

# Supporting Information

## Pure Aliphatic Polycarbonate Networks via Photoinduced Anionic Ring-Opening Polymerization at Elevated Temperatures

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### Table of content

2.2 Monomer synthesis.....	2
2.2.1 General Procedure .....	2
2.2.2 Synthesis of PBG.....	8
3.2 Reactivity studies .....	11
3.2.1 Photo-DSC.....	11
3.2.3 Photorheology .....	12
3.3 Thermal and (thermo-)mechanical analysis.....	13
Literature .....	14

## 2.2 Monomer synthesis

### 2.2.1 General Procedure

#### 2.2.1.1 -Synthesis of 5,5-diethyl-1,3-dioxane-2-one (Et-C)

The synthesis of Et-C was investigated in two different approaches. The first approach was performed by **transesterification** of diethyl carbonate with 2,2-diethylpropane-1,3-diol using sodium hydride as catalyst. For this, 1.88 g (16 mmol, 1.4 eq) of diethyl carbonate were charged into a 10 mL three necked round-bottom flask (RBF) equipped with a magnetic stirring bar. 0.1 eq sodium hydride in paraffin were added at room temperature under N<sub>2</sub> atmosphere, followed by the addition of 1.50 g 2,2-diethylpropane-1,3-diol. The reaction was stirred at room temperature for five minutes before equipping the RBF with a distillation apparatus. Formed ethanol was distilled off at 120 °C. After complete distillation of ethanol, the reaction solution was cooled down to room temperature. Excess diethyl carbonate was then distilled off under reduced pressure at 60 °C, increasing the temperature gradually to 220 °C. The product was then purified *via* Kugelrohr distillation at 180-200 °C and 0.1 mbar to yield 1.29 g (71.9%).

The second approach for the synthesis of Et-C was conducted via the CDI method as described in section 2.2.1.1 of the manuscript. The synthesis *via* the CDI method was scalable up to 8 g of starting materials, in contrast to the limiting factor of the transesterification method requiring Kugelrohr distillation. 7.6 g (80%) of the pure product were obtained as white crystals.

Melting point [2] and <sup>1</sup>H-NMR (Figure S1, Figure S2)[3] are consistent with literature reports.

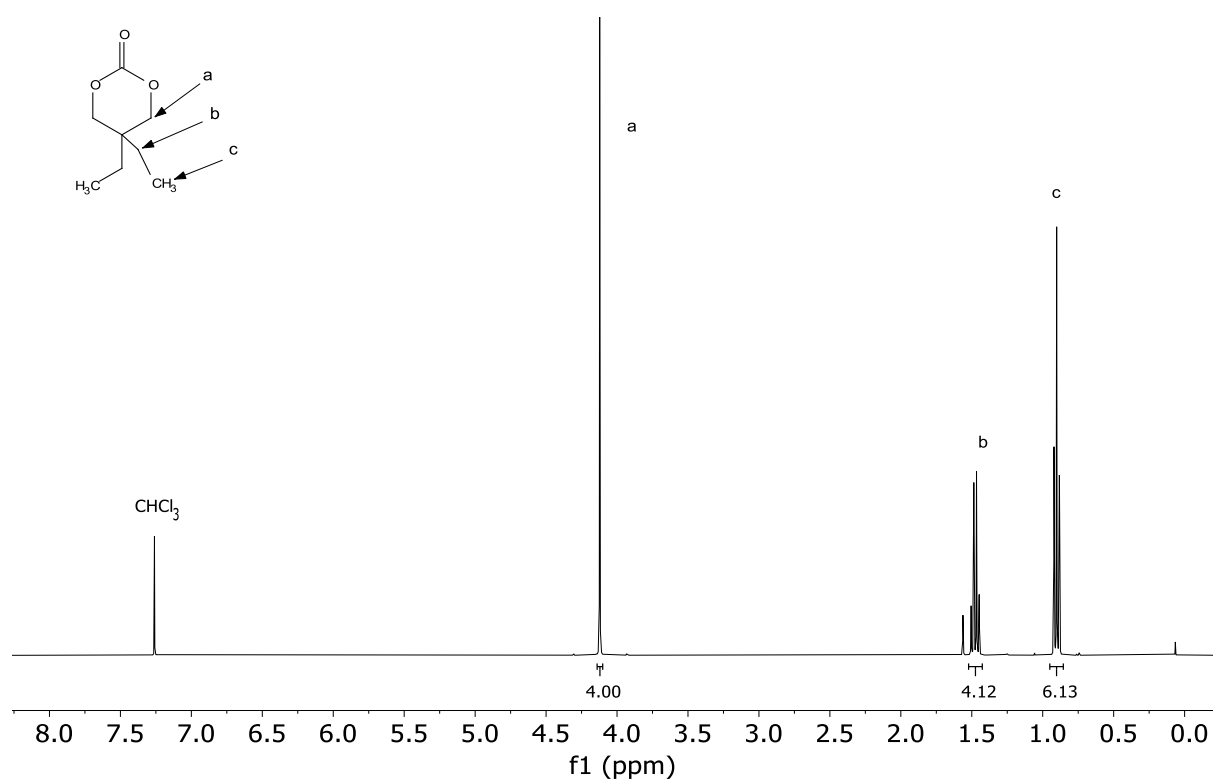


Figure S1:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) of the purified reactive diluent Et-C

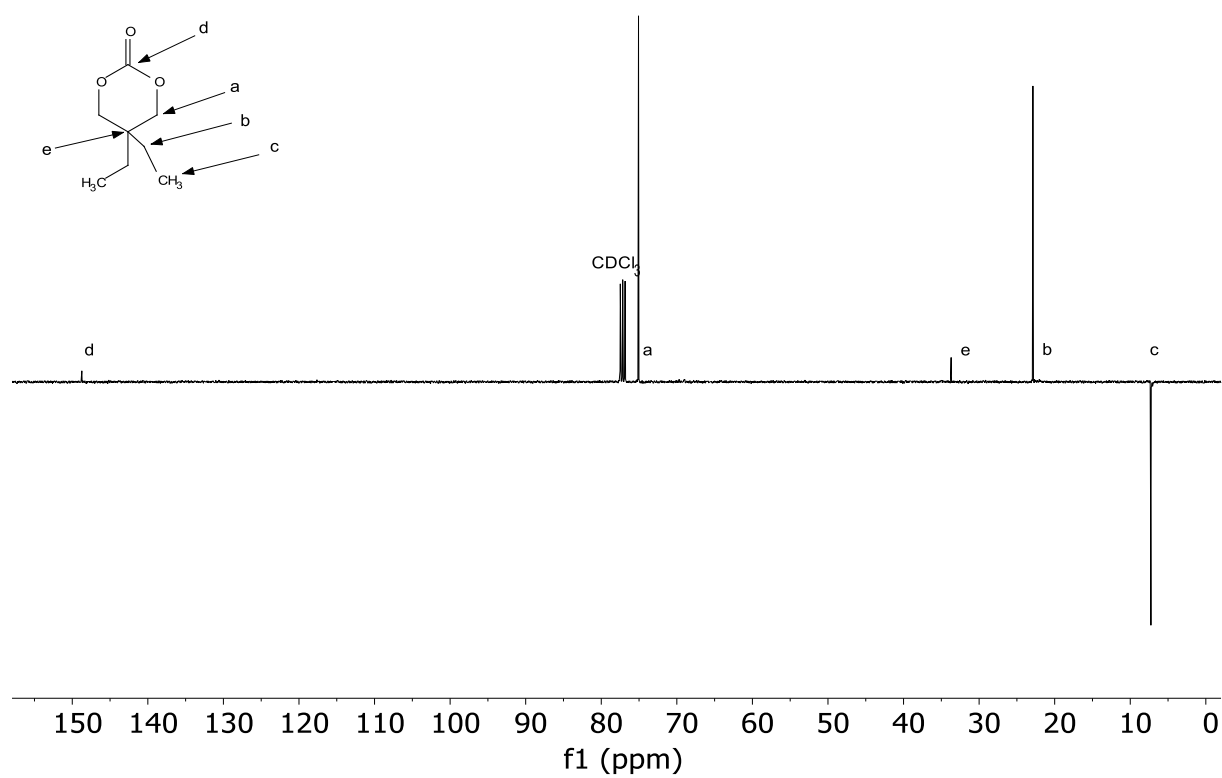


Figure S2:  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ) of the purified reactive diluent Et-C in APT mode

### 2.2.1.2 Synthesis of 5-phenyl-1,3-dioxane-2-one (Ar-C)

The synthesis of Ar-C was conducted via the transesterification method using diethyl carbonate or diphenyl carbonate as carbonate sources. For this, the transesterification was performed as in 2.2.1.1. However, even at temperatures of up to 220 °C no distillate was observed in the Kugelrohr apparatus. STA measurements of the reaction product showed formation of linear poly(Ar-C), which was stable beyond 250 °C, whereas the monomeric cyclic carbonate would exhibit a boiling point of 240 °C at atmospheric pressure (Figure S3).

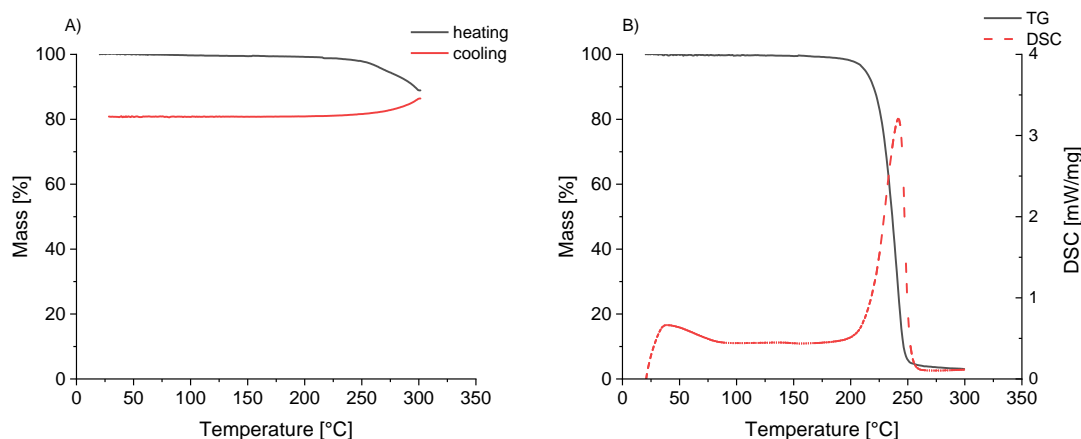


Figure S3: STA measurements of the linear polymer (A) and the corresponding cyclic monomer (B).

The alternative pathway of transesterification using diphenyl carbonate led to the formation of the cyclic carbonate, as indicated by TLC analysis, however, purification *via* column chromatography was not possible as excess diphenyl carbonate and formed phenol are too similar to Ar-C to ensure complete separation.

The synthesis was successfully achieved *via* the CDI method as stated in section 2.2.1.2 of the manuscript. It is noteworthy that precipitate forms in ethyl acetate during the first step of the reaction. The reaction will produce a precipitate, which reacts with the addition of acetic acid to yield a soluble intermediate. 7.84 g (66%) of a colourless oil were obtained.

NMR (Figure S4 and Figure S5) data were in accordance with literature reports. [4]

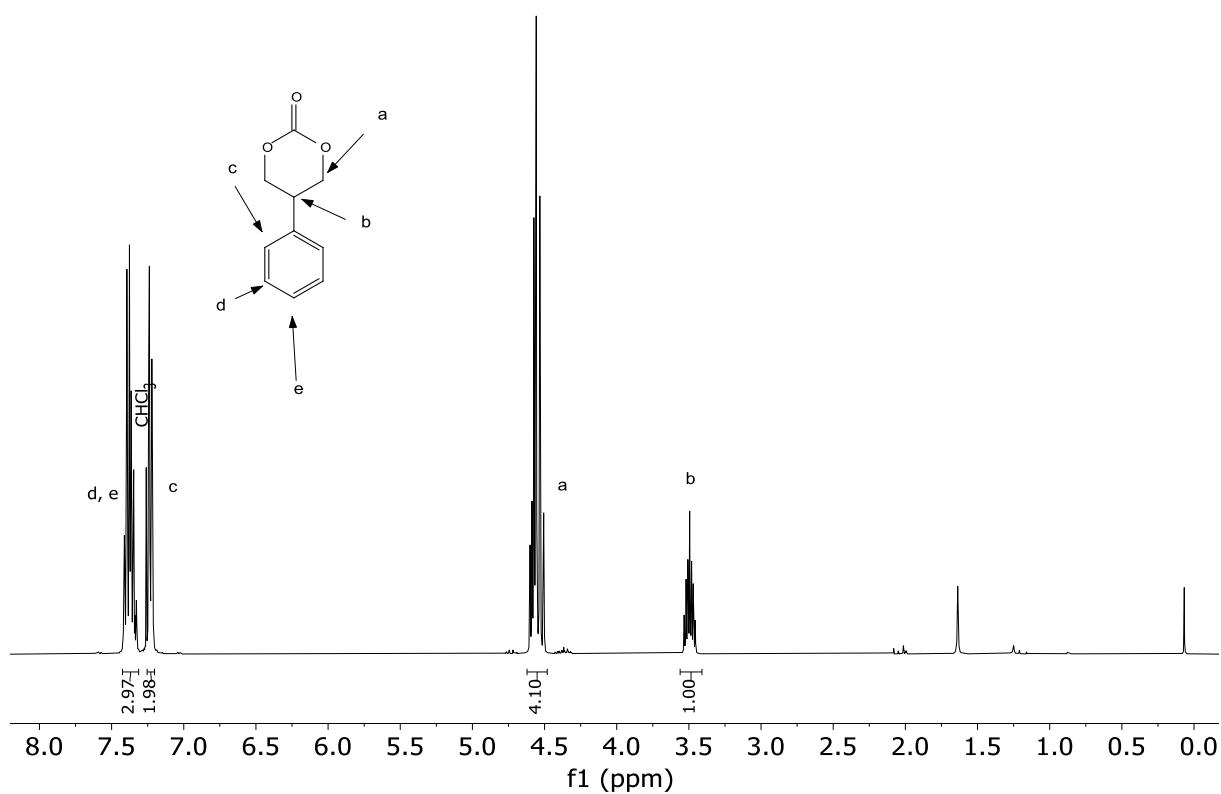


Figure S4:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) of the purified reactive diluent Ar-C

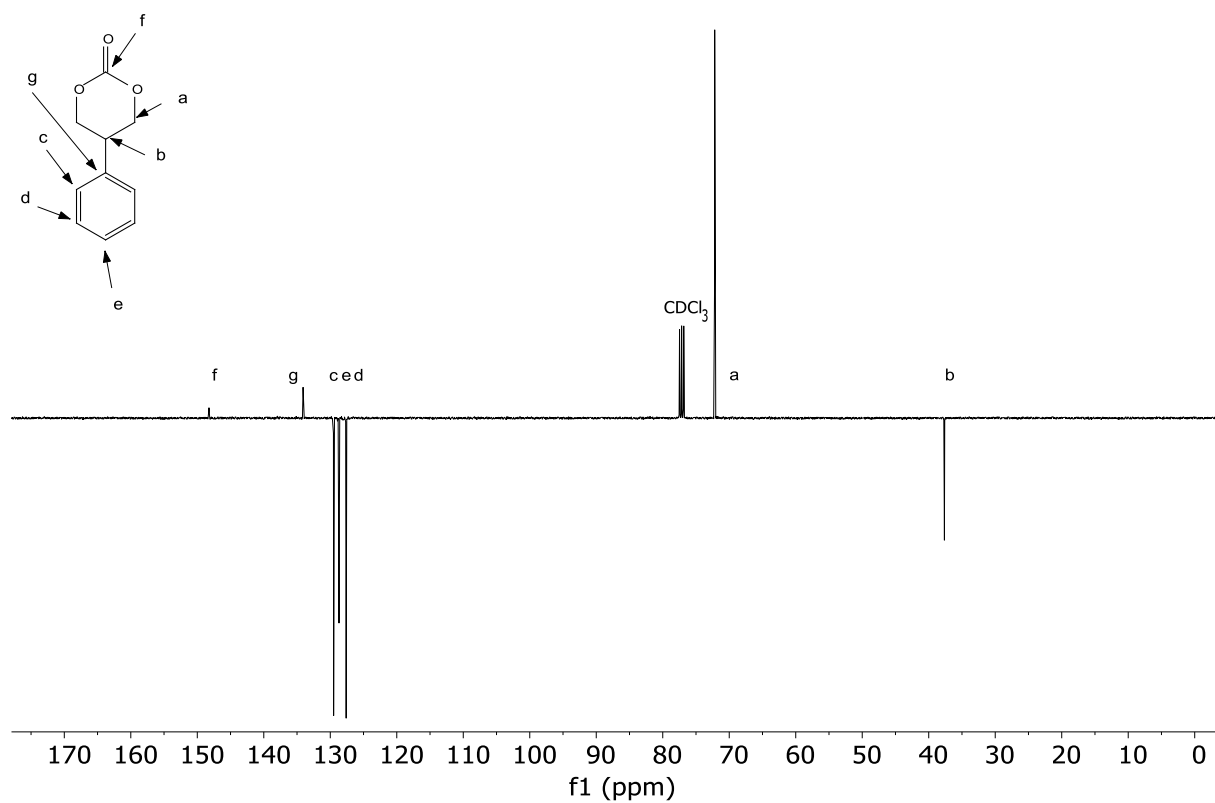


Figure S5:  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ) of Ar-C in APT mode

### 2.2.1.3 Synthesis of 5,5'-(oxybis(methylene))bis(5-ethyl-1,3-dioxane-2-one) (Di-C)

The synthesis of the crosslinker was achieved by transesterification using diphenyl carbonate as described in [5]. In short, 15.4 g (72 mmol, 6 eq) of diphenyl carbonate were heated to 140 °C in a 20 mL penicillin vial equipped with a magnetic stirrer. At the given temperature, 3 g (12 mmol, 1 eq) of di(trimethylolpropane) were added and the vial was sealed. The reaction proceeded for 48 h. After cooling to room temperature, the reaction mixture was dissolved in ethyl acetate and purified by column chromatography (eluent: petroleum ether:ethyl acetate = 2:3, v/v) followed from recrystallisation in a 1:3 mixture of petroleum ether and ethyl acetate. The product was obtained as white crystals in 84% yield (3.05 g).

The second approach was performed using the CDI method explained in section 2.2.1.3 of the manuscript. It is noteworthy that di(trimethylolpropane) is not soluble in ethyl acetate but the reaction will proceed as heterogeneous reaction between the solid material and the dissolved 1,1'-carbonyldiimidazole until all starting material is dissolved, which takes roughly 40 min on a 20 g scale. This indicates the completion of the first step of the reaction and acetic acid was then added to the reaction according to the protocol. The CDI method did not result in an increase of yield with 86% of yield, however, the time decreased from roughly 60 h from the transesterification to 6 h to obtain a purified product.

Melting point and NMR (Figure S6 and Figure S7) data were in accordance with literature. [5]

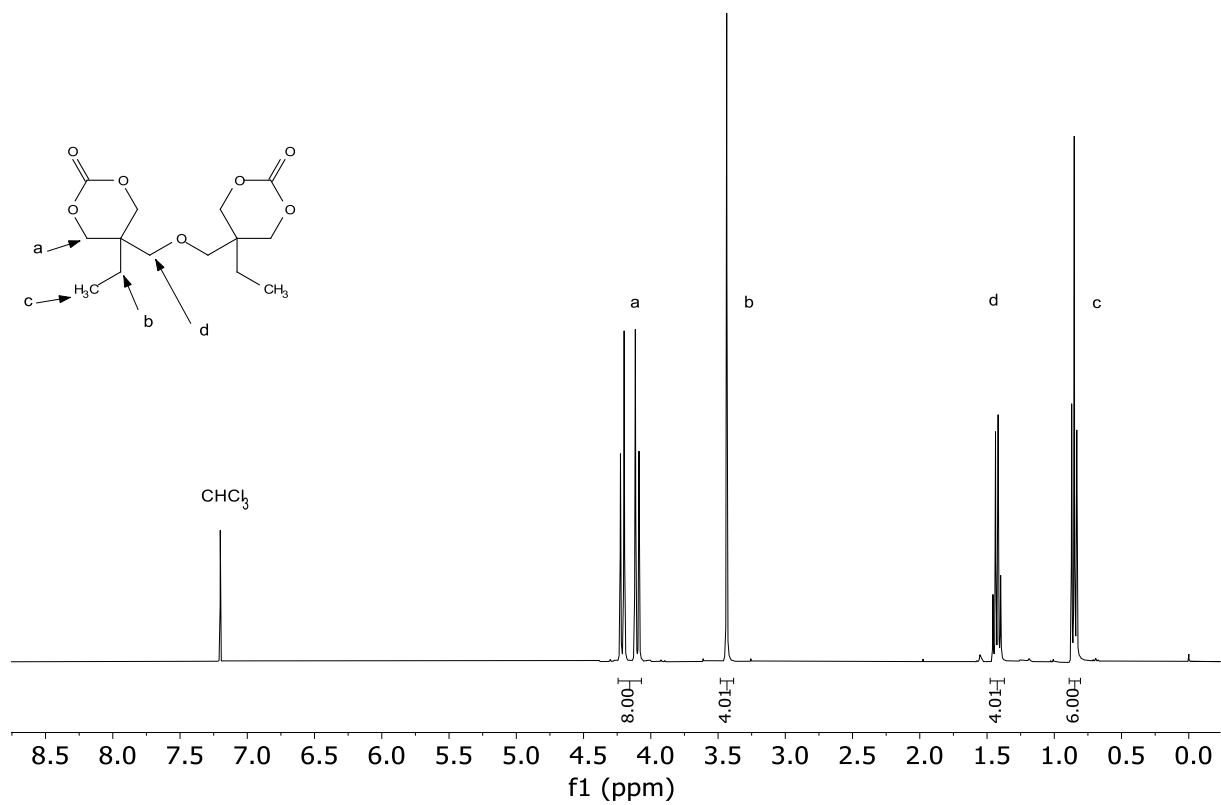


Figure S6:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) of Di-C

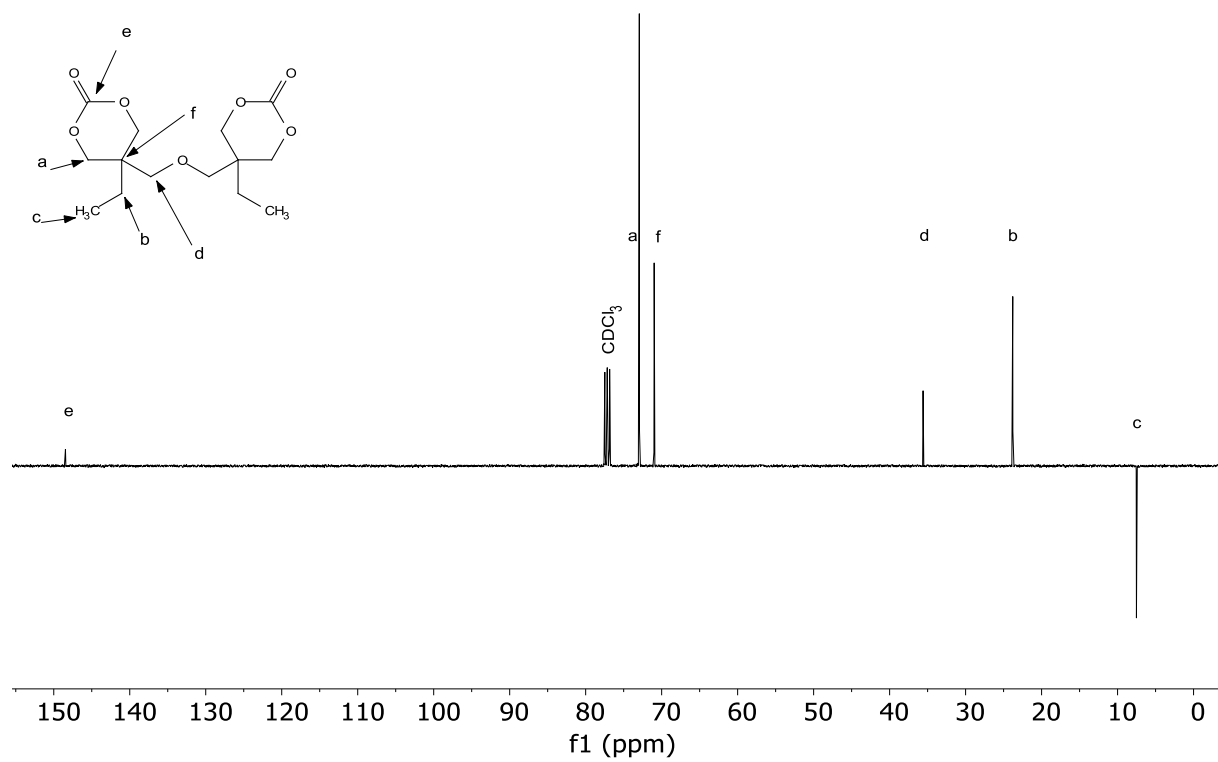


Figure S7:  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ) of Di-C in APT mode

## 2.2.2 Synthesis of PBG

### 2.2.2.1 Synthesis of octahydropyrrolo[1,2-a]pyrimidine (RDBN)

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR of RDBN can be seen in Figure S8 and Figure S9, respectively. The NMR data were in accordance with literature reported data. [6]

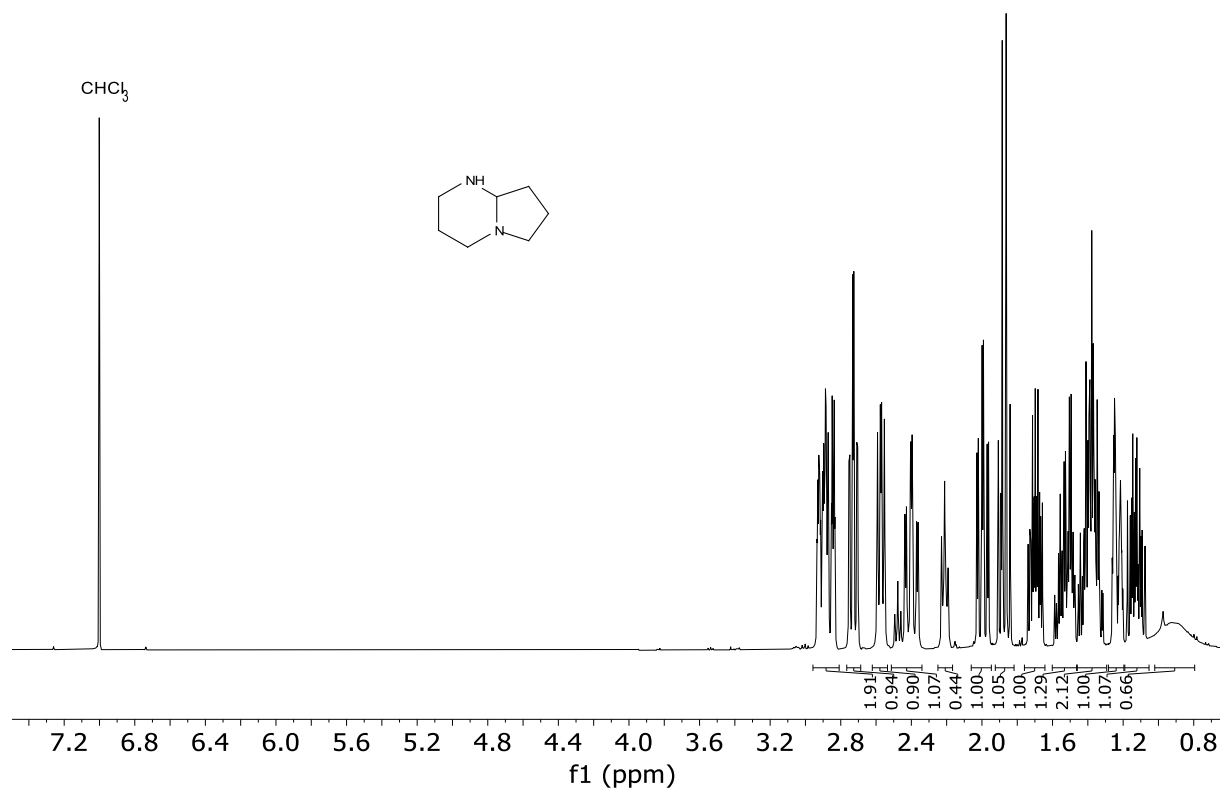


Figure S8:  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of RDBN.



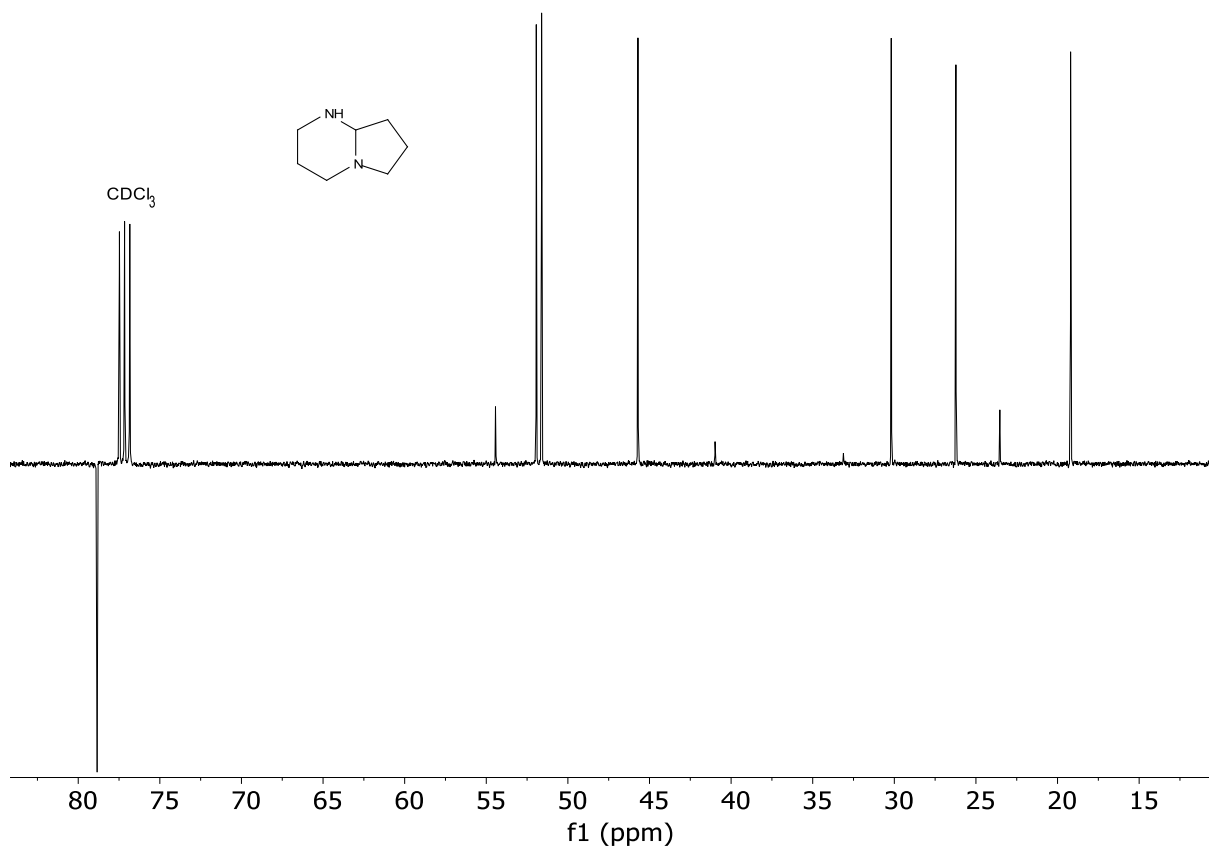


Figure S9: <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) of RDBN in APT mode.

### 2.2.2.2 Synthesis of methyl 4-((hexahydropyrrolo[1,2-a]pyrimidin-1(2H)-yl)methyl)benzoate (PBG)

The synthesis of the photo-base generator was performed according to literature [7, 8] and the analysis data were in accordance with literature. [7, 8]

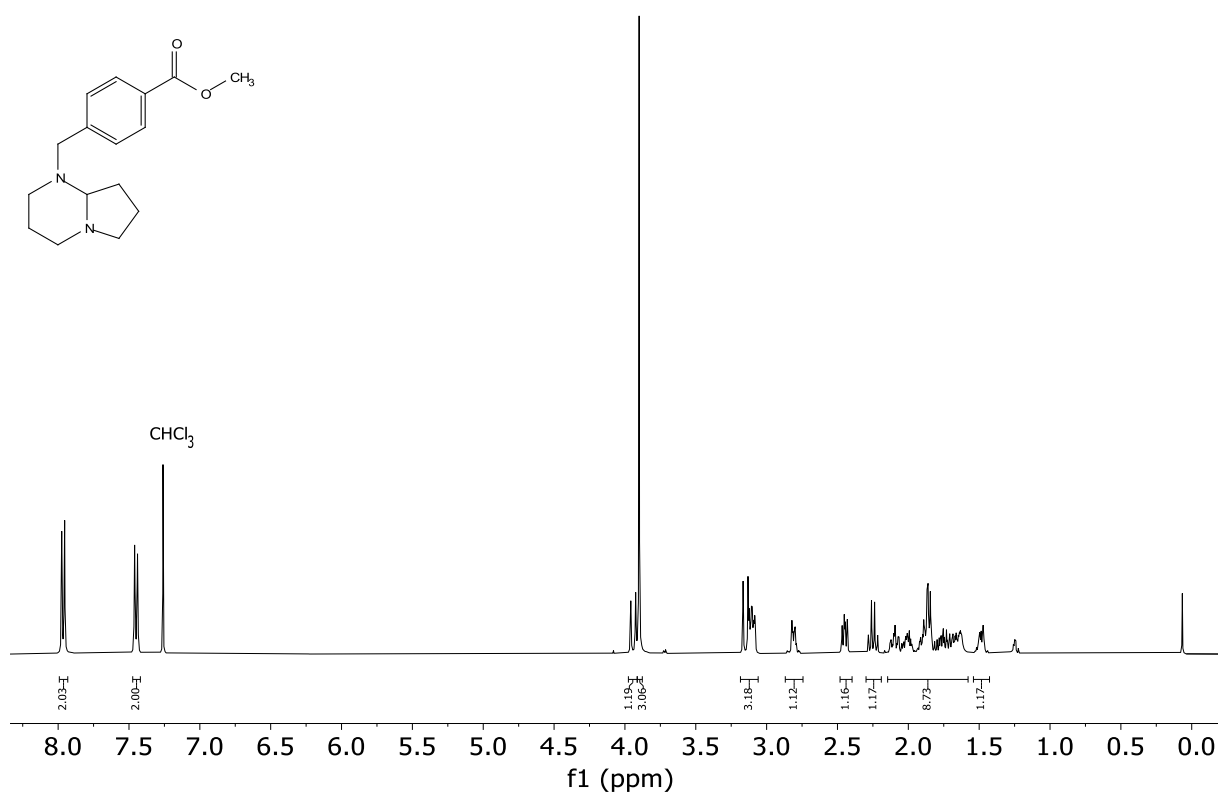


Figure S10:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) of PBG

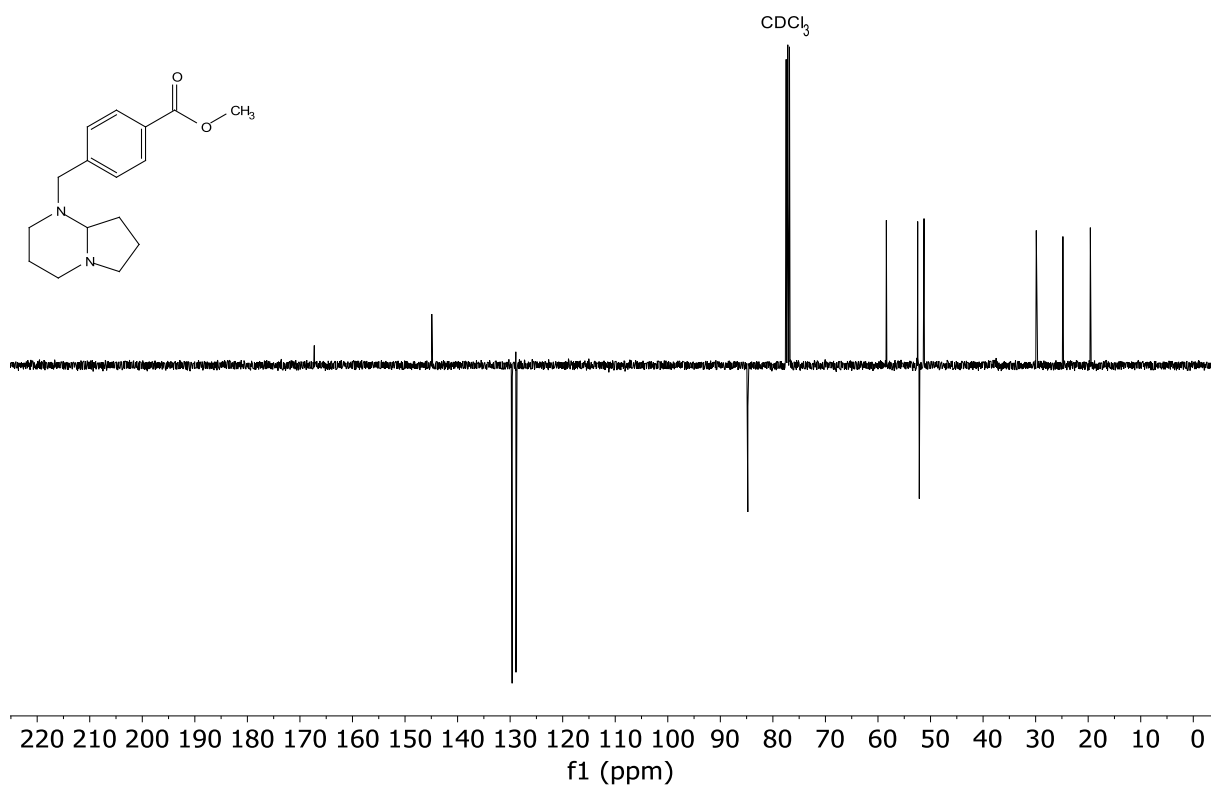


Figure S11:  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ) in APT mode of PBG

## 3.2 Reactivity studies

### 3.2.1 Photo-DSC

The photo-DSC experiments were performed according to the procedure described in the manuscript. The  $^1\text{H-NMR}$  of Ar-C during these experiments are summed up in Figure S12. Noteworthy is the influence of coupling of the  $\text{CH}_2$  groups experiencing ring-strain of the cyclic carbonate and the freedom of rotation in the linear polycarbonate. The signal changes from a multiplet to a doublet, as shown in Figure S12. The comparison of all tested temperatures during the photo-DSC analysis can be seen in Figure S13.

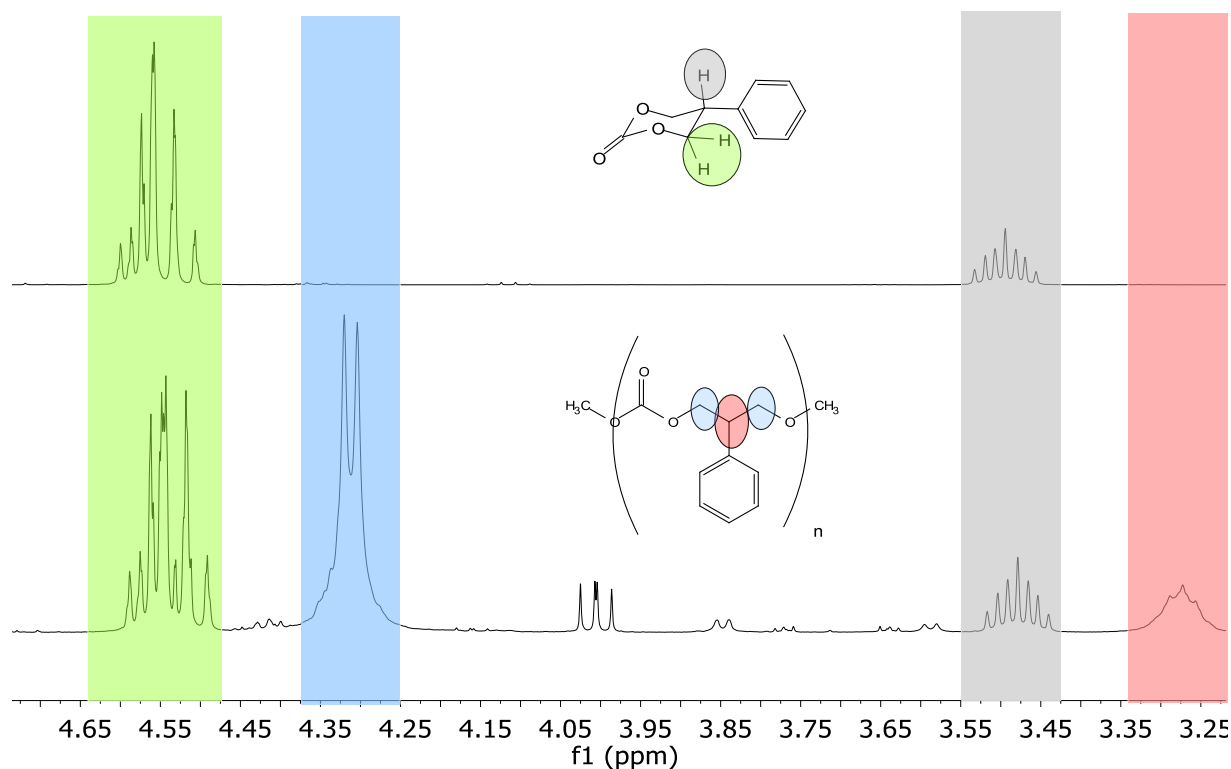


Figure S12: Comparison of the  $^1\text{H-NMR}$  signals of the cyclic monomer and the linear polycarbonate as indicated by a single monomeric unit. (400 MHz,  $\text{CDCl}_3$ )

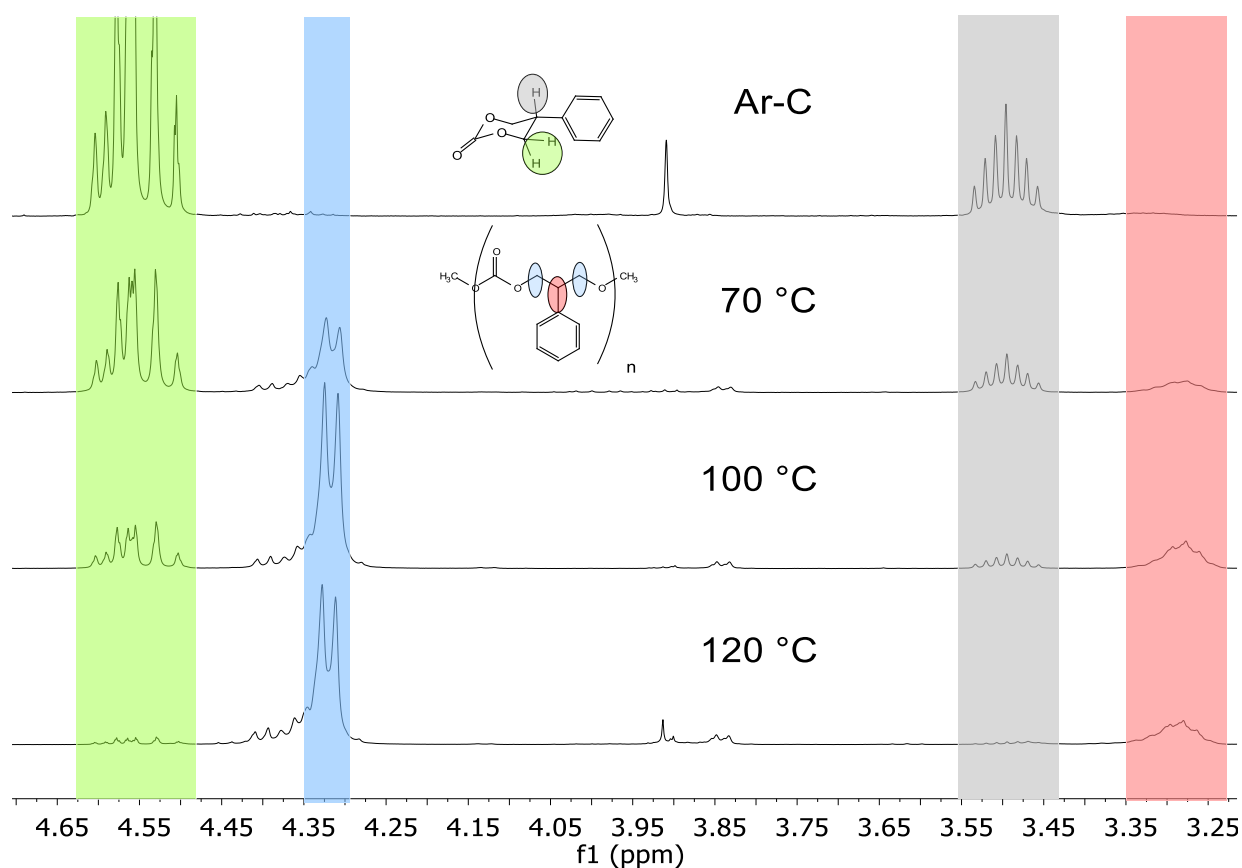


Figure S13: Comparison of all  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) obtained after the photo-DSC studies of Ar-C

### 3.2.3 Photorheology

The photorheological measurements were performed with a light intensity of  $50 \text{ mW cm}^{-2}$  (320-500 nm) on the sample surface and an irradiation time of 15 min. The same initiator concentration was used as in photo-DSC experiments (5 mol%). For the photorheological experiments, the glass surface, protected with a heatproof PE tape, was first heated to  $110 \text{ }^\circ\text{C}$ , and  $130 \text{ }\mu\text{L}$  of the samples were added. The temperature was chosen based on higher conversions observed during the photo-DSC experiments. For the experiments, different concentrations of reactive diluent (0-63 mol%) were tested to investigate its influence on the gelation properties of the formulation. The curves for the storage modulus ( $G'$ ) of the investigated formulations can be seen in Figure S14. In all formulations containing the reactive diluent the increase of  $G'$  happens very fast once the photobase generator reacted. The curve shapes suggest that the limiting factor was the diffusivity of the sensitizer and PBG. It can also be assumed that the solubility of PBG in pure Di-C was lower than in the reactive diluent Et-C, which could cause the delay in reaction. The decrease of the storage modulus of the formulation containing 63 mol% Et-C might be caused by

delamination of the PE tape from the glass plate as well as the expulsion of unreacted resin from underneath the stamp.

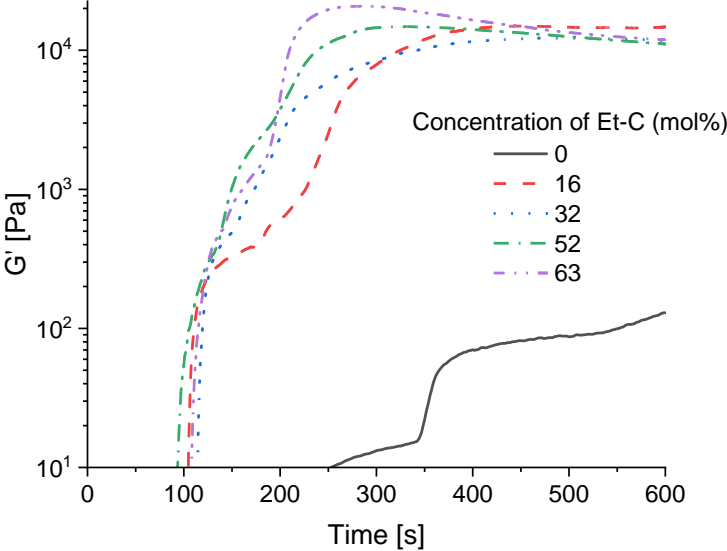


Figure S14: The storage modulus as function of time for all investigated formulation with different concentrations of reactive diluent Et-C at 120 °C.  $t = 0$  marks the beginning of irradiation

### 3.3 Thermal and (thermo-)mechanical analysis

In addition to the evaluation of  $T_{5\%}$ , all TGA curves are summarized in Figure S15.

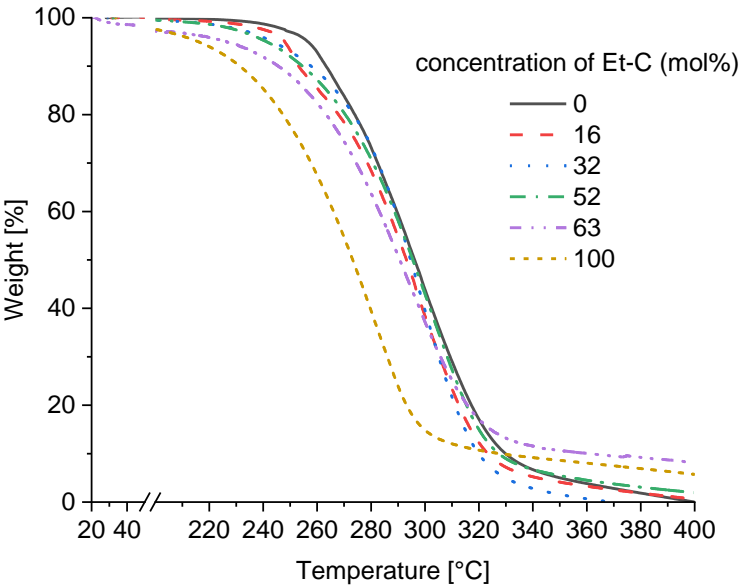


Figure S15: The thermal degradation behavior as indicated by TGA for all tested formulations

## Literature

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