Electronic Supporting Information

for

Fast curing polyhydroxyurethanes via ring opening polyaddition of low viscous cyclic carbonates and amines

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Table of content

Materials

Trimethylolpropane triglycdiyl ether (technical grade), neopentylglycol diglycidyl ether (technical grade), tetrabutylammonium iodide (reagent grade, 98%), branched polyethylenimine (average M_w ~ 800 by LS, average M_n ~ 600 by GPC) and 1,2,4,5-tetramethylbenzene (standard for quantitative NMR, TraceCERT®) were purchased from Sigma-Aldrich. 1,4-cyclohexanedimethanol diglycidyl ether and 1,6-hexanediol diglycidyl ether were brought from Carbosynth Europe. Tris(2-aminoethyl)amine was purchased from TCI Chemicals Europe. Dimethylsulfoxide-d_6 (99,8%) in ampoules were purchased from Deutero GmbH. Priamine™ 1071 from Croda were kindly provided by Dentsply Sirona. Dry ice purchased from Linde AG was used as carbon dioxide source. All chemicals were used as received. Double chamber syringes and static mixers (5 ml) were purchased from Adchem GmbH.

Instrumentation

^{1}H-NMR: (^{1}H-Nuclear Magnetic Resonance Spectroscopy) NMR spectra were recorded in deuterated DMSO on a 600 MHz Bruker Avance III with a strength of 14.1 Tesla, 64 scan rates and a d_1 pulse time of 10 seconds. Chemical shifts of all NMR spectra were reported in delta (δ) expressed in parts per million (ppm). The following abbreviations are used to indicate the multiplicities: t: triplet; m: multiplet. MestReNova was used to evaluate the spectra.

Rheology: Rheological studies were performed on a HAAKE MARS II rheometer, using a heatable parallel plate construction (35 mm). The measurements were performed in an oscillation experiment with frequency of 1 Hz and deformation of γ_0 = 0.03 +/- 0.005. For evaluation, storage modulus (G'), loss modulus (G'') and dynamic viscosity ($|\eta^*|$) were plotted against time by using Origin Pro 2019 9.6.0.172.

FTIR: (Fourier Transform Infrared Spectroscopy) Nicolet FT-IR-6700 from Thermo Fisher was used in the range of 400-4000 cm^{-1}. For evaluation, Omnic 7.4 as a software was used.

ESI-MS: (Electrospray Ionization Mass Spectrometer) Measurements were performed on an Agilent 1260 Infinity instrument coupled to a 6120 Quadrupole LC/MS containing an Electrospray Ionization (ESI) source. Measurements were operated in positive ionization mode in a m/z range of 200 to 2000. OpenLab ChemStation software from Agilent Technologies was used for evaluation.

DSC: (Differential Scanning Calorimetry) Measurements were performed with DSC3 from Mettler Toledo equipped with autosampler. Indium and zinc were employed as calibrants. 40 µl standard aluminum crucibles were punctured before use and all experiments were conducted under nitrogen atmosphere with a flow of 30 ml/min. Glass transition temperatures were evaluated by heating/cooling rate of 10 K/min from 223.15 K to 423.15 K with three cycles to give an average value for Tg.

General Methods

Synthesis of cyclic carbonate monomers (1-4)

As described in literature[1, 2], respective glycidyl ether was stirred and cooled in a flask for a few minutes using an ice bath. Subsequently, 2.5 mol% tetrabutylammonium iodide (TBAI) was added in small portions. After the flask was sealed with a septum, cannula gas in- and outlets were installed. Carbon dioxide was bubbled through the mixture at room temperature for a few minutes and the CO_2-insertion was continued while heating the reaction mixture up to 85 °C. After complete conversion of oxirane moieties, revealed by ^{1}H-NMR spectroscopy, the reaction was stopped. The products were recovered as viscous oils in quantitative yields. Since ammonium compounds also catalytically favour the aminolysis of cyclic carbonates, TBAI is not extracted from the products.[3] Each cyclic carbonate product therefore contains 2.5mol% TBAI.

Transcarbonylation of comparatively pure 1,4-butanediglycidyl ether as an example for CC without or less by-products:

The glycidyl ethers used in this work were technical products with lower oxirane values. An exception was 1,4-butanediglycidyl ether, which was the only starting compound used with a comparatively high purity of >95%. Transcarbonylation of low-viscous 1,4-butanediglycidyl ether resulted in a waxy product. The reaction mixture solidified during the synthesis at 85 °C after reaching a conversion of about 89% and could not be liquefied again even after increasing the reaction temperature up to 100 °C. The conversion-related increase of viscosity correlates with the CO_2 addition and the associated increasing polarity of the components. It is conceivable that this effect has a stronger influence on the viscosity of compounds with comparatively low molecular weights, as in the case of 1,4-butanediglycidyl ether. This leads to a first assumption that glycidyl ethers with a high purity tend to form solid CCs. The by-products contained in technical glycidyl ethers and CCs probably reduce their crystallization tendency and lead to rather viscous oils. By-products such as hydrolyzed oxiranes cannot participate in PHU network forming reactions, and thus may reduce the curing capacity and act as internal or external plasticizers.

Quantitative ^{1}H-qNMR experiments

The sample to be examined was weighed precisely into a microreaction vessel and subsequently, 1,2,4,5-tetramethylbenzene (TMB) as an internal standard compound was added. The ratio of sample and internal standard was one-third the mass of the sample. Then, 2.5 ml of DMSO-d_6, were taken off with a precision pipette and introduced into the microreaction vessel in countercurrent of nitrogen. After mixing the compounds thoroughly on a vortex mixer, the container is centrifuged for one minute at 1000 rpm. Then 4x 0.6 ml of the solution were removed with a 1 ml syringe and added in NMR tubes while using nitrogen countercurrent. Samples are measured in a 600 MHz NMR with a strength of 14.1 Tesla, 64 scan rates and a d_1 pulse time of 10 seconds. After measuring, the program MestReNova was used to normalize the spectra to the solvent signal (here DMSO-d_6, 2.5 ppm) and to perform a baseline correction (Whittaker Smoother). Then, the methyl proton signal of TMB and the cyclic carbonate- or glycidyl ether signal of the sample was integrated.

Exemplary evaluation description for cyclic carbonate content:

1. Calculation of n(TMB) from m(TMB) and M(TMB) and therefrom c(TMB) by dividing with V(DMSO-d_6)
2. Multiply the integral of the signal to be considered (determined in the spectrum) by c(TMB) calculated under 1. and obtain c(CC).
3. The c(CC) obtained in 2. is multiplied by V(DMSO-d_6) to obtain n(CC).
4. If n(CC) is divided by m(sample), the CC content of the sample is obtained with the unit mmol/mg.
5. All four NMR samples of the cyclic carbonate monomer to be considered are examined according to the above calculation, validated and averaged for the final CC content.

By this method, cyclic carbonate content, glycidyl ether content and therefrom the conversion of transcarbonylation was examined. (Tab. S1)

*Table S1: Conversion of cyclic carbonates **1-4** examined by quantitative ^{1}H-qNMR*

CC	Conversion [%]
1	98
2	96
3	95
4	99

Rheology experiments

To prepare the cyclic carbonate-amine mixtures, the corresponding cyclic carbonate monomer was weighed precisely in a glass container. Then, the amine component was added in equimolar amounts based on the functional groups and the mixture was stirred thoroughly with a spatula for one minute. The mixture was subsequently applied to the pre-tempered 35 mm plate at 40 °C and the rheological experiment was started. The measurements were performed in an oscillation experiment with frequency of 1 Hz and deformation of γ_0 = 0.03 +/- 0.005. For evaluation, storage modulus (G'), loss modulus (G'') and dynamic viscosity ($|\eta^*|$) were plotted against time. The intersection of G' and G'' corresponds to the rheological definition of gelation time (t_{gel}) on the x-axis. The reached plateau of G' after 12h is taken as the final hardness of the cured mixture. The pot life (t_{pot}) is the time until the mixture can be processed before the viscosity increases up to a specific value (here 300 Pa*s).

Rheological data for application-oriented mixture (CC: 40 wt% of 1 and 60 wt% of 3 / Amine: 86 mol% of BPEI (6) and 14 mol% of PA71 (7)) at 20 °C and 37 °C:

Table S2: Rheological data for application-oriented mixture (CC: 40 wt% of 1 and 60 wt% of 3 / Amine: 86 mol% of BPEI (6) and 14 mol% of PA71 (7)) at 20 °C and 37 °C.

Temperature [°C]	t_{gel} [1] [min]	t_{pot} [2] [min]	G' plateau [3] [Pa]	Tg [4] [°C]
20	116	6.8	4.3×10^6	-16; 32
37	16	6.4	2.1×10^6	-17; 31

[1]: time at intersection of G' and G'', [2]: time at η = 300 Pa·s, [3]: G' at t = 12 h, [4]: Tg measured by DSC

Water uptake studies of PHUs

To determine water absorption, pieces of PHUs were first cut out the same size and weighed using a precision balance. The pieces were then transferred separately into glass containers and 5 ml of distilled water was added to each. After 24 hours at room temperature, the PHUs were removed with

tweezers, carefully dabbed with a lint-free cloth and the weight determined. The pieces were then placed back into the water medium and the mass determination repeated after one week. The obtained masses and calculated water uptake for **1** and **3** containing PHUs are shown in table S3.

*Table S3: Masses of **1**, **3** and TAEA containing PHUs and calculated water uptake.*

1 [wt%]	**3** [wt%]	$Mass_{dry}$ [mg]	$Mass_{24h}$ [mg]	Water uptake$_{24h}$ [wt%]	$Mass_{1week}$ [mg]	Water uptake$_{1week}$ [wt%]
100	0	63.06	84	33.2	84.1	33.4
75	25	89.06	117.3	31.7	117.3	31.7
50	50	84.72	109.2	28.9	109.2	28.9
25	75	88.96	114.1	28.3	114	28.1
0	100	103.55	132.7	28.2	132.8	28.2

Calculation of water uptake:

$$Water\ uptake_{24h\ or\ 1week}\ [wt\%] = \left(\frac{m_{24h\ or\ 1week}}{m_{dry}} - 1\right) * 100$$

Analytical Data

For the synthesis of desired cyclic carbonate monomers, glycidyl ether compounds in technical grade were used without further purification. Attempts to purify desired precursors by one-step vacuum distillation were not efficient. We assume that hydroxy group containing byproducts from hydrolyzed oxiranes are contained in the cyclic carbonate monomers. For this reason, cyclic carbonate functionality rather than product purity will be evaluated below. ^{1}H-NMR analysis of cyclic carbonates **1-4** show broadened signals around 3-4 ppm proving the assumed existence of non-desired hydroxy groups.

Cylic carbonate monomer **1**

4,4'-(((2-Ethyl-2-(((2-oxo-1,3-dioxolan-4 yl)methoxy)methyl)propane 1,3 diyl)bis(oxy))bis(methylene))- bis(1,3-dioxolan-2-one)

1
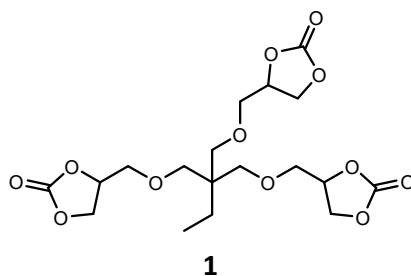
^{1}H-NMR (600 MHz, DMSO-d$_6$): δ [ppm] = 0.76-0.85 (m, -C$\underline{H_3}$, 3.3H); 1.21-1.37 (m, -C$\underline{H_2}$CH$_3$, 2.5H); 3.11-3.93 (m, -OC$\underline{H_2}$-); 4.21-4.56 (m, -C$\underline{H_2}$OC(=O)O-, 6H); 4.88-4.95 (m, -C$\underline{H}$OC(=O)O-, 3H).

ESI-MS: calculated M_{exact} (m/z) = 434.13; found [M+H$^+$] (m/z) = 435 and [M+Na$^+$] (m/z) = 457

FTIR: 1782 cm^{-1} (C=O, cycl.)

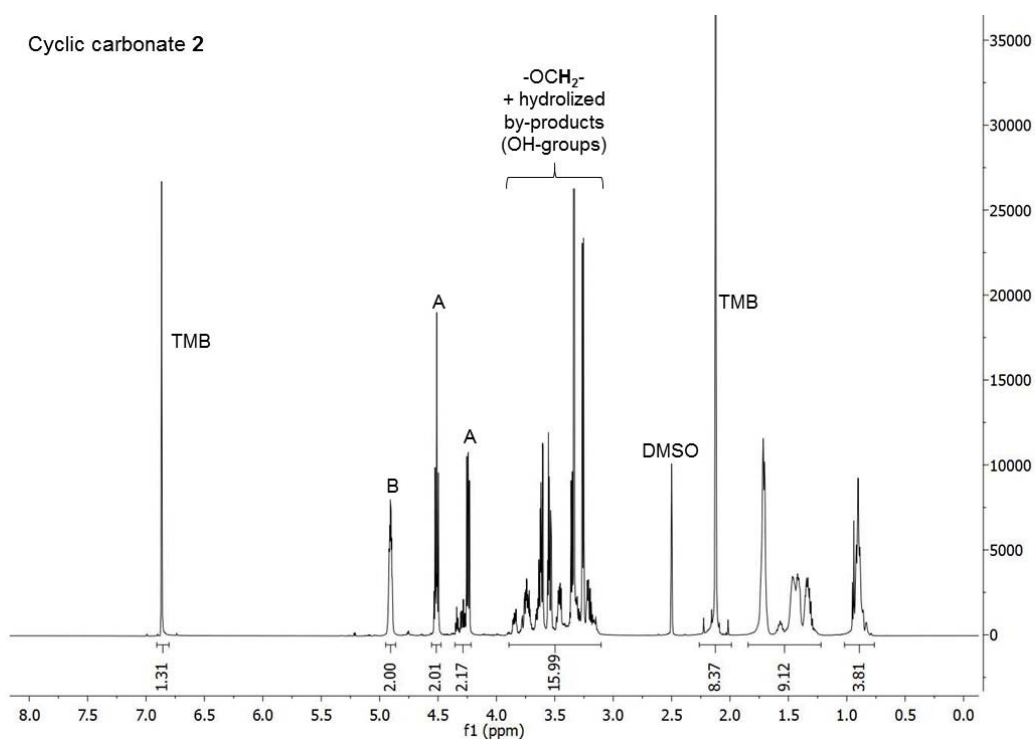*Figure S1: 600 MHz ^{1}H-NMR spectra of cyclic carbonate **1** in deuterated DMSO (contains TMB as internal standard). Signals A and B mark cyclic carbonate protons.*
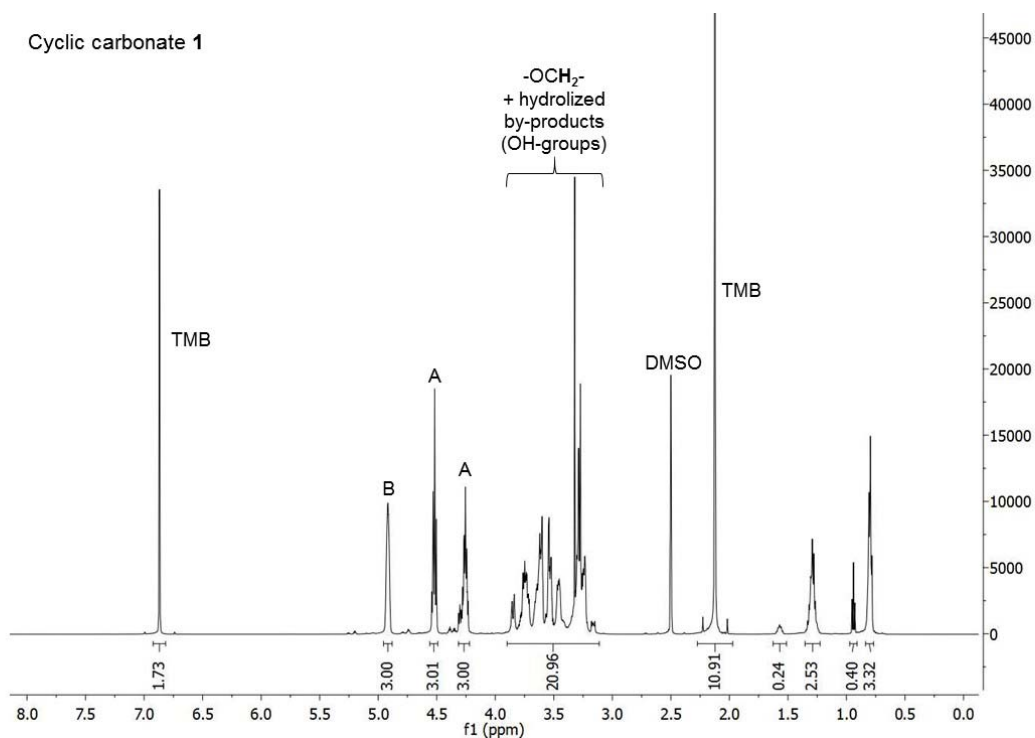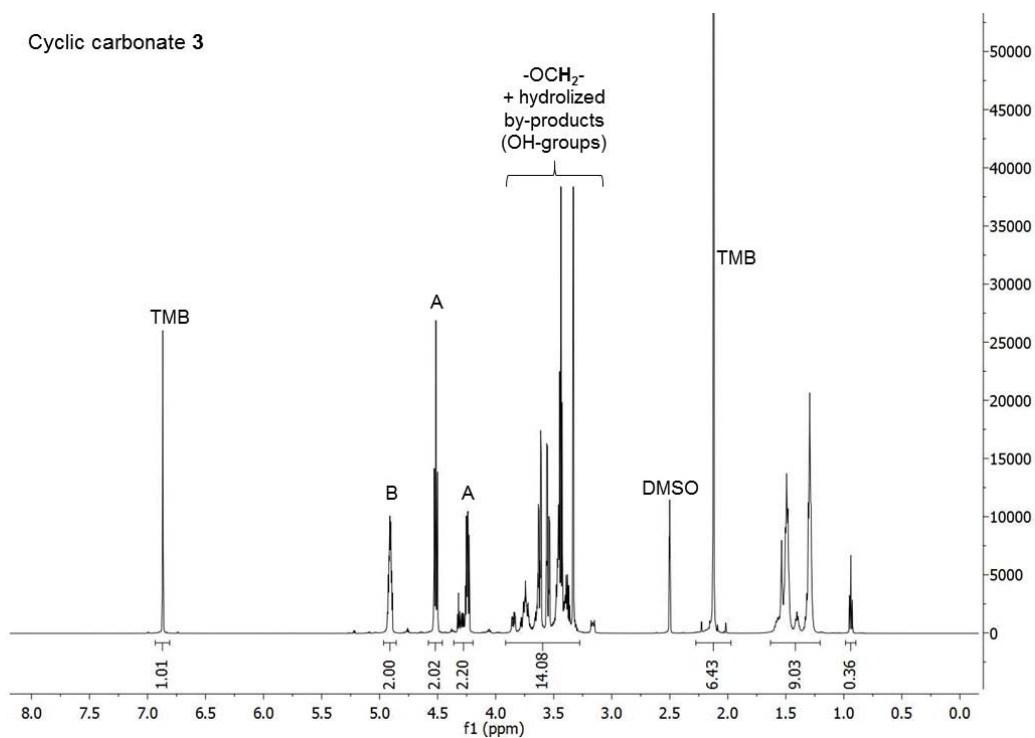
Cylic carbonate monomer 2

4,4'-(((Cyclohexane-1,4-diylbis(methylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one)
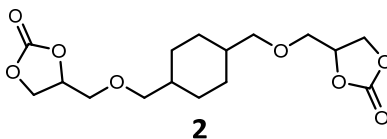
^{1}H-NMR (600 MHz, DMSO-d$_6$): δ [ppm] = 0.80-1.81 (m, -CH-, -CH$_2$-, 12.9H); 3.10-3.91 (m, -OCH$_2$-); 4.21-4.55 (m, -CH$_2$OC(=O)O-, 4.2H); 4.86-4.95 (m, -CHOC(=O)O-, 2H).

ESI-MS: calculated M$_{exact}$ (m/z) = 344.15; found [M+H$^+$] (m/z) = 345 and [M+Na$^+$] (m/z) = 367

FTIR: 1782 cm^{-1} (C=O, cycl.)

*Figure S2: 600 MHz ^{1}H-NMR spectra of cyclic carbonate **2** in deuterated DMSO (contains TMB as internal standard). Signals A and B mark cyclic carbonate protons.*

Cylic carbonate monomer **3**

4,4'-((Hexane-1,6-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one)

3
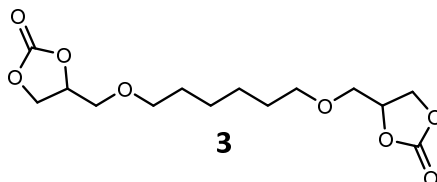
^{1}H-NMR (600 MHz, DMSO-d$_6$): δ [ppm] = 1.22-1.63 (m -C$\underline{H}_2$-, 9H); 3.32-3.88 (m, -OC$\underline{H}_2$-); 4.20-4.55 (m, -C$\underline{H}_2$OC(=O)O-, 4.2H); 4.88-4.95 (m, -C$\underline{H}$OC(=O)O-, 2H).

ESI-MS: calculated M$_{exact}$ (m/z) = 318.13; found [M+H$^+$] (m/z) = 319 and [M+Na$^+$] (m/z) = 341

FTIR: 1783 cm^{-1} (C=O, cycl.)

*Figure S3: 600 MHz ^{1}H-NMR spectra of cyclic carbonate **3** in deuterated DMSO (contains TMB as internal standard). Signals A and B mark cyclic carbonate protons.*

Cylic carbonate monomer **4**

4,4'-(((2,2-Dimethylpropane-1,3-diyl)bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one)

4
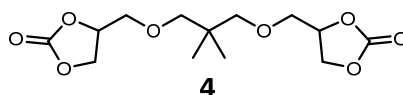
^{1}H-NMR (600 MHz, DMSO-d$_6$): δ [ppm] = 0.77-0.87 (m, -C$\underline{H}_3$, 8.4H); 3.10-3.92 (m, -OC$\underline{H}_2$-); 4.22-4.57 (m, -C$\underline{H}_2$OC(=O)O-, 4H); 4.87-4.96 (m, -C$\underline{H}$OC(=O)O-, 2H).

ESI-MS: calculated M$_{exact}$ (m/z) = 304.12; found [M+H$^+$] (m/z) = 305 and [M+Na$^+$] (m/z) = 327

FTIR: 1786 cm^{-1} (C=O, cycl.)

Cyclic carbonate **4**

-OC**H**₂- + hydrolized by-products (OH-groups)
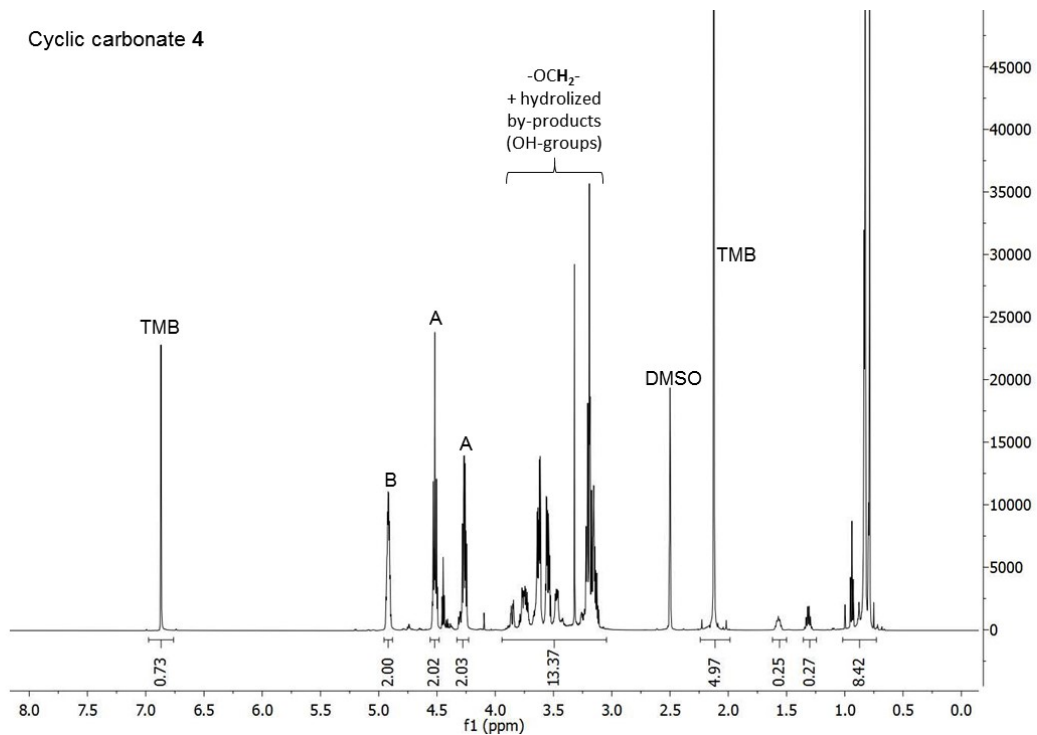
*Figure S4: 600 MHz ¹H-NMR spectra of cyclic carbonate **4** in deuterated DMSO (contains TMB as internal standard). Signals A and B mark cyclic carbonate protons.*

Rheology Data

Viscosity of cyclic carbonates **1**-**4** at 25 °C

*Table S4: Viscosity of cyclic carbonates **1**-**4***

CC	Viscosity [Pa*s]
1	300
2	30
3	1
4	5

Cyclic carbonates **1**-**4** with TAEA at 40 °C
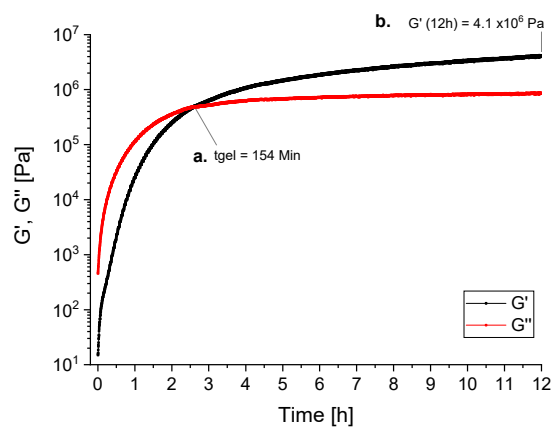
Figure S5: Cyclic carbonate 2 with TAEA at 40°C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)
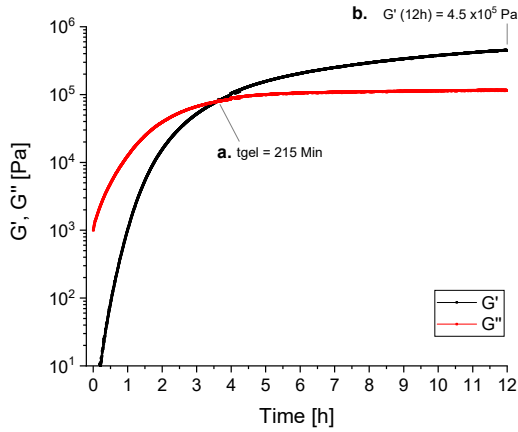
Figure S6: Cyclic carbonate 3 with TAEA at 40°C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)
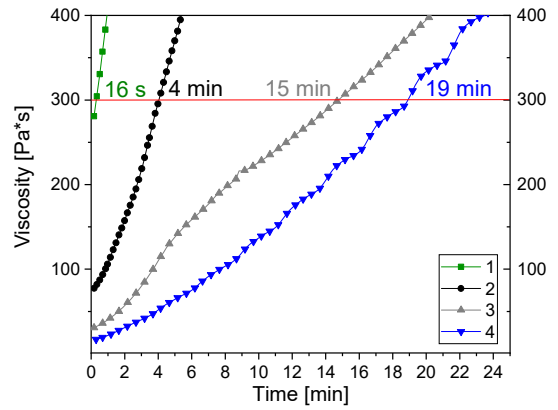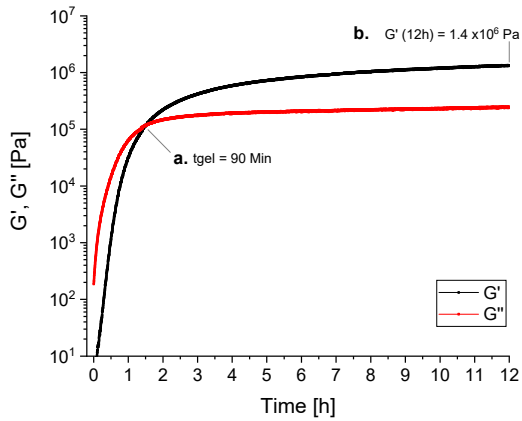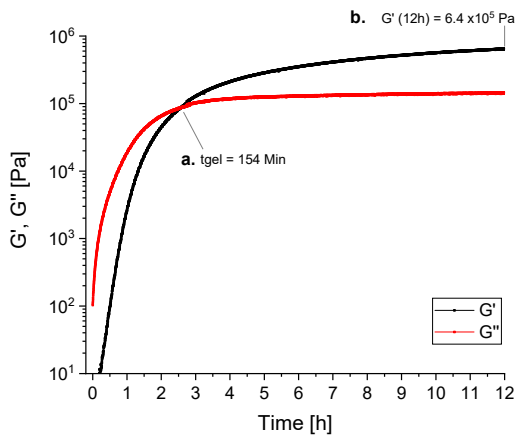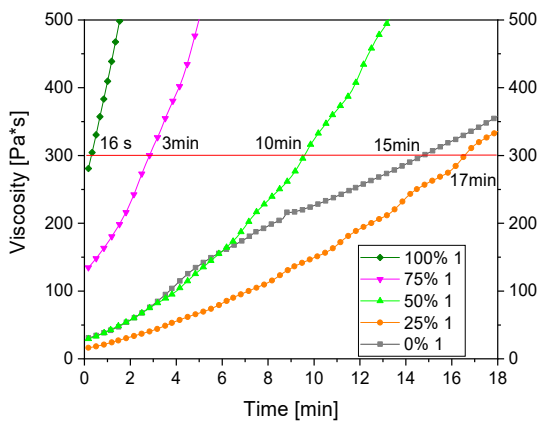

*Figure S9: Determination of pot life of cyclic carbonates 1-4 with TAEA at 40 °C (pot life limit at 300 Pa*s)*

Cyclic carbonates **1** and **3** as mixtures with TAEA at 40 °C
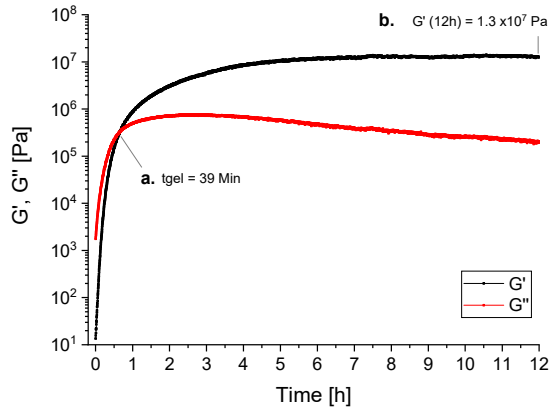
Figure S7: Cyclic carbonate 1 with TAEA at 40°C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)
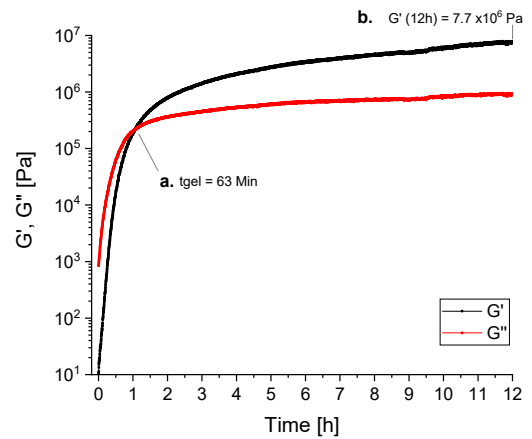
Figure S10: Cyclic carbonate mixture of 75 wt% 1 and 25 wt% 3 with TAEA at 40°C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)
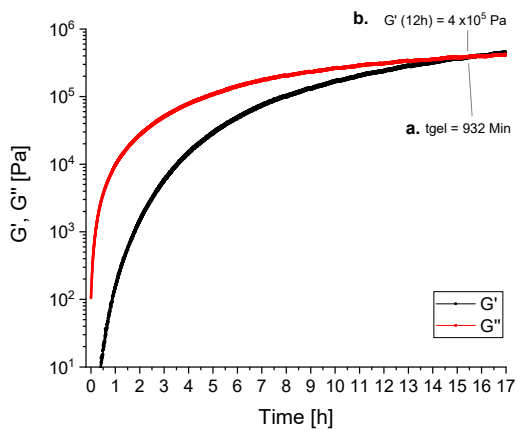
Figure S8: Cyclic carbonate 4 with TAEA at 40°C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)

Figure S11: Cyclic carbonate mixture of 50 wt% 1 and 50 wt% 3 with TAEA at 40°C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)
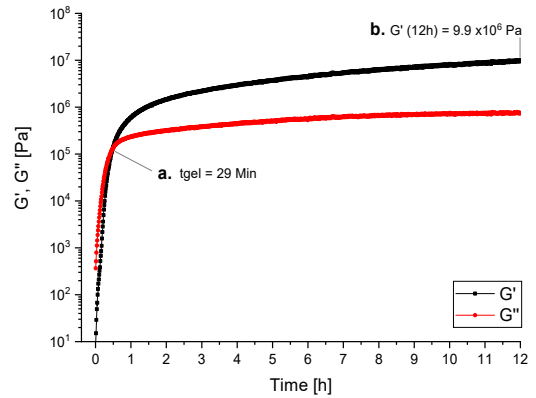

Figure S14: 100 mol% BPEI with cyclic carbonate 2 at 40 °C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)
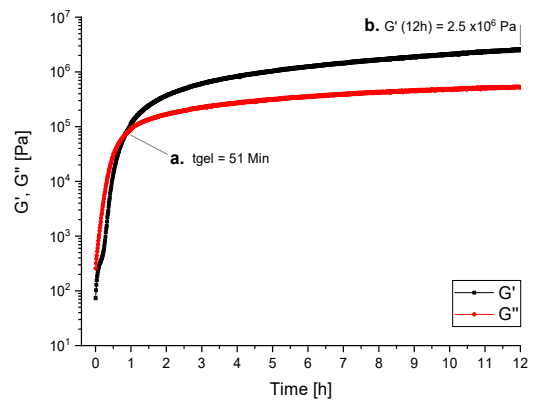

Figure S12: Cyclic carbonate mixture of 25 wt% 1 and 75 wt% 3 with TAEA at 40°C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)

Figure S15: 75 mol% BPEI and 25 mol% PA71 with cyclic carbonate 2 at 40 °C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)
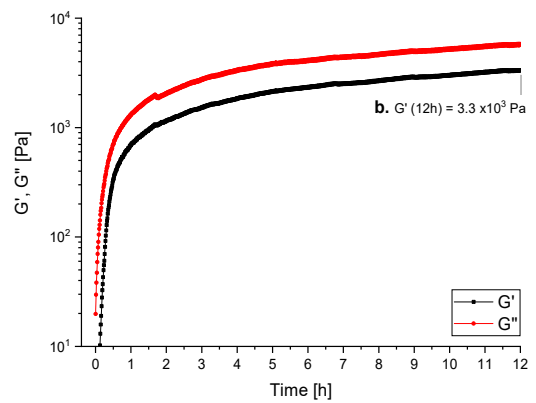

*Figure S13: Determination of pot life of cyclic carbonate mixtures of cyclic carbonate 1 and 3 with TAEA at 40 °C (pot life limit at 300 Pa*s)*

Figure S16: 50 mol% BPEI and 50 mol% PA71 with cyclic carbonate 2 at 40 °C; Determination of final storage modulus G' at 12h (b.)
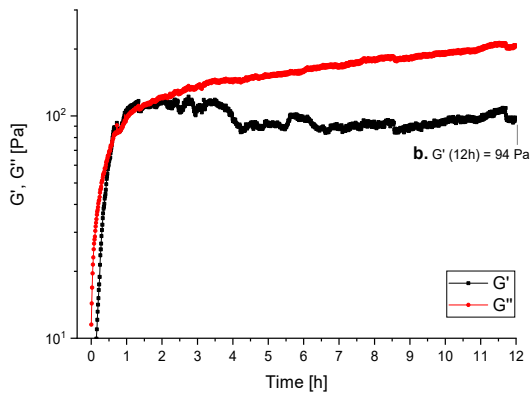
11

Figure S17: 100 mol% PA71 with cyclic carbonate 2 at 40 °C; Determination of final storage modulus G' at 12h (b.)
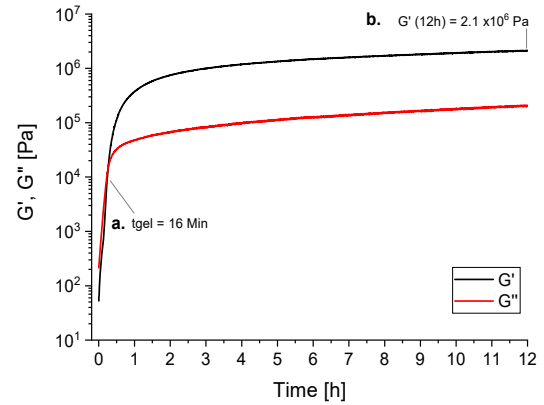

Figure S19: Cyclic carbonate 1 (40 wt%) and 3 (60 wt%) with BPEI (86 mol%) and PA71 (14 mol%) at 40 °C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)
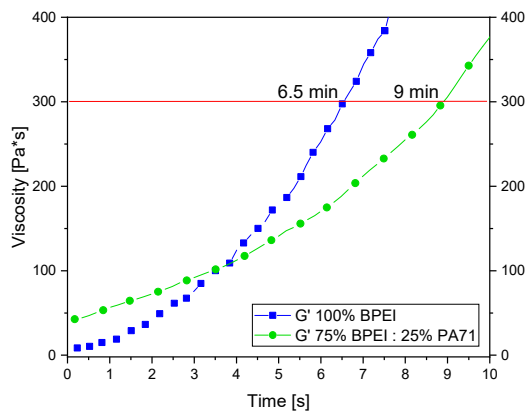

*Figure S18: Determination of pot life of cyclic carbonate 2 with BPEI and PA71 at 40 °C (pot life limit at 300 Pa*s)*
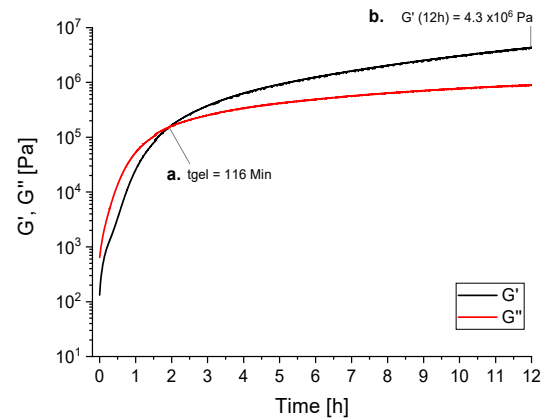

Figure S20: Cyclic carbonate 1 (40 wt%) and 3 (60 wt%) with BPEI (86 mol%) and PA71 (14 mol%) at 20 °C; Determination of gelation time (a.) and final storage modulus G' at 12h (b.)

12

DSC Thermogram
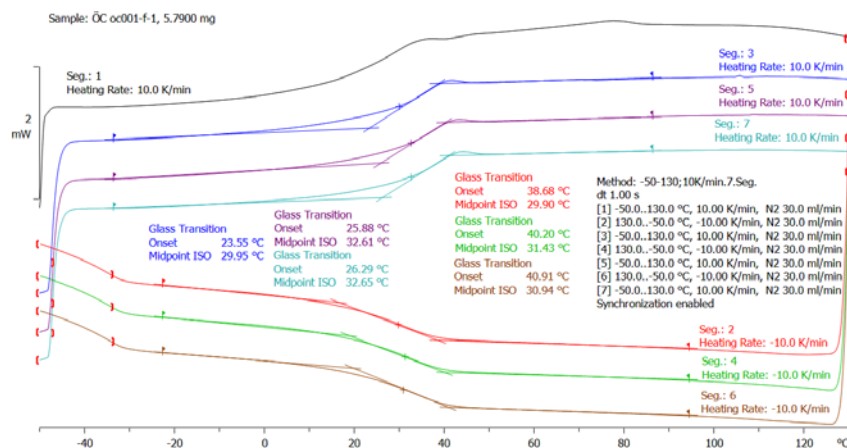
Exemplary for cyclic carbonate monomer **2** with TAEA

Figure S21: Thermogram of PHU made of cyclic carbonate 2 with TAEA at 40°C. Determination of Tg.

FTIR Spectra

Exemplary for PHU based on 40 wt% of **1** and 60 wt% of **3** and 86 mol% of BPEI (**6**) and 14 mol% of PA71 (**7**) cured at 37 °C. No cyclic carbonate signal (v(C=O) ~ 1780 cm^{-1}) can be detected.

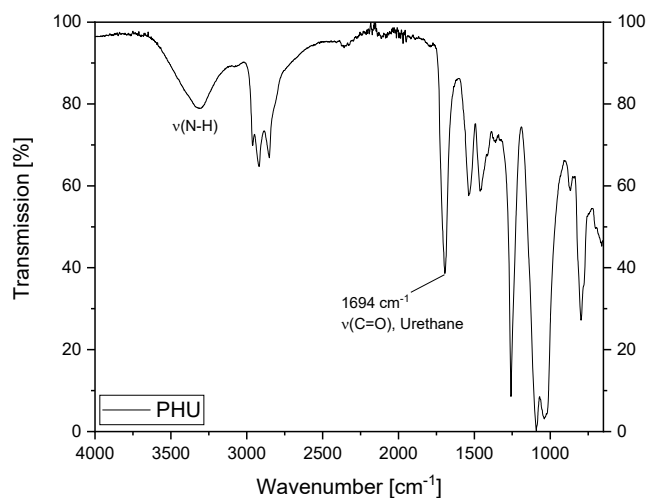*Figure S22: PHU based on 40 wt% of 1 and 60 wt% of 3 and 86 mol% of BPEI (6) and 14 mol% of PA71 (7) cured at 37 °C.*

Literature

1.   N. Kihara, N. Hara and T. Endo, *The Journal of Organic Chemistry*, 1993, **58**, 6198-6202.
2.   M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing and C. Detrembleur, *Catalysis Science & Technology*, 2017, **7**, 2651-2684.
3.   C. D. Diakoumakos and D. L. Kotzev, *Macromolecular Symposia*, 2004.