc.*, 2008, **130**, 6749–6754.