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## Supplementary Materials for

### **A coating from nature**

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# Materials and Methods

## General Information

**Commercial reagents and solvents:** Unless stated otherwise, all commercially available reagents and solvents were purchased from the commercial sources: Sigma–Aldrich, Acros, Macron, AkzoNobel Coatings BV, Linde-gas and were used as received. Dry solvents for the reactions were of quality puriss., p.a.. Anhydrous solvents were purified by passage through solvent purification columns (47) (MBraun SPS-800). For aqueous solutions, demineralized water was used.

**Reagents:** Furfural (99%), methylene blue, hexanol anhydrous ( $\geq 99\%$ ), 2-propanol anhydrous (99.5%), (-)-menthol (99%), p-toluenesulfonic acid ( $\geq 98.5\%$ ), sodium bisulfite, 1,3,5-trimethoxybenzene ( $\geq 99\%$ ), bis(trimethylsilyl)benzene (96%), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Omnirad 819, 97%), dodecyl vinyl ether (98%), diethylene glycol divinyl ether (99%), ethylene glycol vinyl ether (97%), methyl methacrylate (99%, stabilized), styrene ( $\geq 99\%$ , stabilized), butyl acrylate ( $\geq 99\%$ , stabilized), butyl crotonate (99%), butyl methacrylate (99%, stabilized), maleic anhydride (99%), furfuryl alcohol (98%), 2(5H)-furanone (98%), 2,5-dimethoxy-2,5,-dihydrofuran (97%), were purchased from *Sigma-Aldrich* (Zwijndrecht, The Netherlands).

Oxygen compressed (technical grade) was purchased from *Linde-gas* (Schiedam, The Netherlands).

Methanol anhydrous (99,8%) was purchased from *Acros* (Geel, Belgium).

Vinyl neodecanoate (Veova-10) and tert-Butyl peroxy-3,5,5-trimethylhexanoate (Trigonox 42S) were obtained from *AkzoNobel Car Refinishes BV* (Sassenheim, The Netherlands).

**Solvents:** Methanol anhydrous (MeOH, 99%, AR grade), ethyl acetate (EtOAc, HPLC grade), n-pentane (99%), n-heptane (HPLC grade) and diethyl ether (Et<sub>2</sub>O, stabilized with BHT, AR grade) were purchased from *Macron*.

1-Methoxy-2-propanol ( $\geq 99.5\%$ ) and butyl acetate (anhydrous,  $\geq 99\%$ ) were purchased from *Sigma-Aldrich*.

**Equipment:** Unless stated otherwise, all equipment used is commercially available.

Red LED-strip (150 lm) as light source for Immersion Well photooxidation setup.

TL-bulbs (1350 lm each) as light source for continuous flow setup.

Oxygen pressure regulator (0-15 bar) for continuous flow setup.

Brooks (SLA5850S1CAB1B2A1, 4NML/M) mass flow controllers for continuous flow setup.

Halogen lamp (8000 lm) as light source for rotary evaporator photooxidation setup.

Led lamps (575 lm each) as light source for rotary evaporator photooxidation setup.

LED beacon ROHS CE IP65 (12 LEDS WW 22 °C,  $\lambda_{\text{irr}}=395$  nm) as light source for UV-curing of coatings.

Byk Applicator (50-200  $\mu\text{m}$ , 10 cm) to apply coatings.

**Preparation of non-commercial compounds:** Unless stated otherwise, all reactions were carried out in oven- and flame-dried glassware using standard Schlenk techniques and were run under nitrogen atmosphere. The reaction progress was monitored by <sup>1</sup>H-NMR-spectroscopy.

**Reaction setups:** Photooxidation reactions were performed in dedicated setups described in **Photooxidation Setups (Figs. S2–S4)**.

Condensation reactions were performed in a 500 mL round bottom flasks with condensers, under a nitrogen atmosphere. In cases where azeotropic removal of water was required, a Dean-Stark apparatus was installed.

Polymerization reactions were performed in a 4 mL glass vial with screw cap and septum, which were purged with nitrogen.

Coating formation experiments were performed on glass plates (10x20 cm).

**General Considerations:** Thin Layer Chromatography analyses were performed on commercial Kieselgel 60, F254 silica gel plates with fluorescence-indicator UV<sub>254</sub> (Merck, TLC silica gel 60 F<sub>254</sub>). For detection of components, UV light at 254 nm or 365 nm was used. Alternatively, oxidative staining using aqueous basic potassium permanganate solution (KMnO<sub>4</sub>) was used. Drying of solutions was performed with MgSO<sub>4</sub> and volatiles were removed with a rotary evaporator. Flash column chromatography was conducted with a Revelis X2 Flash Chromatography system at room temperature and using n-pentane/EtOAc, unless stated otherwise.

**General Analytical Information:** Nuclear Magnetic Resonance spectra were measured with an Agilent Technologies 400-MR (400/54 Premium Shielded) spectrometer (400 MHz). All spectra were measured at room temperature (22–24 °C). Chemical shifts for the specific NMR spectra were reported relative to the residual solvent peak [in ppm; CDCl<sub>3</sub>:  $\delta_{\text{H}} = 7.26$ ; CDCl<sub>3</sub>:  $\delta_{\text{C}} = 77.16$ ]. (48) The multiplicities of the signals are denoted by *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), *br s* (broad signal), *app* (apparent). All <sup>13</sup>C-NMR spectra are <sup>1</sup>H-broadband decoupled.

High-resolution mass spectrometric measurements were performed using a Thermo scientific LTQ OrbitrapXL spectrometer with ESI ionization. The molecule-ion M<sup>+</sup>, [M + H]<sup>+</sup> and [M–X]<sup>+</sup>, respectively, are given in *m/z*-units.

Raman spectra were measured with a PerkinElmer RamanStation400F.

GPC spectra were measured with a Agilent Polypore, THF/acetic acid (99/1), 1 mL/min, RI detector, 50  $\mu$ L injection.

Glass temperatures (*T<sub>g</sub>*) were measured with a Differential Scanning Calorimeter (DSC) Q2000 (TA Instruments) in a modulated way according to ASTM method D3418.

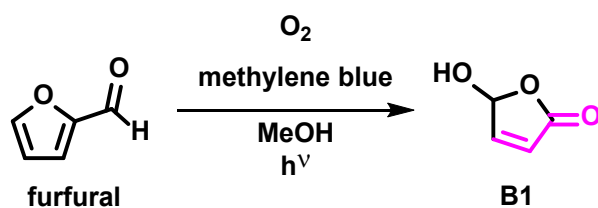
Pendulum hardness (Persoz hardness) of the cured coatings were determined according to ISO 1522.

The cured coating were subjected to Dynamic Mechanical Thermal Analysis (DMTA) according to ISO 6721-11, using a TA Instruments RSA3 dynamic mechanical analyzer.

## Supplementary Text

### Photooxidation of furfural, reaction setups and optimization

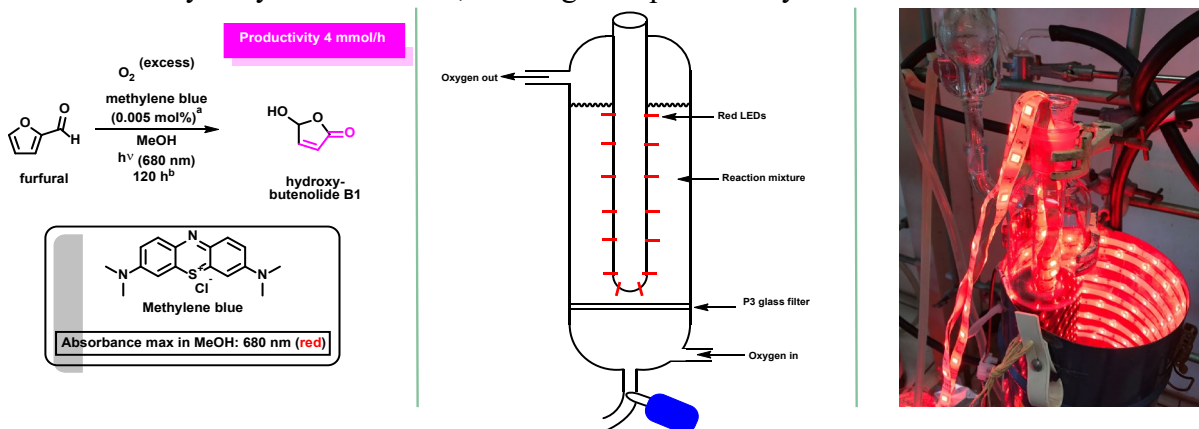
Here are described, the three photooxidation setups and their optimization. The setups were mainly optimized for concentration, catalyst loading and reaction time. The Immersion Well setup is largely unoptimized, the rotary evaporator setup is optimized for concentration, catalyst loading and volume and the continuous flow setup is optimized for concentration, catalyst loading, residence time flows of solution and oxygen.



**Fig. S1.** General reaction scheme for the photooxidation of furfural to hydroxybutenolide **B1** using methylene blue as photosensitizer.

#### Immersion Well Setup

The simple immersion well setup for the photooxidation of furfural (shown below) for the photooxidation of furfural, consists of a standard column chromatography glass piece with an extra inlet and outlet and the bottom and top, respectively. Irradiation is done by a red LED strip inside a glass tube that can be inserted. An oxygen cylinder, connected to a pressure regulator, is connected to the inlet at the bottom. Homogeneous stirring is achieved by bubbling oxygen through the P3 glass filter in the column. Using this setup, 50 gram of furfural could be quantitatively converted to hydroxybutenolide **B1**, resulting in a productivity of 4 mmol/h.



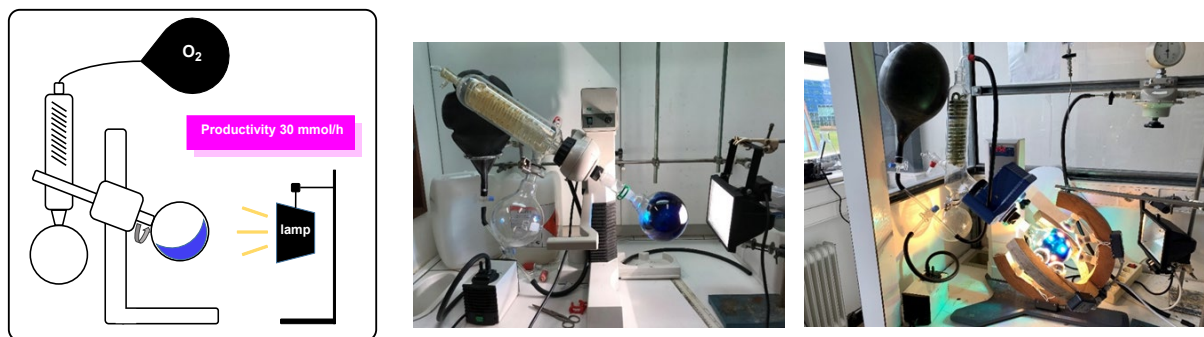
**Fig. S2.** Reaction scheme of photooxidation of furfural to hydroxybutenolide **B1**, productivity of the setup and structure of methylene blue. Reaction conditions: 1 M furfural, 6 mmol% methylene blue, excess oxygen (bubbling), irradiation  $\lambda_{\text{irr}} = 635 \text{ nm}$  (left). Schematic representation of Immersion Well setup (middle). Immersion Well reactor in operation (right). a) Low catalyst



loading resulted in a faster conversion due to the poor penetration of the light. b) Upon photo-bleaching of the catalyst, an additional catalyst loading of 5 mmol% was added during the reaction.

### Rotary evaporator setup and reaction optimization

The simple rotary evaporator setup for the photooxidation of furfural consists of a standard rotary evaporator, put under an oxygen atmosphere. A lamp is placed in front of rotating flask, irradiating the reaction mixture for 20 minutes.



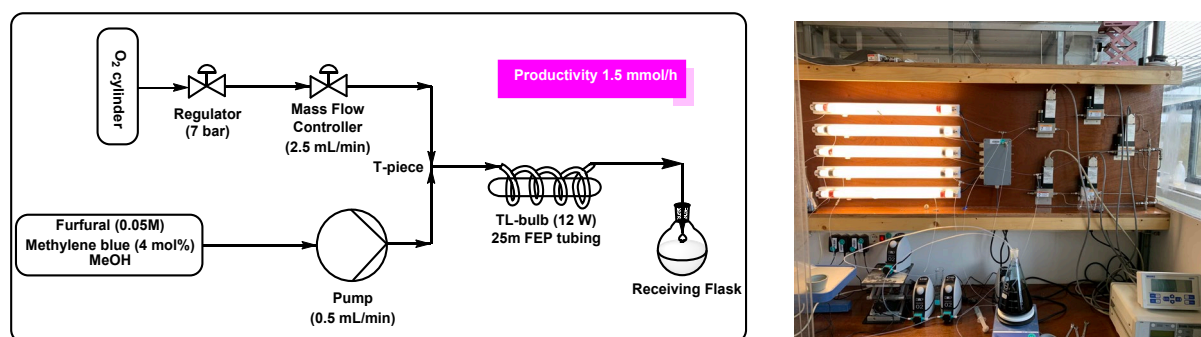
**Fig. S3.** General rotary evaporator photooxidation setup scheme and productivity of the setup (left). Rotary evaporator photooxidation setup with 400 W halogen lamp in operation (middle). Rotary evaporator photooxidation setup with 10 x 80 W LEDs in operation (right).

**Table S1.** Rotary evaporator reaction optimization. a) Reaction time of 30 min. 10 x 80 W LED with a wooden construction built for optimal irradiation of the mixture (**Fig. S4** right). The use of LEDs could be placed closer to the rotating flask due to less heat generated from the lamps. c) Lower catalyst loading resulted generally in higher conversion due to increased light penetration.

<b>Entry</b>	<b>Concentration (M)</b>	<b>Volume (mL)</b>	<b>Cat. Loading (mol%)</b>	<b>Lamp setup</b>	<b>Conversion (%)</b>
<b>1</b>	<b>1</b>	<b>10</b>	<b>1</b>	<b>400 W halogen lamp</b>	<b>37</b>
<b>2</b>	<b>1</b>	<b>10</b>	<b>5</b>	<b>400 W halogen lamp</b>	<b>23</b>
<b>3</b>	<b>1</b>	<b>5</b>	<b>1</b>	<b>400 W halogen lamp</b>	<b>72</b>
<b>4</b>	<b>1</b>	<b>5</b>	<b>5</b>	<b>400 W halogen lamp</b>	<b>48</b>
<b>5</b>	<b>1</b>	<b>10</b>	<b>0.5</b>	<b>400 W halogen lamp</b>	<b>65</b>
<b>6</b>	<b>1</b>	<b>10</b>	<b>0.1</b>	<b>400 W halogen lamp</b>	<b>62</b>
<b>7<sup>a</sup></b>	<b>1</b>	<b>10</b>	<b>0.5</b>	<b>400 W halogen lamp</b>	<b>100</b>
<b>8</b>	<b>1</b>	<b>5</b>	<b>1</b>	<b>10 x 80 W LED</b>	<b>100</b>
<b>9<sup>b</sup></b>	<b>1</b>	<b>10</b>	<b>1</b>	<b>10 x 80 W LED</b>	<b>90</b>
<b>10<sup>c</sup></b>	<b>1</b>	<b>10</b>	<b>0.5</b>	<b>10 x 80 W LED</b>	<b>100</b>
<b>11</b>	<b>1</b>	<b>10</b>	<b>0.1</b>	<b>10 x 80 W LED</b>	<b>97</b>
<b>12</b>	<b>1.5</b>	<b>10</b>	<b>0.5</b>	<b>10 x 80 W LED</b>	<b>90</b>

### Continuous flow setup and reaction optimization

The continuous flow setup for the photooxidation of furfural consists of thin Fluorelated Ethylene Propylene (FEP) tubing (1/16 inch ID) wrapped around a standard 18W TL-bulb. A line for the reaction mixture, consisting of methylene blue as photosensitizer and furfural dissolved in methanol, is mixed with a line of oxygen in a Swagelock T-piece. The solution is pumped by a Simdos O2 dosing pump. The oxygen flow is downregulated from the cylinder to 7 bar by a pressure regulator and the flow is controlled by a Mass Flow Controller of Brooks (SLA5850S1CAB1B2A1, 4NML/M).



**Fig. S4.** Continuous flow scheme for the photooxidation of furfural to hydroxybutenolide **B1** under optimized conditions: 0.05 M furfural in methanol, methylene blue (4 mol%), solution flow 0.5 mL/min, oxygen (7 bar) flow 2.5 mL/min, 25 m of FEP tubing wrapped around 18 W TL-bulb (left). Continuous flow setup in operation (right).

**Table S2.** Continuous flow reaction optimization. a) Maximum length of FEP tubing wrapped around standard TL-bulb. b) Highest productivity, however high catalyst loading resulted in precipitation of the catalyst during the reaction, clogging the dosing pumps. c) Same concentration of catalyst, 2 mM, as entry 7 d) Same concentration of catalyst, 4 mM, as entry 8.

Entry	Concentration (M)	Cat. Loading (mol %)	FEP length (m)	Flow sol. (mL/min)	Flow O <sub>2</sub> (mL/min)	Conversion (%)
1	0.05	1	7.5	1	5	28
2	0.05	1	15	1	5	51
3	0.05	1	15	0.5	2.5	65
4	0.05	1	25 <sup>a</sup>	0.5	2.5	89
5	0.05	1	25	0.5	5.0	77
6	0.05	1	25	0.5	1.5	88
7	0.05	4	25	0.5	2.5	96
8 <sup>b</sup>	0.1	4	25	0.5	2.5	94
9	0.1	2 <sup>c</sup>	25	0.5	2.5	85
10	0.2	2 <sup>d</sup>	25	0.5	2.5	61

## Experimental Procedures

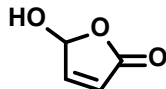
### General Procedure A: (Co)polymerization

To a 4 mL vial with screwcap with septum were added, alkoxybutenolide **B2-5** (2 mmol, 1 eq.), the corresponding comonomer (2 mmol, 1 eq.) and 1-methoxy-2-propanol (1 mL). 1,3,5-Trimethoxybenzene (181 mg, 1 mmol, 0.5 eq.) was added as an internal standard for <sup>1</sup>H-NMR measurements. The mixture was heated to 120 °C and Trigonox 42S (0.03 mg, 0.033 μL, 6 mol%, 0.06 eq.) was added as an initiator. The mixture was refluxed for 10 min – 4 h depending on the desired polymer. At regular intervals a sample of 50 μL was taken from the mixture and put in a small vial which was flash frozen (–18 °C) in order to stop polymerization. The reaction kinetics were followed and the conversion was determined by <sup>1</sup>H NMR spectroscopy. In case of homo-polymerization, the concentration of the monomer was doubled to account for the net concentration of alkenes in the reaction mixture.

### General Procedure B: UV-curing of coatings

To a 5 mL vial were added alkoxybutenolide **B2-5** (2 mmol, 1 eq.), di(ethylene glycol) divinyl ether (1 mmol, 0.5 eq.) and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Omnirad 819, 60 μmol, 3 mol%) and stirred until the reaction mixture became homogeneous. The mixture was applied on a glass surface and the surface (10 x 20 cm) was coated with a Byk applicator (100–150 μm thickness). The glass surface was irradiated with UV-A light (LED beacon ROHS CE IP65, 12 LEDs, WW, 22 °C, λ<sub>irr</sub>=395 nm) at 10 cm distance for 5 min (total irradiance of 4.5 mW/cm<sup>2</sup>).

### 5-hydroxy-2(5H)-furanone (hydroxybutenolide) **B1** (Immersion Well setup)

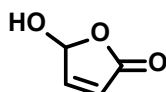


To the large photo-oxygenation setup shown in **Fig. S2** was added freshly distilled (50 °C,  $1.5 \times 10^{-2}$  mbar) furfural (50.0 g, 0.52 mol, 1 eq.) dissolved in 500 mL oxygen enriched methanol. Methylene blue (10 mg, 0.032 mmol, 0.005 mol%) was added to the reaction mixture. An oxygen line was connected to the bottom inlet of the setup and oxygen was bubbled through the solution with a controlled flow. Red LEDs (150 lm,  $\lambda=680$  nm) were inserted in the glass tube and the glass tube was put in the setup. The resulting mixture was bubbled with oxygen for 120 h while irradiated by red light. The reaction was followed by  $^1\text{H-NMR}$  until all furfural was consumed. The solvent was evaporated after under reduced pressure. The obtained oil solidified upon standing. The product 5-hydroxy-2(5H)-furanone **B1** could be used without further purification. Removal of the photosensitizer was done by filtration in diethyl ether over silica and charcoal. After evaporation the compound was recrystallized at  $-78^\circ\text{C}$  to form the product 5-hydroxy-2(5H)-furanone **B1** as an off-white crystalline solid (52.1 g, 0.52 mol, quantitative).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (dd,  $J = 5.7, 1.2$  Hz, 1H,  $\text{H}_2$ ), 6.25 (s, 1H,  $\text{H}_3$ ), 6.21 (dd,  $J = 5.6, 1.1$  Hz, 1H,  $\text{H}_1$ ), 5.89 – 5.24 (m, 1H, OH).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.02 (1C,  $\text{C}_4$ ), 152.92 (1C,  $\text{C}_2$ ), 122.75 (1C,  $\text{C}_3$ ), 98.70 (1C,  $\text{C}_1$ ). HRMS calcd 99.00767, found 99.00912.

### 5-hydroxy-2(5H)-furanone (hydroxybutenolide) **B1** (Continuous flow setup)

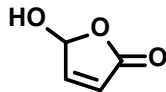


A solution of freshly distilled (50 °C,  $1.5 \times 10^{-2}$  mbar) furfural (10.0 g, 104 mmol, 1 eq.) and methylene blue (128 mg, 0.4 mmol, 4 mol%) in 2000 mL oxygen enriched methanol was prepared in a 2 L Erlenmeyer. The reaction mixture was stirred for 30 min before the lines of the dosing pumps were put in the solution. The dosing pumps was primed with the solution and was set to a flow of 0.5 mL/min. The reaction mixture was pumped through the reaction line together with a flow (2.5 mL/min) of oxygen and irradiated by a TL-bulb. The resulting reaction mixture was received and transferred to a round bottom flask. The solvent was evaporated under reduced pressure and the crude blue oil was distilled to remove unreacted furfural (50 °C,  $1.5 \times 10^{-2}$  mbar). The obtained blue oil solidified upon standing. The product 5-hydroxy-2(5H)-furanone **B1** could be used without further purification. Removal of the photosensitizer was done by filtration in diethyl ether over silica and charcoal. After evaporation the compound was recrystallized at  $-78^\circ\text{C}$  to form the product 5-hydroxy-2(5H)-furanone **B1** as an off-white crystalline solid (10.2 g, 102 mmol, 98%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (dd,  $J = 5.7, 1.2$  Hz, 1H,  $\text{H}_2$ ), 6.25 (s, 1H,  $\text{H}_3$ ), 6.21 (dd,  $J = 5.6, 1.1$  Hz, 1H,  $\text{H}_1$ ), 5.89 – 5.24 (m, 1H, OH).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.02 (1C,  $\text{C}_4$ ), 152.92 (1C,  $\text{C}_2$ ), 122.75 (1C,  $\text{C}_3$ ), 98.70 (1C,  $\text{C}_1$ ). HRMS calcd 99.00767, found 99.00912.

### 5-hydroxy-2(5H)-furanone (hydroxybutenolide) **B1** (Rotary evaporator setup)

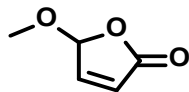


A solution of freshly distilled (50 °C,  $1.5 \times 10^{-2}$  mbar) furfural (1.0 g, 10 mmol, 1 eq.) and methylene blue (17 mg, 52  $\mu\text{mol}$ , 0.5 mol%) in 10 mL oxygen enriched methanol was prepared in a 1000 mL round bottom flask. The mixture was put under an oxygen atmosphere in a standard lab rotary evaporator (175 rpm) and irradiated by 8 x 80 W LED lamps for 20 min. The light sources were placed at a distance of 5 cm from the flask (see **Fig. S4**). The solvent was evaporated after under reduced pressure. The obtained oil solidified upon standing. The product 5-hydroxy-2(5H)-furanone **B1** could be used without further purification. Removal of the photosensitizer was done by filtration in diethyl ether over silica and charcoal. After evaporation the compound was recrystallized at -78 °C to form the product 5-hydroxy-2(5H)-furanone **B1** as an off-white crystalline solid (1.0 g, 10 mmol, quantitative).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (dd,  $J = 5.7, 1.2$  Hz, 1H,  $\text{H}_2$ ), 6.25 (s, 1H,  $\text{H}_3$ ), 6.21 (dd,  $J = 5.6, 1.1$  Hz, 1H,  $\text{H}_1$ ), 5.89 – 5.24 (m, 1H, OH).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.02 (1C,  $\text{C}_4$ ), 152.92 (1C,  $\text{C}_2$ ), 122.75 (1C,  $\text{C}_3$ ), 98.70 (1C,  $\text{C}_1$ ). HRMS calcd 99.00767, found 99.00912.

### 5-methoxy-2(5H)-furanone (methoxybutenolide) **B2**



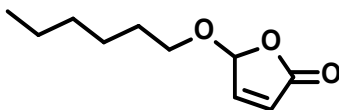
5-Hydroxy-2(5H)-furanone **B1** (100.0 g, 1 mol) was dissolved in 500 mL dry methanol and heated at reflux for 20 h. The conversion was followed by  $^1\text{H}$  NMR until all 5-hydroxy-2(5H)-furanone **B1** was consumed. The solvent was evaporated under reduced pressure and the crude was distilled under reduced pressure (70 °C,  $1.0 \times 10^{-2}$  mbar) yielding 5-methoxy-2(5H)-furanone **B2** (86.5 g, 0.76 mol, 76%) as a slightly yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (dd,  $J = 5.7, 1.2$  Hz, 1H,  $\text{H}_2$ ), 6.24 (dd,  $J = 5.7, 1.2$  Hz, 1H,  $\text{H}_1$ ), 5.86 (t,  $J = 1.2$  Hz, 1H,  $\text{H}_3$ ), 3.58 (s, 3H,  $\text{H}_8$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.87 (1C,  $\text{C}_4$ ), 150.20 (1C,  $\text{C}_2$ ), 125.41 (1C,  $\text{C}_3$ ), 104.17 (1C,  $\text{C}_1$ ), 57.23 (1C,  $\text{C}_8$ ).

HRMS calcd 115.03897, found 115.038892

### 5-hexyloxy-2(5H)-furanone (hexyloxybutenolide) **B3**



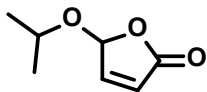
5-Hydroxy-2(5H)-furanone **B1** (62.0 g, 0.62 mol, 1 eq.) and anhydrous hexanol (104.5 g, 1.02 mol, 1.65 eq.) were dissolved in 180 mL toluene and heated at reflux under azeotropic removal of water for 20 h. The solvent was evaporated under reduced pressure and the crude was fractionally distilled under reduced pressure (100 °C,  $1.0 \times 10^{-2}$  mbar) yielding a yellow oil. The yellow oil was further purified by column chromatography (silica gel, n-pentane: ethyl acetate / 90 : 10) yielding 5-hexyloxy-2(5H)-furanone **B3** (60.4 g, 0.33 mol, 53%) as a slightly yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (dd,  $J = 5.7, 1.2$  Hz, 1H,  $\text{H}_2$ ), 6.22 (dd,  $J = 5.7, 1.2$  Hz, 1H,  $\text{H}_1$ ), 5.92 (t,  $J = 1.2$  Hz, 1H,  $\text{H}_3$ ), 3.86 (dt,  $J = 9.4, 6.6$  Hz, 1H,  $\text{H}_8''$ ), 3.67 (dt,  $J = 9.4, 6.7$  Hz, 1H,  $\text{H}_8'$ ), 1.67 – 1.55 (m, 2H,  $\text{H}_9', 11'$ ), 1.41 – 1.22 (m, 6H,  $\text{H}_9'', 11'', 10, 12$ ), 0.88 (d,  $J = 7.0$  Hz, 3H,  $\text{H}_{13}$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.68 (1C,  $\text{C}_4$ ), 150.47 (1C,  $\text{C}_2$ ), 125.14 (1C,  $\text{C}_1$ ), 103.52 (1C,  $\text{C}_3$ ), 70.80 (1C,  $\text{C}_8$ ), 31.62 (1C,  $\text{C}_{10}$ ), 29.56 (1C,  $\text{C}_9$ ), 25.67 (1C,  $\text{C}_{11}$ ), 22.67 (1C,  $\text{C}_{12}$ ), 14.13 (1C,  $\text{C}_{13}$ ).

HRMS calcd 185.11722, found 185.11701.

### 5-isopropoxy-2(5H)-furanone (isopropoxybutenolide) **B4**



5-Hydroxy-2(5H)-furanone **B1** (70.0 g, 0.7 mol, 1 eq.) was dissolved in anhydrous 2-propanol 250 mL and heated at refluxed for 20 h. The solvent was evaporated under reduced pressure and the crude was fractionally distilled under reduced pressure (90 °C,  $1.4 \times 10^{-2}$  mbar) yielding a yellow oil. The yellow oil was further purified by column chromatography (silica gel, n-pentane: ethyl acetate / 90 : 10) yielding 5-isopropoxy-2(5H)-furanone **B4** (44.6 g, 0.31 mol, 45%) as a colourless oil.

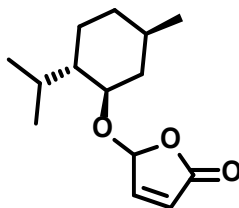
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 (dd,  $J = 5.7, 1.3$  Hz, 1H,  $\text{H}_2$ ), 6.20 (dd,  $J = 5.7, 1.3$  Hz, 1H,  $\text{H}_1$ ), 5.99 (t,  $J = 1.3$  Hz, 1H,  $\text{H}_3$ ), 4.15 – 4.04 (m, 1H,  $\text{H}_8$ ), 1.31 – 1.15 (m, 6H,  $\text{H}_8, 10$ ).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.68 (1C,  $\text{C}_4$ ), 150.47 (1C,  $\text{C}_2$ ), 125.14 (1C,  $\text{C}_1$ ), 103.52 (1C,  $\text{C}_3$ ), 70.80 (1C,  $\text{C}_8$ ), 31.62 (1C,  $\text{C}_{10}$ ), 29.56 (1C,  $\text{C}_9$ ), 25.67 (1C,  $\text{C}_{11}$ ), 22.67 (1C,  $\text{C}_{12}$ ), 14.13 (1C,  $\text{C}_{13}$ ).

HRMS calcd 143.07027, found 143.07015.



### 5-menthyloxy-2(5H)-furanone (menthyloxybutenolide) **B5**



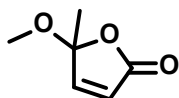
5-Hydroxy-2(5H)-furanone **B1** (60.0 g, 0.6 mol, 1 eq.), (-)-menthol (101.3 g, 0.65 mol, 1.08 eq.) and catalytic amounts of *p*-TsOH (0.57 g, 3 mmol, 0.005 eq.) were dissolved in 175 mL toluene and heated at reflux under azeotropic removal of water for 20 h. The solvent was evaporated under reduced pressure and the crude was fractionally distilled under reduced pressure (120 °C,  $1.4 \times 10^{-2}$  mbar) yielding a yellow oil. An impurity of unsaturated aldehyde was removed from the residue by dissolving the crude yellow oil in an ethereal solution of diethyl ether and a saturated solution of NaHSO<sub>3</sub> for 30 min. The water layer was extracted three times with diethylether. After combining all organic fractions, the organic layer was washed three times with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, filtered and the solvent was evaporated under reduced pressure yielding a slightly yellow oil which solidified upon standing as a white solid (58.6 g, 0.25 mol, 41%) consisting of two diastereomers (ratio 58:43). Recrystallization from *n*-heptane and washing with cold (-18°C) *n*-heptane yielded diastereomerically pure 5-menthyloxy-2(5H)-furanone **B5** as was determined by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. Through combination of the mother liquors and repeating this step multiple crops of diastereomerically pure white crystalline product were obtained.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.16 (dd, *J* = 5.7, 1.2 Hz, 1H, H<sub>2</sub>), 6.19 (dd, *J* = 5.7, 1.2 Hz, 1H, H<sub>1</sub>), 6.08 (t, *J* = 1.2 Hz, 1H, H<sub>3</sub>), 3.65 (td, *J* = 10.7, 4.3 Hz, 1H, H<sub>11</sub>), 2.18 – 2.05 (m, 2H, H<sub>10,14</sub>), 1.71 – 1.63 (m, 2H, H<sub>8,12</sub>), 1.47 – 1.35 (m, 1H, H<sub>9</sub>), 1.32 – 1.21 (m, 1H, H<sub>13</sub>), 1.08 – 0.99 (m, 1H, H<sub>9</sub>), 0.95 (d, *J* = 6.5 Hz, 3H, H<sub>16</sub>), 1.00 – 0.82 (m, 2H), 0.88 (d, *J* = 7.1 Hz, 3H, H<sub>15</sub>), 0.80 (d, *J* = 6.9 Hz, 3H, H<sub>17</sub>).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 170.85 (1C, C<sub>4</sub>), 151.01 (1C, C<sub>2</sub>), 124.92 (1C, C<sub>3</sub>), 100.59 (1C, C<sub>1</sub>), 79.25 (1C, C<sub>8</sub>), 47.93 (1C, C<sub>13</sub>), 40.48 (1C, C<sub>9</sub>), 34.36 (1C, C<sub>11</sub>), 31.63 (1C, C<sub>10</sub>), 25.49 (1C, C<sub>12</sub>), 23.32 (1C, C<sub>14</sub>), 22.36 (1C, C<sub>17</sub>), 21.00 (1C, C<sub>15</sub>), 15.94 (1C, C<sub>16</sub>).

HRMS calcd 239.16417, found 239.16408.

### 5-methoxy-5-methyl-2(5H)-furanone (methoxymethoxybutenolide) **B6**



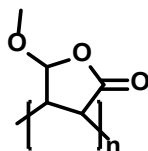
A solution of furfuryl alcohol (1.1 g, 10 mmol, 1 eq.) and methylene blue (17 mg, 52  $\mu\text{mol}$ , 0.5 mol%) in 10 mL oxygen enriched methanol was prepared in a 1000 mL round bottom flask. The mixture was put under an oxygen atmosphere in a standard lab rotary evaporator (175 rpm) and irradiated by 8 x 80 W LED lamps for 30 min. The light sources were placed at a distance of 5 cm from the flask (see **Fig. S4**). The solvent was evaporated after under reduced pressure. The obtained oil was distilled under reduced pressure (60°C,  $1.0 \times 10^{-2}$  mbar) yielding the product 5-methoxy-5-methyl-2(5H)-furanone **B6** in the first fraction as a colourless oil (0.8 gram, 6.5 mmol, 65%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (d,  $J = 5.6$  Hz, 1H), 6.19 (d,  $J = 5.7$  Hz, 1H), 3.23 (s, 3H), 1.66 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.99, 154.20, 124.18, 109.14, 51.31, 23.55

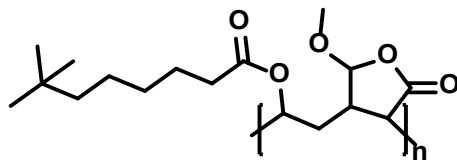
HRMS calcd 129.0546, found 129.0546.

### poly-5-methoxy-2(5H)-furanone **BP1**



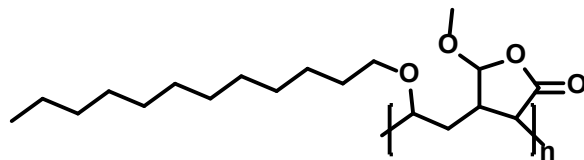
This polymer was prepared via described **General Procedure A**. 5-methoxy-2(5H)-furanone **B2** (490 mg, 4 mmol, 1 eq.) was added to the reaction mixture. The polymer poly-5-methoxy-2(5H)-furanone **BP1** was obtained after heating for 2.5 h at reflux as a slightly yellow oil (53 % conversion).

### 5-methoxy-2(5H)-furanone-VeoVa-10-copolymer **BP2**



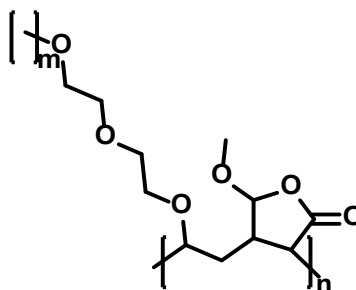
This polymer was prepared via described **General Procedure A**. 5-methoxy-2(5H)-furanone **B2** (245 mg, 2 mmol, 1 eq.) and VeoVa-10 (426 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 5-methoxy-2(5H)-furanone-VeoVa-10-copolymer **BP2** was obtained after heating for 2 h at reflux as a slightly yellow oil (98 % conversion).

### 5-methoxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer BP3



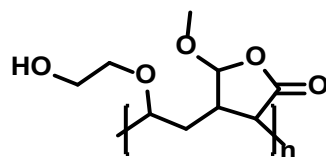
This polymer was prepared via described **General Procedure A**. 5-methoxy-2(5H)-furanone **B2** (245 mg, 2 mmol, 1 eq.) and dodecyl vinyl ether (457 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 5-methoxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer **BP3** was obtained after heating for 50 min at reflux as a slightly yellow oil (95 % conversion).

### 5-methoxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer BP4



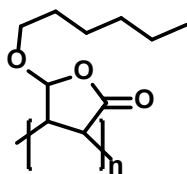
This polymer was prepared via described **General Procedure A**. 5-methoxy-2(5H)-furanone **B2** (245 mg, 2 mmol, 1 eq.) and di(ethylene glycol) divinyl ether (170 mg, 1 mmol, 0.5 eq.) were added to the reaction mixture. The polymer 5-methoxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer **BP4** was obtained after heating for 6 min at reflux as a hard white solid (69 % conversion).

### 5-methoxy-2(5H)-furanone-ethylene-glycol-vinyl-ether BP5



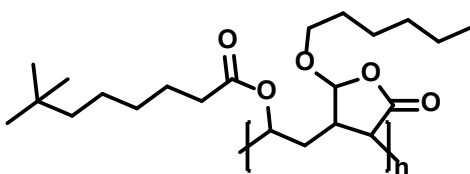
This polymer was prepared via described **General Procedure A**. 5-methoxy-2(5H)-furanone **B2** (245 mg, 2 mmol, 1 eq.) and ethylene glycol vinyl ether (189 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 5-methoxy-2(5H)-furanone-ethylene-glycol-vinyl-ether **BP5** was obtained after heating for 2 h at reflux as a slightly yellow oil (99 % conversion).

### poly-5-hexyloxy-2(5H)-furanone HP1



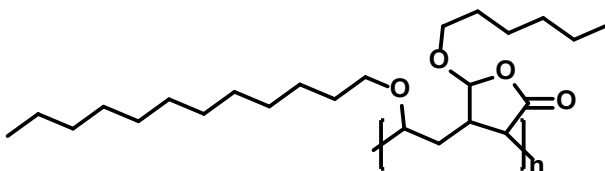
This polymer was prepared via described **General Procedure A**. 5-hexyloxy-2(5H)-furanone **B3** (792 mg, 4 mmol, 1 eq.) was added to the reaction mixture. The polymer poly-5-hexyloxy-2(5H)-furanone **HP1** was obtained after heating for 3 h at reflux as a slightly yellow oil (51 % conversion).

### 5-hexyloxy-2(5H)-furanone-VeoVa-10-copolymer HP2



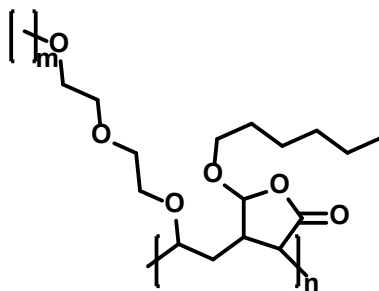
This polymer was prepared via described **General Procedure A**. 5-hexyloxy-2(5H)-furanone **B3** (396 mg, 2 mmol, 1 eq.) and VeoVa-10 (426 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 5-hexyloxy-2(5H)-furanone-VeoVa-10-copolymer **HP2** was obtained after heating for 3.5 h at reflux as a slightly yellow oil (92 % conversion).

### 5-hexyloxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer HP3



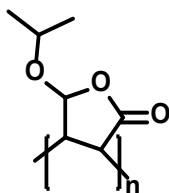
This polymer was prepared via described **General Procedure A**. 5-hexyloxy-2(5H)-furanone **B3** (396 mg, 2 mmol, 1 eq.) and dodecyl vinyl ether (457 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 5-hexyloxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer **HP3** was obtained after heating for 40 min at reflux as a slightly yellow oil (>99 % conversion).

#### 5-hexyloxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer HP4



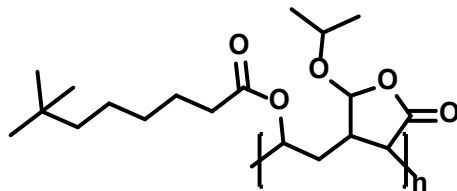
This polymer was prepared via described **General Procedure A**. 5-hexyloxy-2(5H)-furanone **B3** (396 mg, 2 mmol, 1 eq.) and di(ethylene glycol) divinyl ether (170 mg, 1 mmol, 0.5 eq.) were added to the reaction mixture. The polymer 5-hexyloxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer **HP4** was obtained after heating for 10 min at reflux as a viscous slightly yellow oil (88 % conversion).

#### poly-5-isopropoxy-2(5H)-furanone IP1



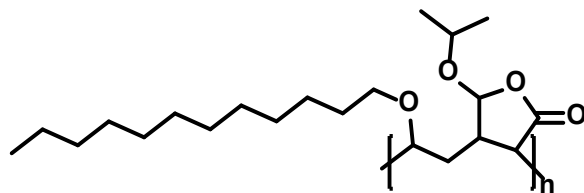
This polymer was prepared via described **General Procedure A**. 5-isopropoxy-2(5H)-furanone **B4** (611 mg, 4 mmol, 1 eq.) was added to the reaction mixture. The polymer poly-5-isopropoxy-2(5H)-furanone **IP1** was obtained after heating for 4 h at reflux as a slightly yellow oil (37 % conversion).

#### 5-isopropoxy-2(5H)-furanone-VeoVa-10-copolymer IP2



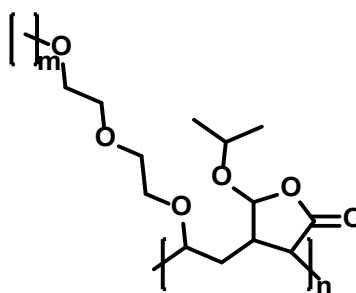
This polymer was prepared via described **General Procedure A**. 5-isopropoxy-2(5H)-furanone **B4** (306 mg, 2 mmol, 1 eq.) and VeoVa-10 (426 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 5-isopropoxy-2(5H)-furanone-VeoVa-10-copolymer **IP2** was obtained after heating for 3 h at reflux as a slightly yellow oil (96 % conversion).

### 5-isopropoxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer IP3



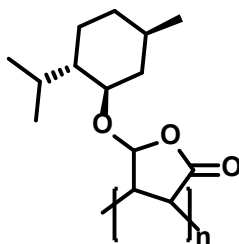
This polymer was prepared via described **General Procedure A**. 5-isopropoxy-2(5H)-furanone **B4** (306 mg, 2 mmol, 1 eq.) and dodecyl vinyl ether (457 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 5-isopropoxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer **IP3** was obtained after heating for 40 min at reflux as a slightly yellow oil (>99 % conversion).

### 5-isopropoxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer IP4



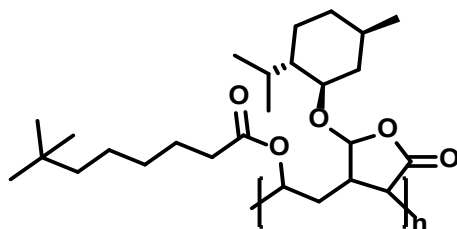
This polymer was prepared via described **General Procedure A**. 5-isopropoxy-2(5H)-furanone **B4** (306 mg, 2 mmol, 1 eq.) and di(ethylene glycol) divinyl ether (170 mg, 1 mmol, 0.5 eq.) were added to the reaction mixture. The polymer 5-isopropoxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer **IP4** was obtained after heating for 20 min at reflux as a viscous off-white oil (91 % conversion).

### poly-5-menthyloxy-2(5H)-furanone MP1



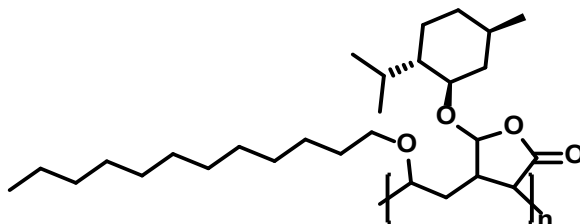
This polymer was prepared via described **General Procedure A**. 5-menthyloxy-2(5H)-furanone **B5** (1.02 g, 4 mmol, 1 eq.) was added to the reaction mixture. The polymer poly-5-menthyloxy-2(5H)-furanone **MP1** was obtained after heating for 90 min at reflux as a slightly yellow oil (30 % conversion).

### 5-menthyloxy-2(5H)-furanone-VeoVa-10-copolymer MP2



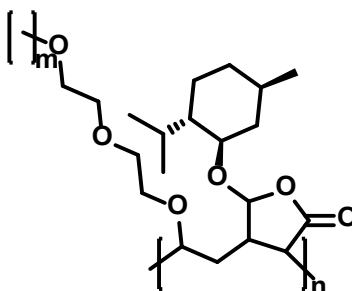
This polymer was prepared via described **General Procedure A**. 5-menthyloxy-2(5H)-furanone **B5** (512 mg, 2 mmol, 1 eq.) and VeoVa-10 (426 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 5-menthyloxy-2(5H)-furanone-VeoVa-10-copolymer **MP2** was obtained after heating for 4 h at reflux as a slightly yellow oil (92 % conversion).

### 5-menthyloxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer MP3



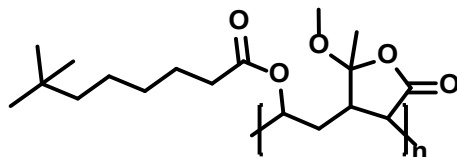
This polymer was prepared via described **General Procedure A**. 5-menthyloxy-2(5H)-furanone **B5** (512 mg, 2 mmol, 1 eq.) and dodecyl vinyl ether (457 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 5-menthyloxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer **MP3** was obtained after heating for 40 min at reflux as a slightly yellow oil (>99 % conversion).

### 5-menthyloxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer MP4



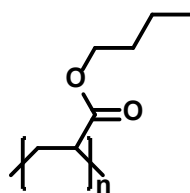
This polymer was prepared via described **General Procedure A**. 5-menthyloxy-2(5H)-furanone **B5** (512 mg, 2 mmol, 1 eq.) and di(ethylene glycol) divinyl ether (170 mg, 1 mmol, 0.5 eq.) were added to the reaction mixture. The polymer 5-menthyloxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer **MP4** was obtained after heating for 15 min at reflux as a viscous slightly yellow oil (>99 % conversion).

### 5-methoxy-5-methyl-2(5H)-furanone-VeoVa-10-copolymer MMP2



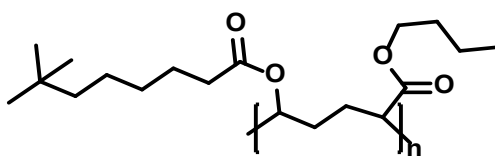
This polymer was prepared via described **General Procedure A**. 5-methoxy-5-methyl-2(5H)-furanone **B6** (275 mg, 2 mmol, 1 eq.) and VeoVa-10 (426 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 5-methoxy-5-methyl-2(5H)-furanone-VeoVa-10-copolymer **MMP2** was obtained after heating for 2.5 h at reflux as a slightly yellow oil (45 % conversion).

### poly-butyl-acrylate BAP1



This polymer was prepared via described **General Procedure A**. Butyl acrylate (551 mg, 4 mmol, 1 eq.) was added to the reaction mixture. The polymer poly-butyl-acrylate **BAP1** was obtained after heating for 6 min at reflux as a viscous colourless oil (90 % conversion).

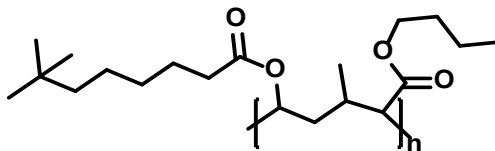
### butyl-acrylate-VeoVa-10-copolymer BAP2



This polymer was prepared via described **General Procedure A**. Freshly distilled butyl acrylate (276 mg, 2 mmol, 1 eq.) and VeoVa-10 (426 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer butyl-acrylate-VeoVa-10-copolymer **BAP2** was obtained after heating for 50 min at reflux as a colourless oil (98 % conversion).

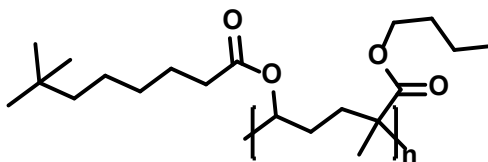


### butyl-crotonate-VeoVa-10-copolymer BCP2



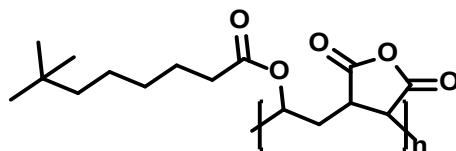
This polymer was prepared via described **General Procedure A**. Butyl crotonate (306 mg, 2 mmol, 1 eq.) and VeoVa-10 (426 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer butyl-crotonate-VeoVa-10-copolymer **BCP2** was obtained after heating for 60 min at reflux as a colourless oil (44 % conversion).

### butyl-methacrylate-VeoVa-10-copolymer BMP2



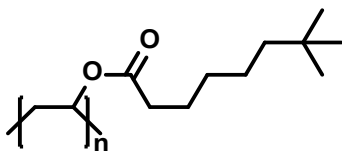
This polymer was prepared via described **General Procedure A**. Freshly distilled butyl methacrylate (306 mg, 2 mmol, 1 eq.) and VeoVa-10 (426 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer butyl-methacrylate-VeoVa-10-copolymer **BMP2** was obtained after heating for 30 min at reflux as a colourless oil (55 % conversion).

### maleic-anhydride-VeoVa-10-copolymer MAP2



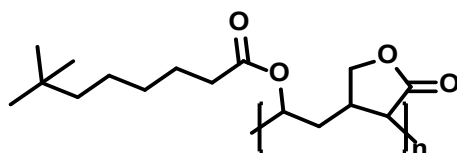
This polymer was prepared via described **General Procedure A**. Maleic anhydride (211 mg, 2 mmol, 1 eq.), VeoVa-10 (426 mg, 2 mmol, 1 eq.) and bis(trimethylsilyl)benzene (48 mg, 0.2 mmol, 0.1 eq.) as internal standard were added to the reaction mixture. The polymer maleic-anhydride-VeoVa-10-copolymer **MAP2** was obtained after heating for 60 min at reflux as a colourless oil (>99 % conversion).

### poly-VeoVa-10 VP1



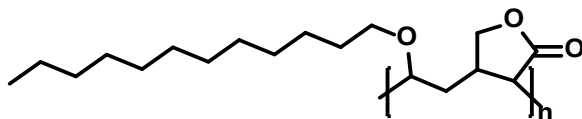
This polymer was prepared via described **General Procedure A**. VeoVa-10 (853 mg, 4 mmol, 1 eq.) was added to the reaction mixture. The polymer poly-VeoVa-10 **VP1** was obtained after heating for 40 min at reflux as a colourless oil (>99 % conversion).

### 2(5H)-furanone-VeoVa-10-copolymer FP2



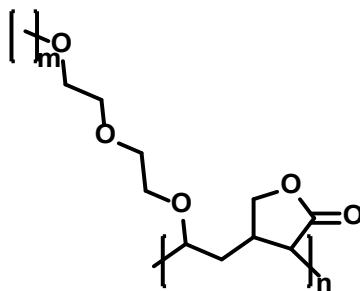
This polymer was prepared via described **General Procedure A**. 2(5H)-furanone (181 mg, 2 mmol, 1 eq.) and VeoVa-10 (426 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 2(5H)-furanone-VeoVa-10-copolymer **FP2** was obtained after heating for 2 h at reflux as a yellow oil (37 % conversion).

### 2(5H)-furanone-dodecyl-vinyl-ether-copolymer FP3



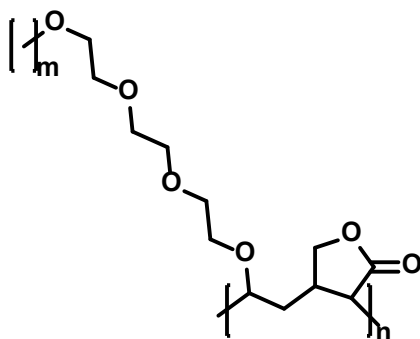
This polymer was prepared via described **General Procedure A**. 2(5H)-furanone (181 mg, 2 mmol, 1 eq.) and dodecyl vinyl ether (457 mg, 2 mmol, 1 eq.) were added to the reaction mixture. The polymer 2(5H)-furanone-dodecyl-vinyl-ether-copolymer **FP3** was obtained after heating for 60 min at reflux as a yellow oil (58 % conversion).

#### 2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer FP4



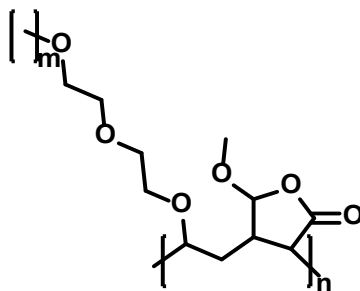
This polymer was prepared via described **General Procedure A**. 2(5H)-furanone (181 mg, 2 mmol, 1 eq.) and di(ethylene glycol) divinyl ether (170 mg, 1 mmol, 0.5 eq.) were added to the reaction mixture. The polymer 2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer **FP4** was obtained after heating for 10 min at reflux as a viscous yellow oil (35 % conversion).

#### 2(5H)-furanone-tri(ethylene glycol)-di-vinyl-ether-copolymer FP6



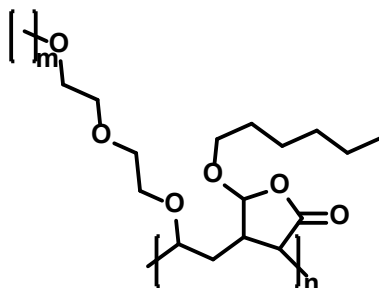
This polymer was prepared via described **General Procedure A**. 2(5H)-furanone (181 mg, 2 mmol, 1 eq.) and tri(ethylene glycol) divinyl ether (217 mg, 1 mmol, 0.5 eq.) were added to the reaction mixture. The polymer 2(5H)-furanone-tri(ethylene glycol)-di-vinyl-ether-copolymer **FP6** was obtained after heating for 20 min at reflux as a viscous yellow oil (36 % conversion).

#### 5-methoxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer BP4 (Coating)



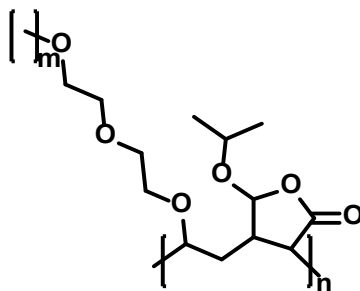
This polymer was prepared via described **General Procedure B**. 5-methoxy-2(5H)-furanone **B2** (490 mg, 4 mmol, 1 eq.), di(ethylene glycol) divinyl ether (340 mg, 2 mmol, 0.5 eq.) and Ommirad 819 (54 mg, 0.1 mmol, 3 mol%) were mixed together. The polymer 5-methoxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer **BP4** was obtained after irradiation for 5 min with an UV-lamp ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ) as a hard clear colourless coating.

#### 5-hexyloxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer HP4 (Coating)



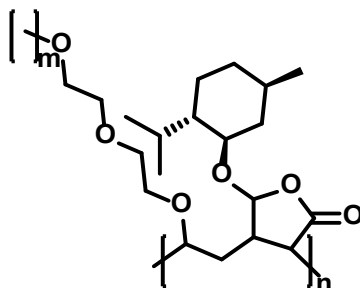
This polymer was prepared via described **General Procedure B**. 5-hexyloxy-2(5H)-furanone **B3** (792 mg, 4 mmol, 1 eq.), di(ethylene glycol) divinyl ether (340 mg, 2 mmol, 0.5 eq.) and Ommirad 819 (54 mg, 0.1 mmol, 3 mol%) were mixed together. The polymer 5-hexyloxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer **HP4** was obtained after irradiation for 5 min with an UV-lamp ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ) as a hard clear colourless coating.

### 5-isopropoxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer IP4 (Coating)



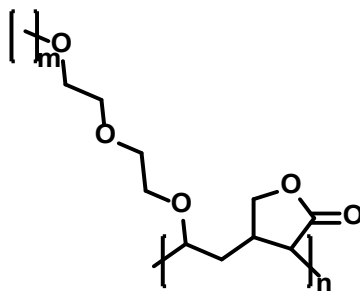
This polymer was prepared via described **General Procedure B**. 5-isopropoxy-2(5H)-furanone **B4** (611 mg, 4 mmol, 1 eq.), di(ethylene glycol) divinyl ether (340 mg, 2 mmol, 0.5 eq.) and Omirad 819 (54 mg, 0.1 mmol, 3 mol%) were mixed together. The polymer 5-isopropoxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer **IP4** was obtained after irradiation for 5 min with an UV-lamp ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ) as a hard clear colourless coating.

### 5-menthyloxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer MP4 (Coating)



This polymer was prepared via described **General Procedure B**. 5-menthyloxy-2(5H)-furanone **B5** (1.02 g, 4 mmol, 1 eq.), di(ethylene glycol) divinyl ether (340 mg, 2 mmol, 0.5 eq.), Omirad 819 (54 mg, 0.1 mmol, 3 mol%) and 0.3 mL (23 w%) of butyl acetate were mixed together. The polymer 5-menthyloxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer **MP4** was obtained after irradiation for 5 min with an UV-lamp ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ) as a hard clear colourless coating.

**2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer FP4 (coating)**

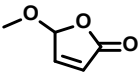
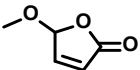
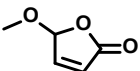
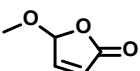
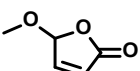
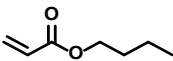
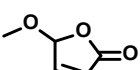
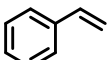
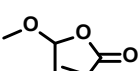
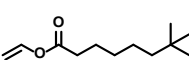
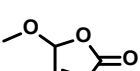
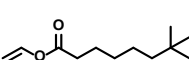
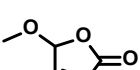
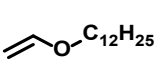
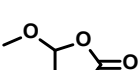
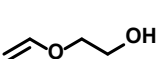


This polymer was prepared via described **General Procedure B**. 2(5H)-furanone (300 mg, 4 mmol, 1 eq.), di(ethylene glycol) divinyl ether (282 mg, 2 mmol, 0.5 eq.) and Omnirad 819 (45 mg, 0.1 mmol, 3 mol%) were mixed together. The polymer 2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer **FP4** was obtained after irradiation for 5 min with an UV-lamp ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ) as a hard clear colourless coating.

### Optimization of (co)polymerization

The (co)polymerization of alkoxybutenolides was optimized for solvent, time and comonomer. All reactions were performed at reflux conditions (butyl acetate bp. 126 °C, 1-methoxy-2-propanol bp. 120 °C.)

**Table S3.** Optimization of the (co)polymerization of methoxybutenolide **B2**. Reaction conditions: methoxybutenolide-comonomer (1:1 ratio) Trigonox 42S (6 mol%) (in case of homopolymerization 3 mol%), 2.15 M in solvent (in case of homopolymerization 4.3 M in solvent), reflux a) Mainly respective homopolymer obtained.

Entry	Monomer 1	Monomer 2	Time (min)	Solvent	Conversion (%)
1		/	120	Butyl acetate	17
2		/	210	Butyl acetate	34
3		/	210	1-methoxy-2-propanol	53
4		/	300	1-methoxy-2-propanol	53
5			10	1-methoxy-2-propanol	0 <sup>a</sup>
6			10	1-methoxy-2-propanol	0 <sup>a</sup>
7			60	1-methoxy-2-propanol	89
8			120	1-methoxy-2-propanol	98
9			120	1-methoxy-2-propanol	95
10			120	1-methoxy-2-propanol	99

## (Co)polymerization of butenolides, reaction kinetics and reactivity

### Reaction kinetics

The rate of polymerization  $R_p$  has been determined for each (co)polymer by:

**Equation S1.** Rate of polymerization.

$$R_p = -\frac{dc_M}{dt} = k_p \cdot \left(f \frac{k_d}{k_t}\right)^{0,5} \cdot c_M \cdot (c_{ini})^{0,5}$$

In the case of copolymerization  $C_M$  was substituted (49) for:

**Equation S2.** Substitution of  $C_M$  in copolymerization.

$$c_M = ([M_1] + [M_2])$$

**Equation S1** is integrated from 0 to t giving:

**Equation S3.** Integration of rate of polymerization from 0 to t.

$$\ln\left(\frac{c_M^0}{c_M}\right) = k_p \left(f \frac{k_d}{k_t} c_{ini}\right)^{0,5} \cdot t$$

The conversion of (co)polymerization is determined by:

**Equation S4.** Conversion of polymer.

$$U = \frac{c_M^0 - c_M}{c_M^0}$$

Substituting  $U$  in **equation S3** and combining the constants and variables we obtain:

**Equation S5.** Rate of polymerization as a function of t.

$$\ln\left(\frac{1}{1-U}\right) = k_{obs} \cdot t$$

By plotting  $\ln\left(\frac{1}{1-U}\right)$  against  $t$  (**equation S5**) it is possible to obtain the rate constant  $k_{obs}$  in  $s^{-1}$ . This rate constant is a combination of different parameters, which are specific to reaction and reaction conditions. It includes:



$k_p \left[ \frac{L}{mol \cdot s} \right]$  = rate constant for propagation

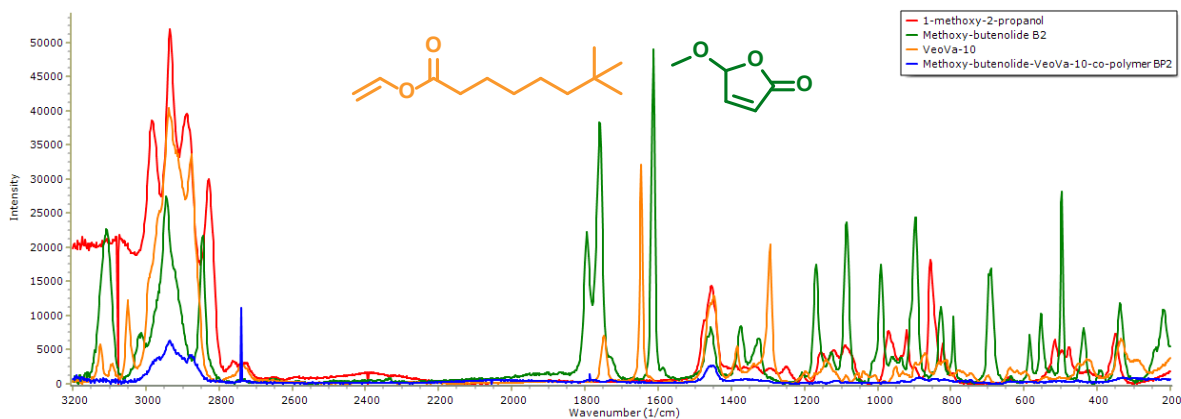
$k_d [s^{-1}]$  = rate constant for dissociation

$k_t \left[ \frac{L}{mol \cdot s} \right]$  = rate constant for termination

Additionally it is assumed that the radical concentration  $c_{ini}$  is constant and does not change over time. A substance specific correction value  $f$  is included as well. Without specific determination of the different rate constants ( $k_p, k_d, k_t$ ), the relative reactivity between the different alkoxybutenolides and the reactivity between butenolides and commonly used monomers can be compared through the comparison of the value for  $k_{obs}$ , provided that these values are obtained under the same reaction conditions.

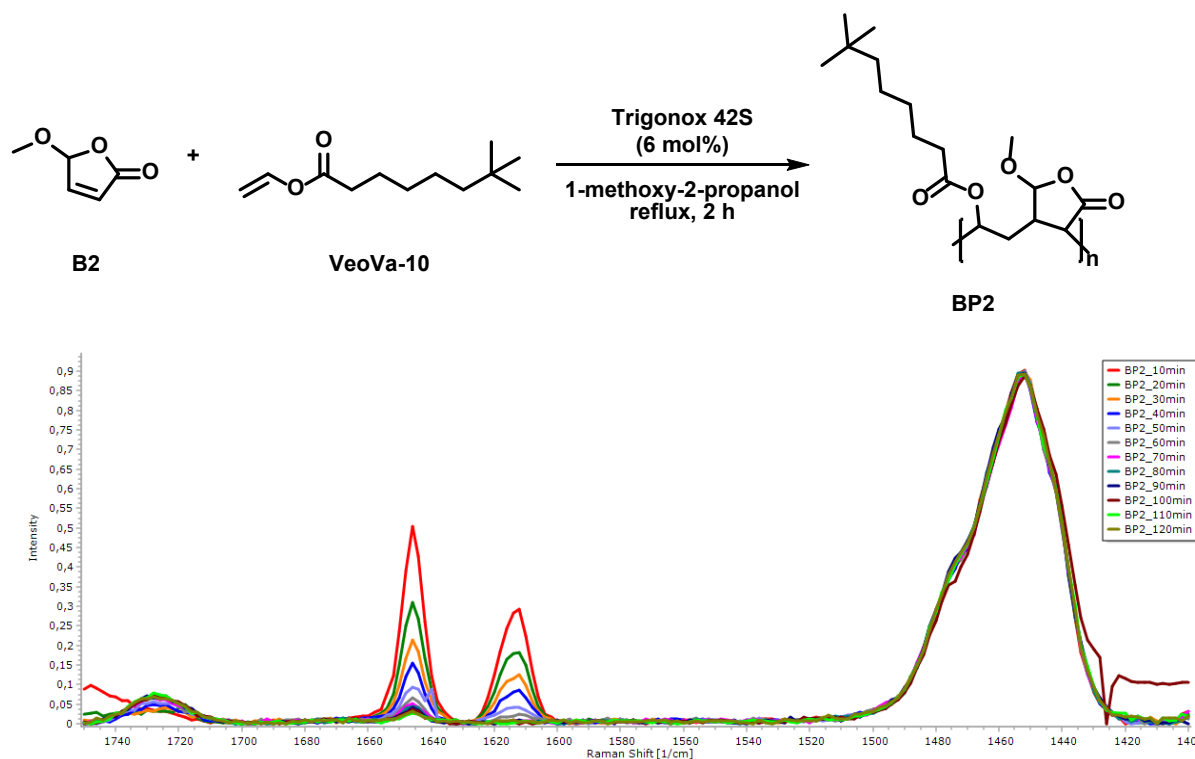
## Raman Spectroscopy

The reaction kinetics of the copolymerization of methoxybutenolide **B2** with VeoVa-10 were determined by Raman Spectroscopy by following the C=C Raman bands of the individual monomers (C=C methoxybutenolide **B2**;  $1612\text{ cm}^{-1}$ , C=C VeoVa-10,  $1646\text{ cm}^{-1}$ ). Integrating these bands against the normalized Raman band of -OH ( $1440\text{ cm}^{-1}$ ) of 1-methoxy-2-propanol, results in the concentrations of the individual monomers. Using the conversion ( $U$ ), that was determined from the concentrations over time,  $\ln(1/(1-U))$  can be plotted against time in which the observed rate constant  $k_{\text{obs}}$  is the slope of the function.



**Fig. S5.** Stacked Raman spectrum of monomers methoxybutenolide **B2** (green), VeoVa-10 (yellow), the solvent 1-methoxy-2-propanol (red) and the resulting copolymer methoxybutenolide-VeoVa-10-copolymer **BP2** (blue).

The polymer methoxybutenolide-VeoVa-10-copolymer **BP2** was synthesized according to **General procedure A**, where samples were taken and flash frozen ( $-18^{\circ}\text{C}$ ) at certain timestamps.

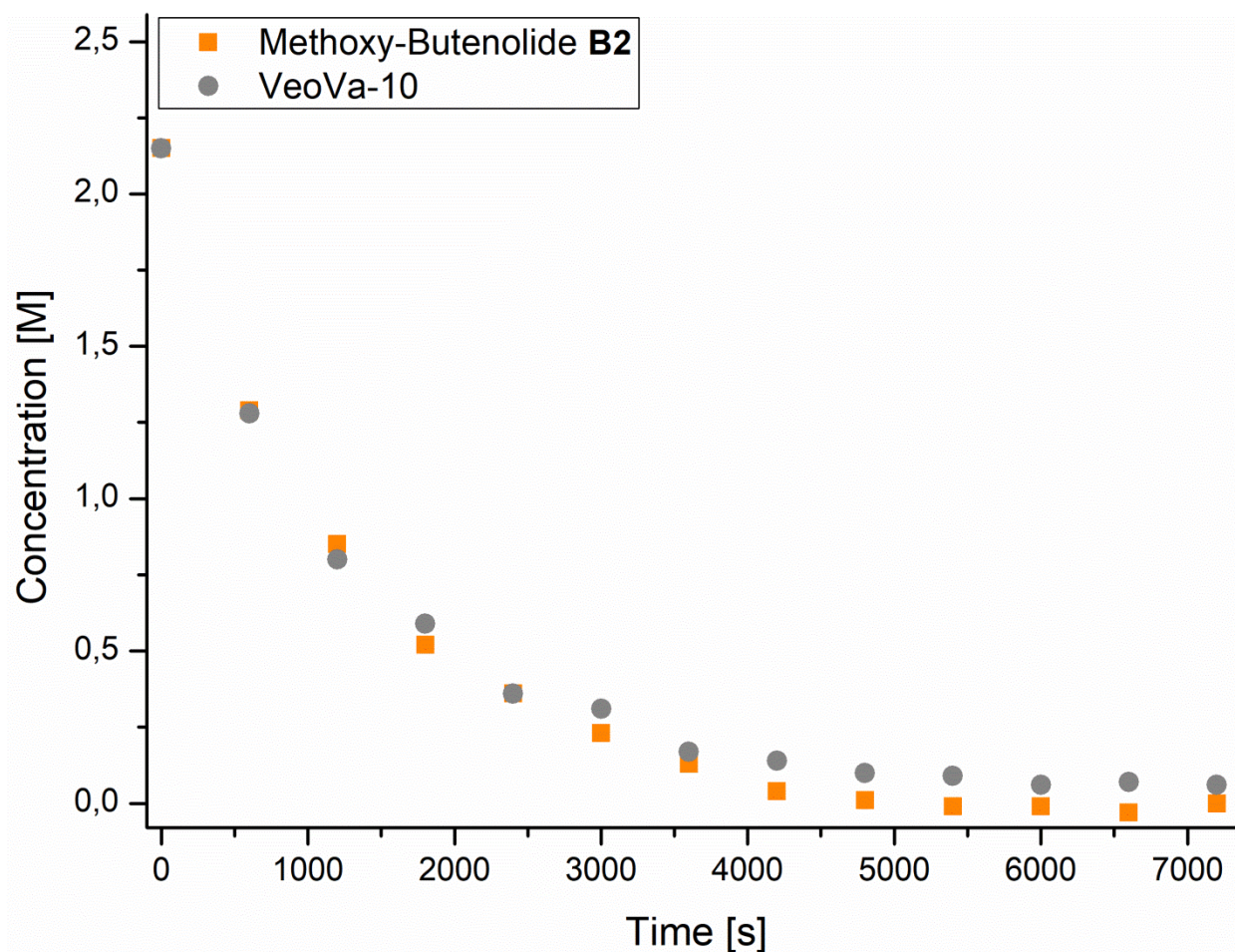


**Fig. S6.** Reaction scheme copolymerization methoxybutenolide **B2** with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h (top). Raman bands (C=C methoxybutenolide **B2**; 1612 cm<sup>-1</sup>, C=C VeoVa-10, 1646 cm<sup>-1</sup>) over time by taking samples and flash freezing (-18°C) them at certain timestamps. Spectrum normalized on -OH Raman band (1440 cm<sup>-1</sup>) of 1-methoxy-2-propanol.

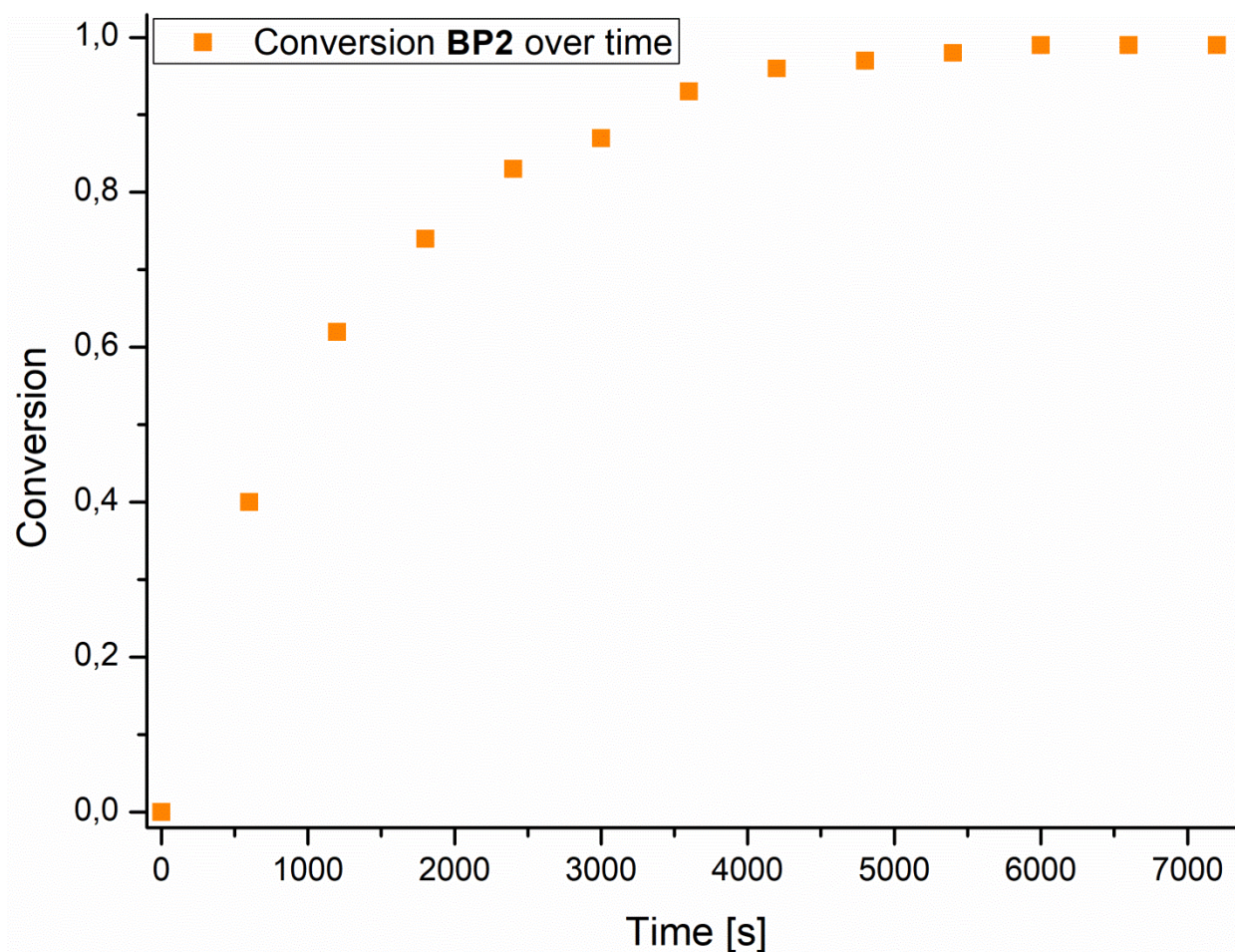
The designated areas of the Raman spectra were integrated and the equations were used to determine the values for  $\ln\left(\frac{1}{1-U}\right)$ . Plotting these values against  $t$  resulted in a linear relation in which the slope of the function is the value for  $k_{obs}$ .

**Table S4.** Kinetic studies of the copolymerization of methoxybutenolide **B2** and VeoVa-10 (1:1 ratio), followed by Raman spectroscopy. Integrated Raman bands (C=C methoxybutenolide **B2**; 1612 cm<sup>-1</sup>, C=C VeoVa-10, 1646 cm<sup>-1</sup>) over time determined by integration against the normalized -OH Raman band (1440 cm<sup>-1</sup>) of 1-methoxy-2-propanol. Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

Methoxybutenolide-VeoVa-10-copolymer BP2						
	Methoxybutenolide <b>B2</b>		VeoVa-10		$k(obs)$	$(7.4 \pm 0.1) \cdot 10^{-4}$ [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	5,34	2,15	7,29	2,15	0,00	0,00
600	3,22	1,29	4,34	1,28	0,40	0,51
1200	2,11	0,85	2,71	0,80	0,62	0,96
1800	1,29	0,52	2,00	0,59	0,74	1,35
2400	0,90	0,36	1,23	0,36	0,83	1,78
3000	0,56	0,23	1,06	0,31	0,87	2,07
3600	0,33	0,13	0,59	0,17	0,93	2,65
4200	0,10	0,04	0,47	0,14	0,96	3,18
4800	0,03	0,01	0,34	0,10	0,97	3,64
5400	-0,02	-0,01	0,32	0,09	0,98	3,93
6000	-0,02	-0,01	0,20	0,06	0,99	4,47
6600	-0,07	-0,03	0,24	0,07	0,99	4,55
7200	-0,01	0,00	0,19	0,06	0,99	4,38

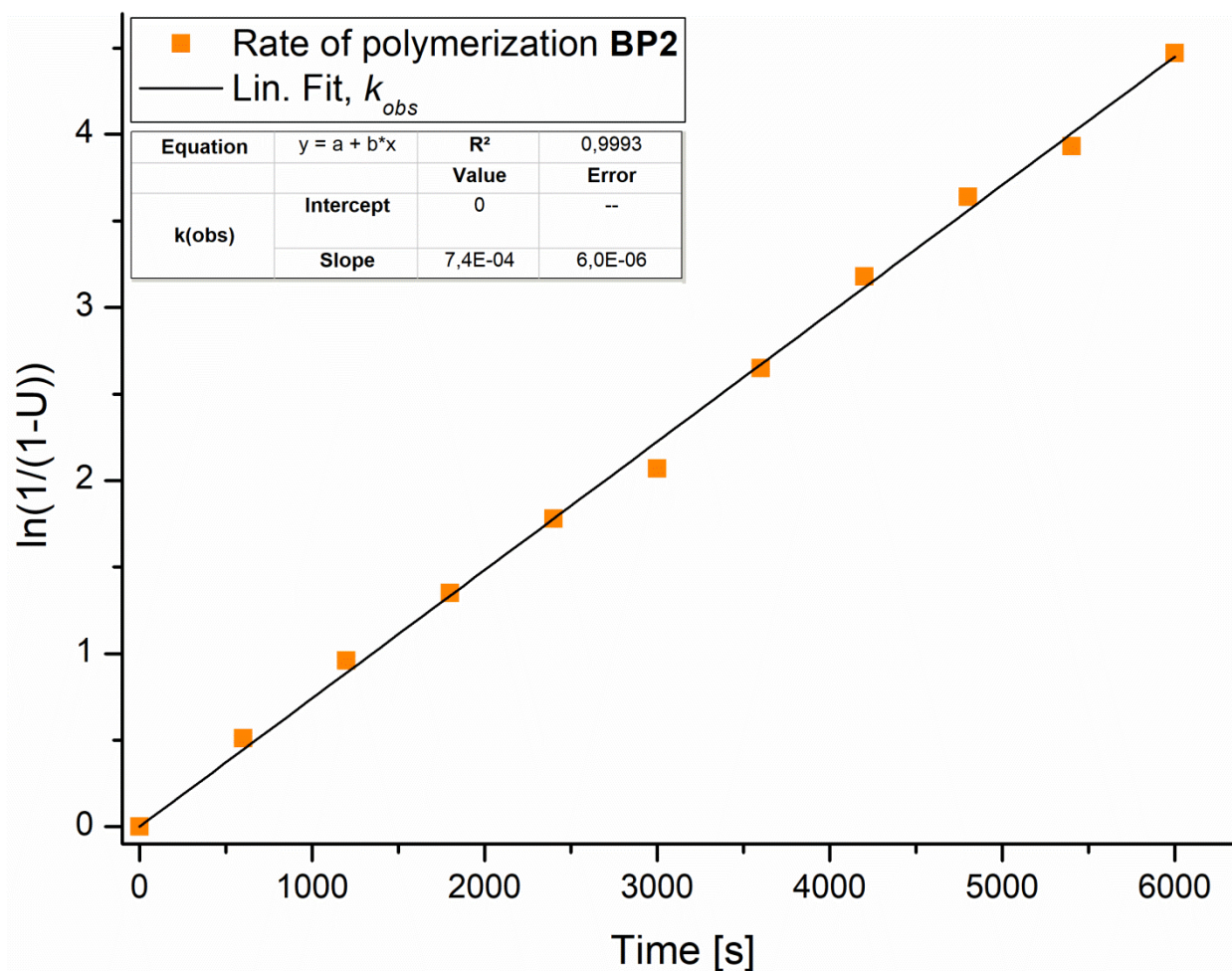


**Fig. S7.** Concentration of monomers over time of the copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) followed by integration of C=C absorption bands (C=C methoxybutenolide **B2**;  $1612\text{ cm}^{-1}$ , C=C VeoVa-10,  $1646\text{ cm}^{-1}$ ) against the normalized  $\text{-OH}$  Raman band ( $1440\text{ cm}^{-1}$ ) of 1-methoxy-2-propanol over time using Raman Spectroscopy by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.



**Fig. S8.** Conversion of polymer **BP2** over time; copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) followed by integration of C=C absorption bands (C=C methoxybutenolide **B2**;  $1612\text{ cm}^{-1}$ , C=C VeoVa-10,  $1646\text{ cm}^{-1}$ ) against the normalized  $\text{-OH}$  Raman band ( $1440\text{ cm}^{-1}$ ) of 1-methoxy-2-propanol over time using Raman Spectroscopy by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

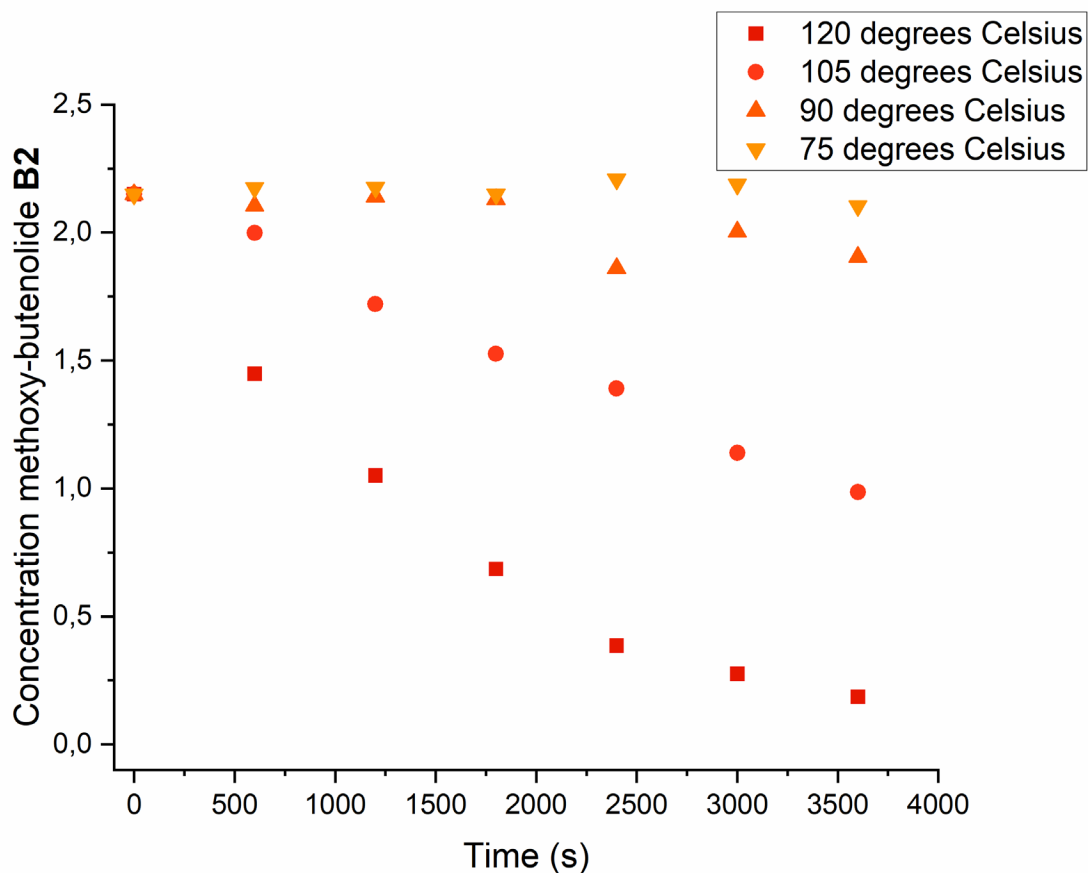




**Fig. S9.** Rate of copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) to **BP2** over time followed by integration of C=C absorption bands (C=C methoxybutenolide **B2**; 1612 cm<sup>-1</sup>, C=C VeoVa-10, 1646 cm<sup>-1</sup>) against the normalized -OH Raman band (1440 cm<sup>-1</sup>) of 1-methoxy-2-propanol over time using Raman Spectroscopy by taking samples and flash freezing (-18°C) them at certain timestamps. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

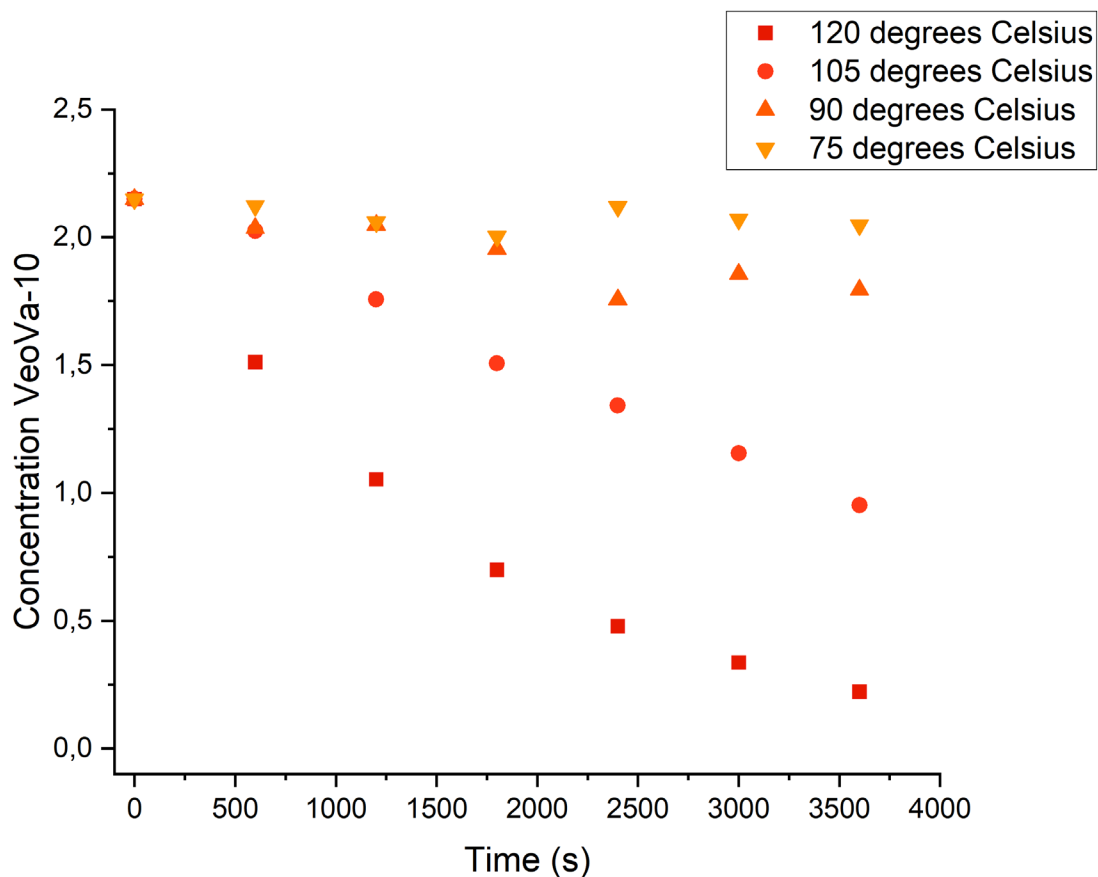
## Temperature effect on reaction kinetics

The copolymerization of methoxybutenolide **B2** and VeoVa-10 was performed at different temperatures, 75, 90, 105 and 120°C (reflux), to determine the effect of the temperature on the reaction kinetics. The effect was measured by Raman spectroscopy in the same manner as described in **General procedure A** and expressed as concentration over time (see **Fig. S10** and **S11**). Since there was no consumption of monomers already at 75°C, flash freezing the samples immediately to -18°C during the (co)polymerization reactions is an effective way to accurately measure the concentration of the monomers at a given time.



**Fig. S10.** The effect of different temperature on the concentration of methoxybutenolide **B2** in the copolymerization of methoxybutenolide **B2** and VeoVa-10 followed by Raman spectroscopy ( $C=C$  methoxybutenolide **B2**;  $1612\text{ cm}^{-1}$ ). Copolymerization performed at 120 °C (dark red square), copolymerization performed at 105 °C (red circle), copolymerization performed at 90 °C (dark orange triangle), copolymerization performed at 75 °C (orange inverted triangle). Reaction conditions: methoxybutenolide-VeoVa-10 (1:1 ratio), Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.





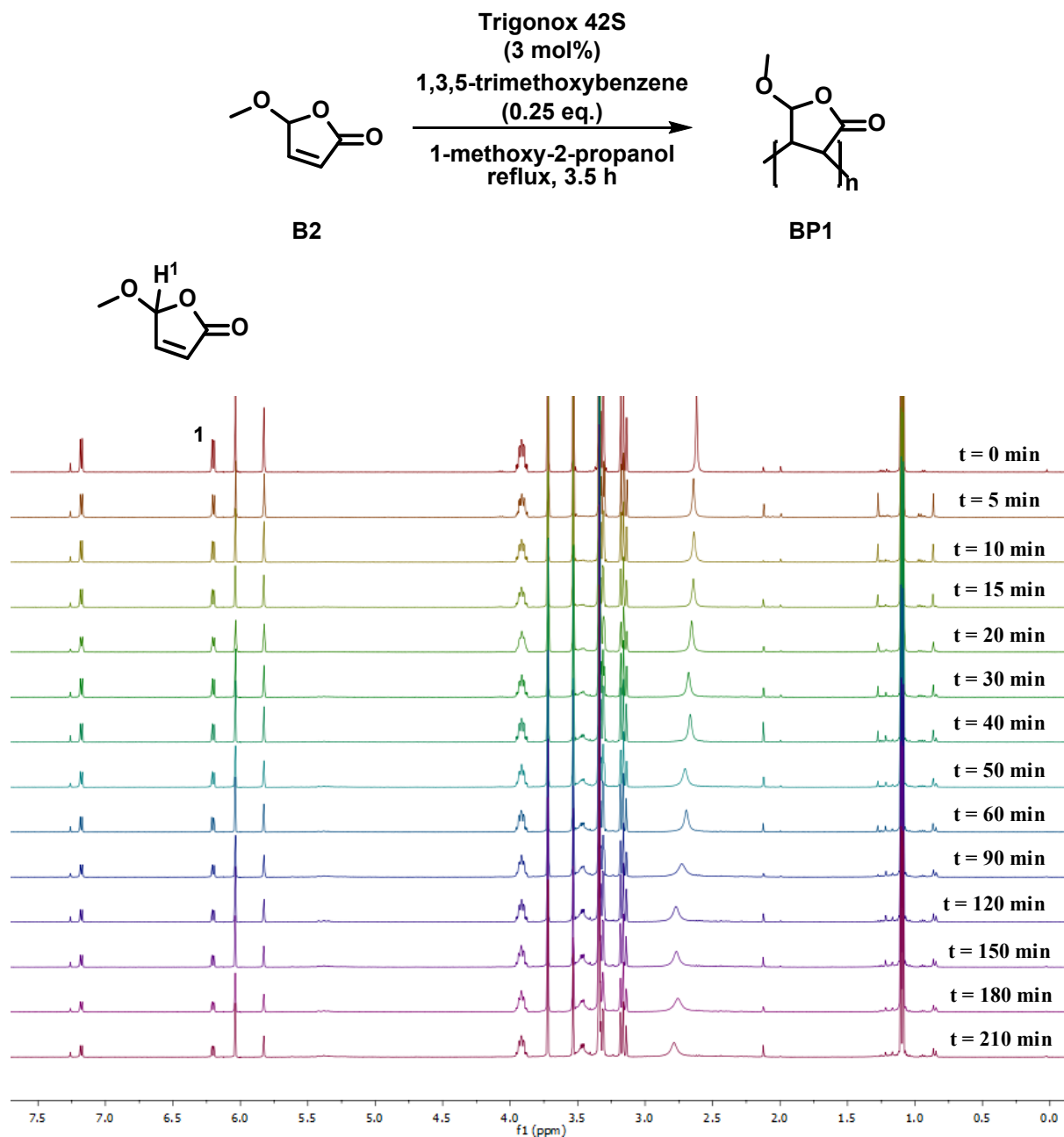
**Fig. S11.** The effect of different temperature on the concentration of VeoVa-10 in the copolymerization of methoxybutenolide **B2** and VeoVa-10 followed by Raman spectroscopy ( $C=C$  VeoVa-10;  $1646\text{ cm}^{-1}$ ). Copolymerization performed at  $120\text{ }^{\circ}\text{C}$  (dark red square), copolymerization performed at  $105\text{ }^{\circ}\text{C}$  (red circle), copolymerization performed at  $90\text{ }^{\circ}\text{C}$  (dark orange triangle), copolymerization performed at  $75\text{ }^{\circ}\text{C}$  (orange inverted triangle). Reaction conditions: methoxybutenolide-VeoVa-10 (1:1 ratio), Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.

## **<sup>1</sup>H-NMR Spectroscopy**

Due to the overlap of the C=C absorption bands of alkoxybutenolides **B3–5** and VeoVa-10 as well as the C=C absorption bands of all alkoxybutenolides **B2–5** with both dodecyl vinyl ether and di(ethylene glycol) divinyl ether, it was decided to change to <sup>1</sup>H NMR spectroscopy as the analytical technique to measure the reaction kinetics. In a similar fashion the concentrations of the monomers were followed by integrating the proton NMR signals. To determine the absolute concentration at a certain point, 1,3,5-trimethoxybenzene, an internal standard, was added to the reaction mixture (0.5 eq.). In the case of copolymerization of maleic anhydride with VeoVa-10, bis(trimethylsilyl)benzene was chosen as the internal standard (0.1 eq.). The equations (**Equations S1–S5**, *vide supra*) were used to determine the values for  $\ln\left(\frac{1}{1-U}\right)$ . Plotting these values against  $t$  resulted in a linear relation in which the slope of the function is the value for  $k_{obs}$ .

<sup>1</sup>H-NMR shifts that have been followed are <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): methoxybutenolide **B2** δ 6.21 (1H), hexyloxybutenolide **B3** δ 6.22 (1H), isopropoxybutenolide **B4** δ 6.20 (1H), menthyloxybutenolide **B5** δ 6.17 (1H), VeoVa-10 δ 4.50 (1H), dodecyl vinyl ether δ 6.43 (1H), di(ethylene glycol) divinyl ether δ 6.46 (2H), tri(ethylene glycol) divinyl ether δ 6.46 (2H), ethylene glycol vinyl ether δ 6.43 (1H), butyl acrylate δ 6.36 (1H), butyl crotonate δ 5.81 (1H), butyl methacrylate δ 5.53 (1H), maleic anhydride δ 7.00 (2H), 2(5H)-furanone δ 7.55 (1H).

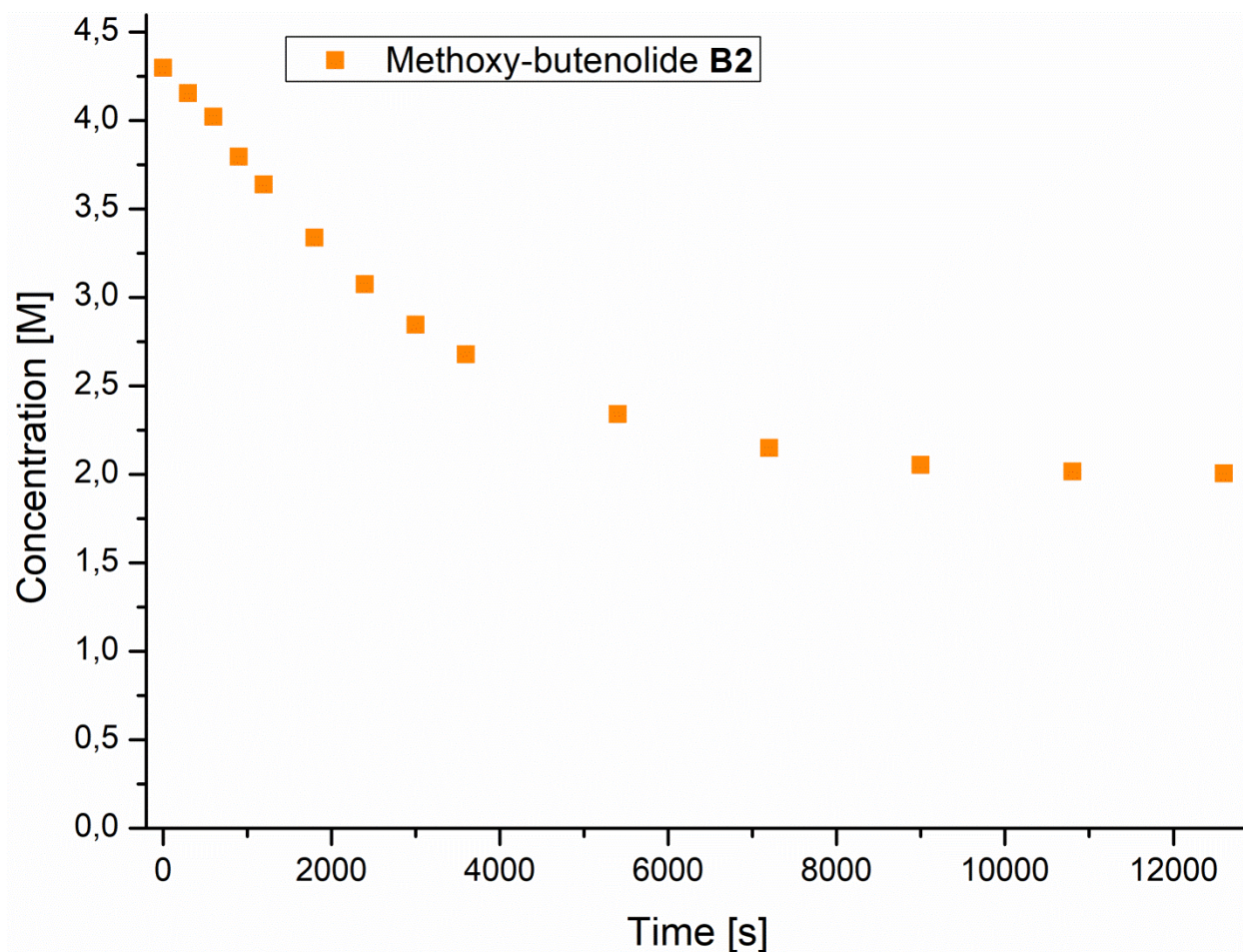
poly-5-methoxy-2(5H)-furanone BP1



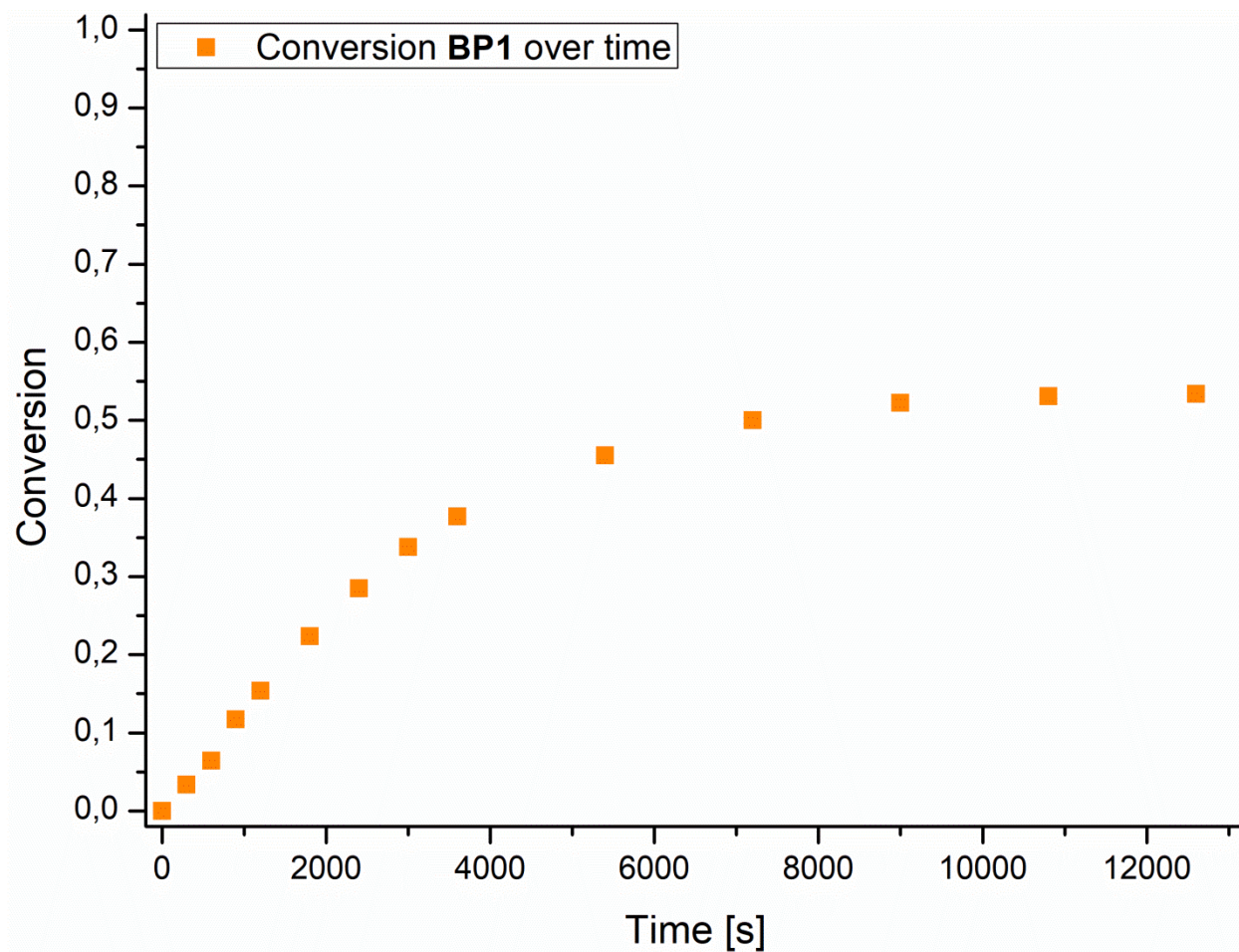
**Fig. S12.** Reaction scheme scheme homopolymerization methoxybutenolide **B2** (2 eq.), reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 3.5 h (top).  $^1\text{H NMR}$  signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard (bottom).

**Table S5.** Kinetic studies of the homopolymerization of methoxybutenolide **B2** (2 eq.), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.25 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 3.5 h.

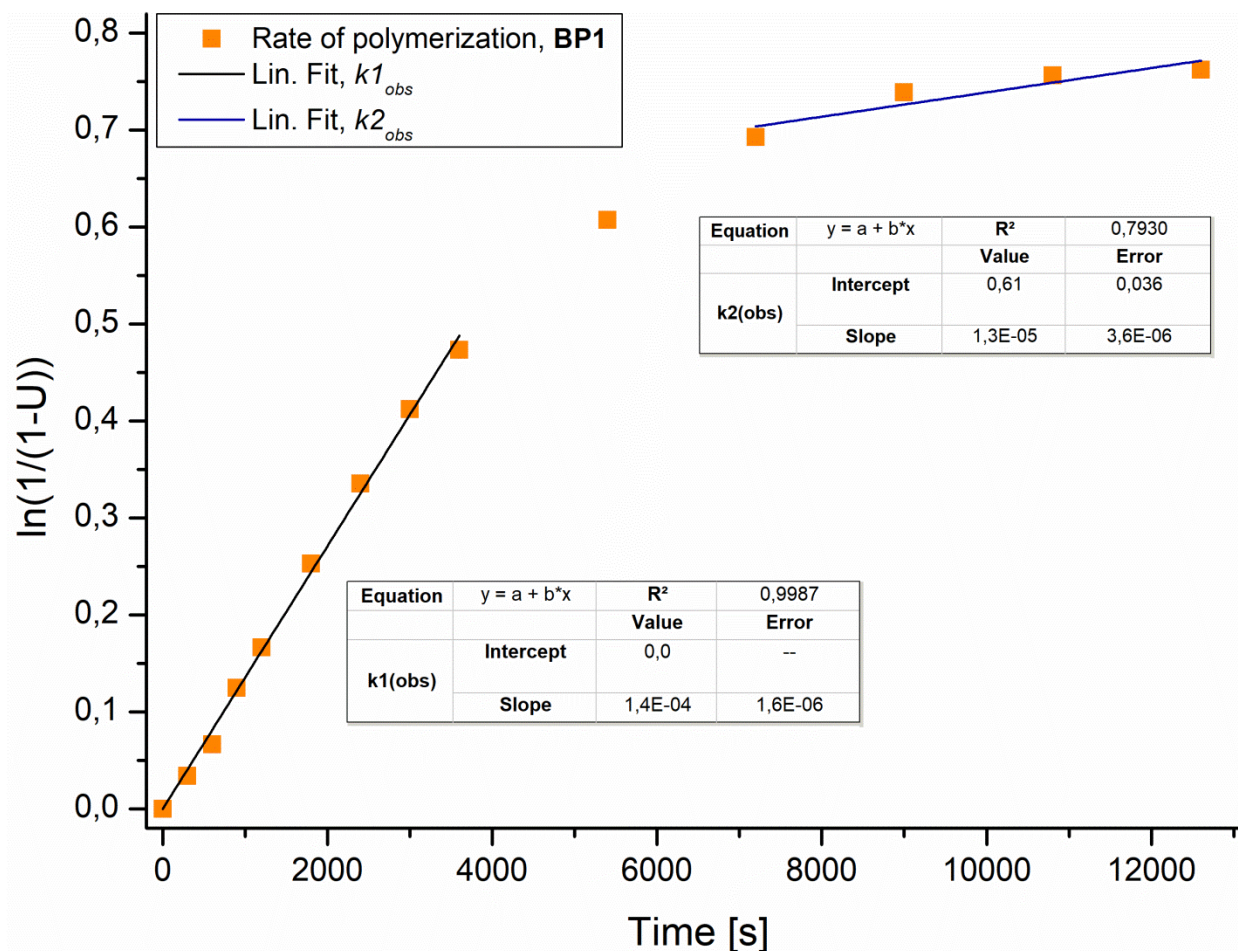
Methoxybutenolide-polymer BP1			k1(obs)	(1.4±0.1)·10 <sup>-4</sup> [s <sup>-1</sup> ]
Methoxybutenolide B2			k2(obs)	(1.3±0.4)·10 <sup>-5</sup> [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,90	4,30	0,00	0,00
300	0,87	4,15	0,03	0,03
600	0,84	4,02	0,06	0,07
900	0,79	3,79	0,12	0,12
1200	0,76	3,64	0,15	0,17
1800	0,70	3,34	0,22	0,25
2400	0,64	3,07	0,28	0,34
3000	0,59	2,85	0,34	0,41
3600	0,56	2,68	0,38	0,47
5400	0,49	2,34	0,46	0,61
7200	0,45	2,15	0,50	0,69
9000	0,43	2,05	0,52	0,74
10800	0,42	2,02	0,53	0,76
12600	0,42	2,01	0,53	0,76



**Fig. S13.** Concentration of the monomer methoxybutenolide **B2** over time followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 3.5 h.

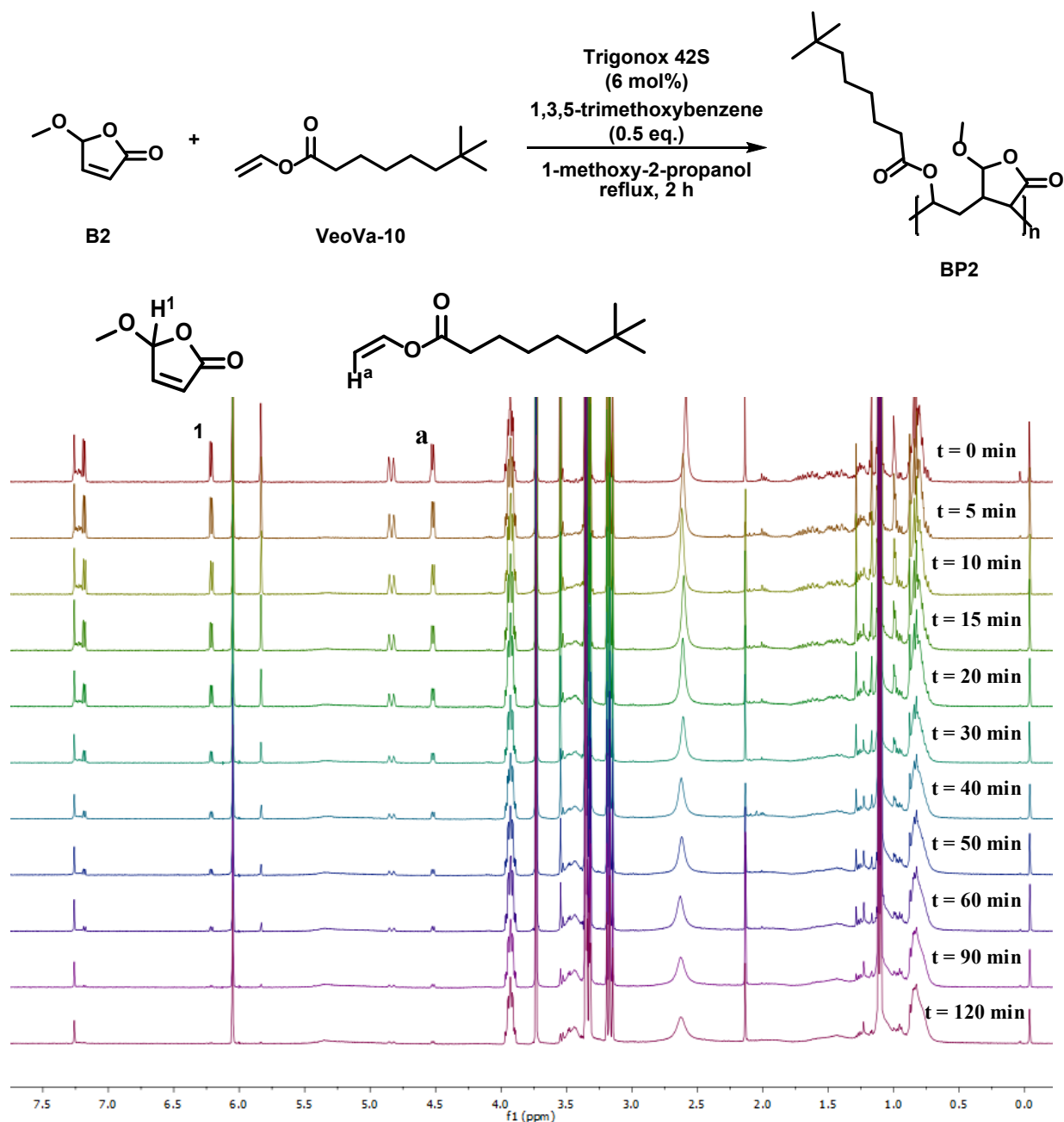


**Fig. S14.** Conversion of polymer **BP1** over time; homo-polymerization of methoxybutenolide **B2** followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 3.5 h.



**Fig. S15.** Rate of homo-polymerization of methoxybutenolide **B2** to **BP1** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 3.5 h.

### 5-methoxy-2(5H)-furanone-VeoVa-10-copolymer BP2

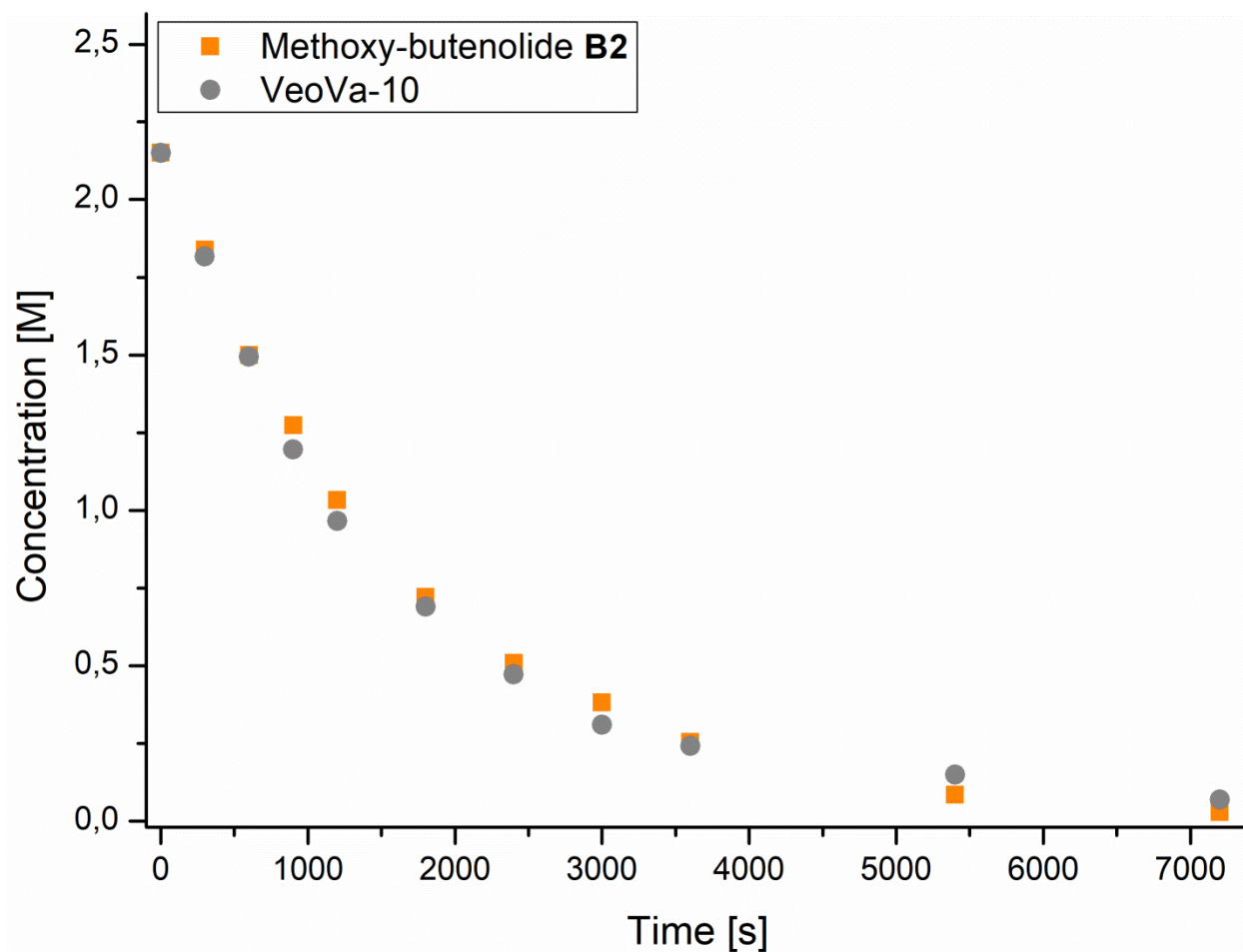


**Fig. S16.** Reaction scheme copolymerization methoxybutenolide **B2** with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

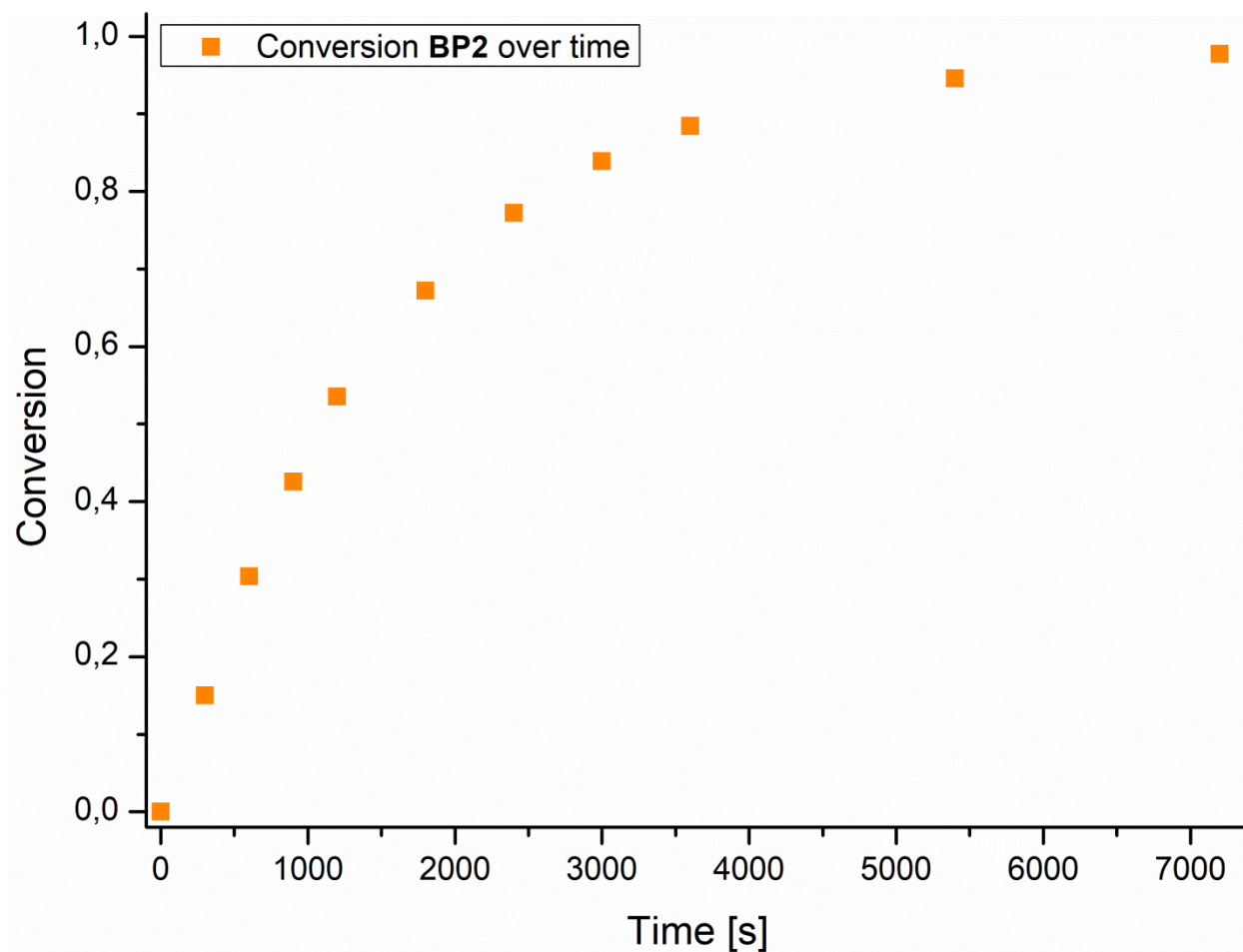


**Table S6.** Kinetic studies of the copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

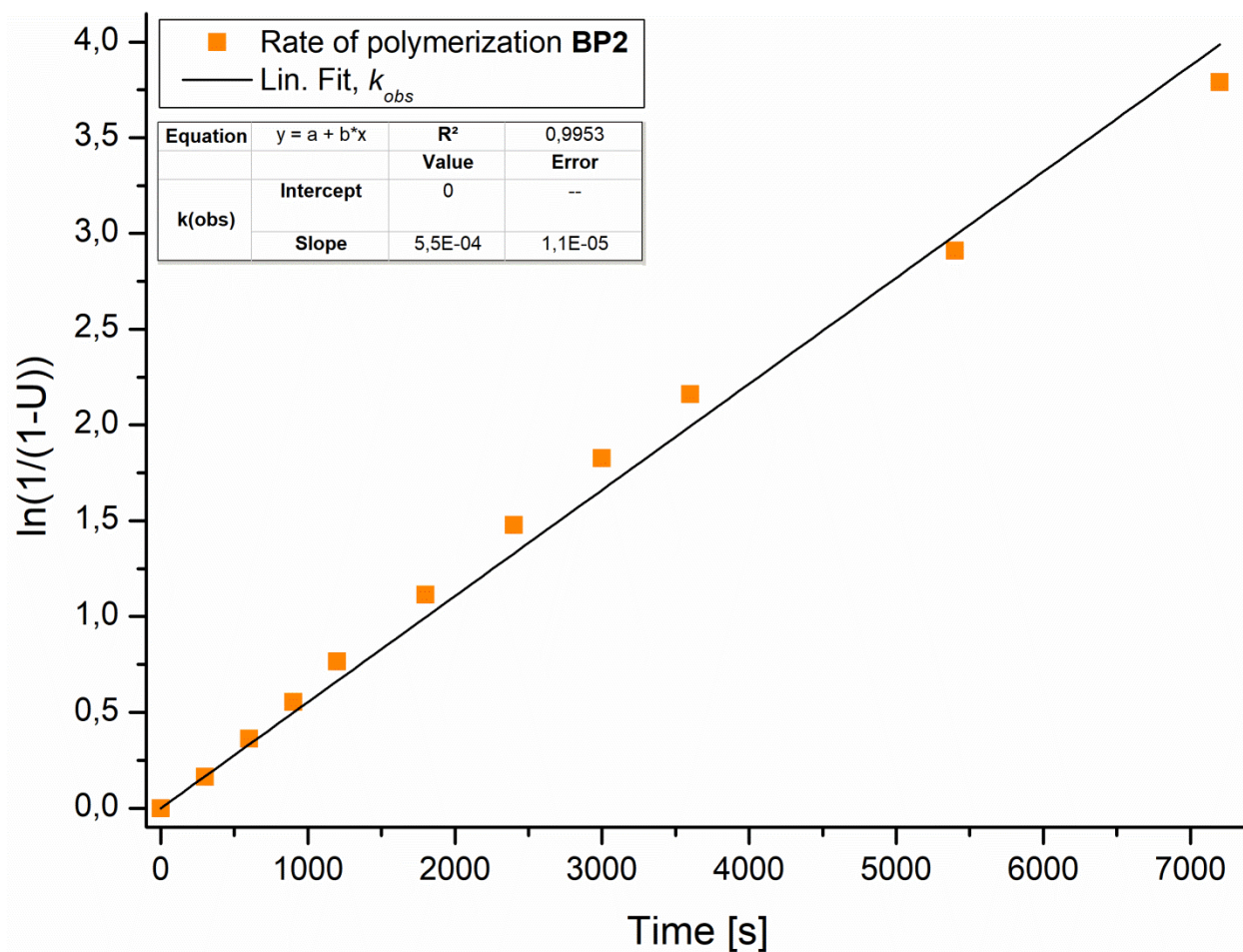
Methoxybutenolide-VeoVa-10-copolymer BP2						
	Methoxybutenolide B2		VeoVa-10		k(obs)	$(5.5 \pm 0.1) \cdot 10^{-4}$ [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	0,76	2,15	0,94	2,15	0,00	0,00
300	0,65	1,84	0,79	1,82	0,15	0,16
600	0,53	1,50	0,65	1,49	0,30	0,36
900	0,45	1,27	0,52	1,20	0,43	0,55
1200	0,37	1,03	0,42	0,97	0,54	0,77
1800	0,26	0,72	0,30	0,69	0,67	1,11
2400	0,18	0,51	0,21	0,47	0,77	1,48
3000	0,14	0,38	0,14	0,31	0,84	1,83
3600	0,09	0,25	0,11	0,24	0,88	2,16
5400	0,03	0,08	0,07	0,15	0,95	2,91
7200	0,01	0,03	0,03	0,07	0,98	3,79



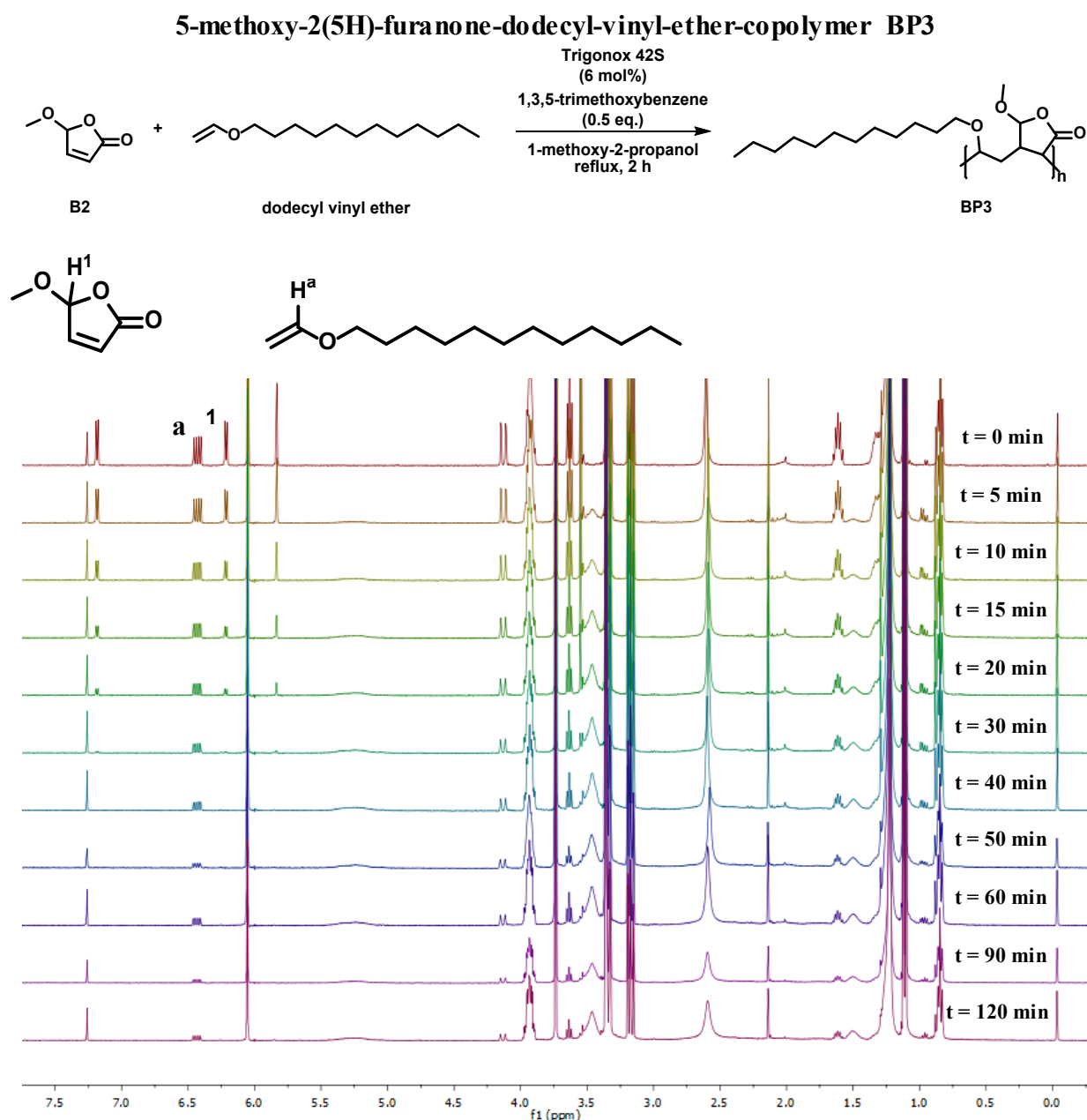
**Fig. S17.** Concentration of monomers over time of the copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.



**Fig. S18.** Conversion of polymer **BP2** over time; copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.



**Fig. S19.** Rate of copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) to **BP2** over time; followed by <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

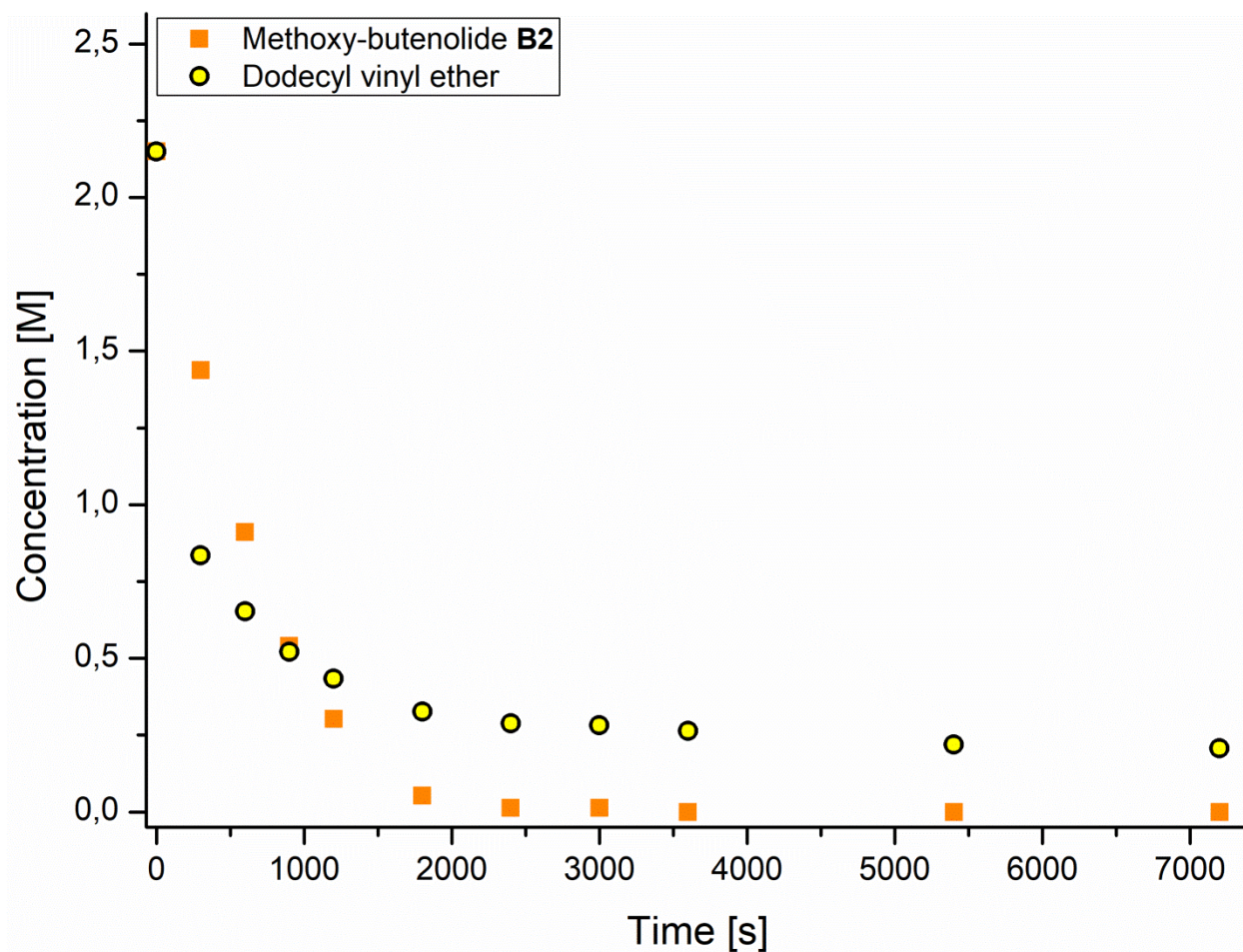


**Fig. S20.** Reaction scheme copolymerization methoxybutenolide **B2** with dodecyl vinyl ether (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

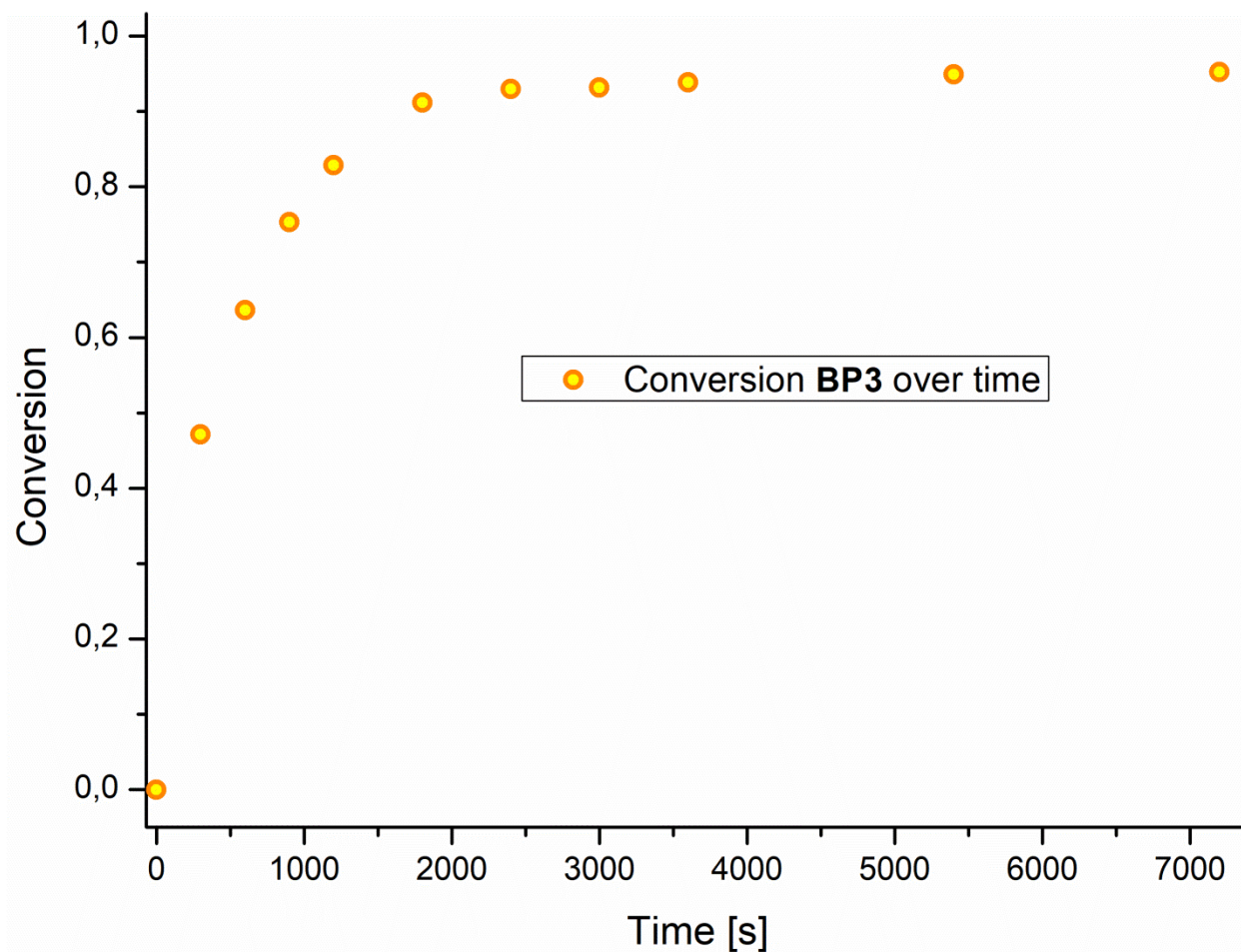
**Table S7.** Kinetic studies of the copolymerization of methoxybutenolide **B2** with dodecyl vinyl ether (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

Methoxybutenolide-dodecyl-vinyl-ether-copolymer BP3					k1(obs)	$(1.4 \pm 0.1) \cdot 10^{-3}$ [s <sup>-1</sup> ]
Methoxybutenolide <b>B2</b>		Dodecyl vinyl ether		k2(obs)	$(8.5 \pm 0.1) \cdot 10^{-5}$ [s <sup>-1</sup> ]	
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	0,82	2,15	0,86	2,15	0,00	0,00
300	0,55	1,44	0,67	0,84	0,47	0,64
600	0,35	0,91	0,52	0,65	0,64	1,01
900	0,21	0,54	0,42	0,52	0,75	1,40
1200	0,12	0,30	0,35	0,43	0,83	1,76
1800	0,02	0,05	0,26	0,33	0,91	2,43
2400	0,01	0,01	0,23	0,29	0,93	2,66
3000	0,01	0,01	0,23	0,28	0,93	2,68
3600	0,00	0,00	0,21	0,26	0,94	2,79
5400	0,00	0,00	0,18	0,22	0,95	2,97
7200	0,00	0,00	0,17	0,21	0,95	3,03



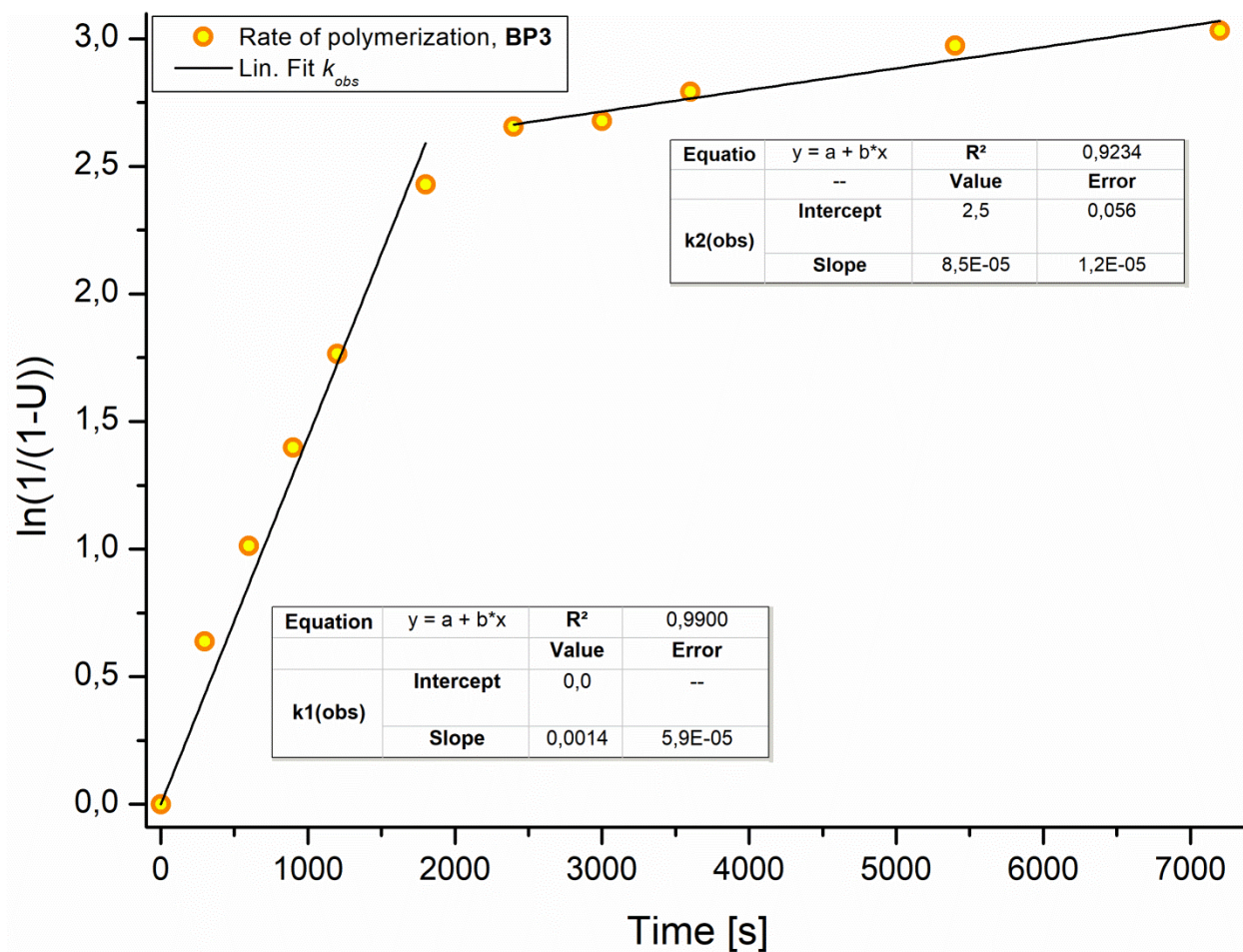


**Fig. S21.** Concentration of monomers over time of the copolymerization of methoxybutenolide **B2** with dodecyl vinyl ether (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.



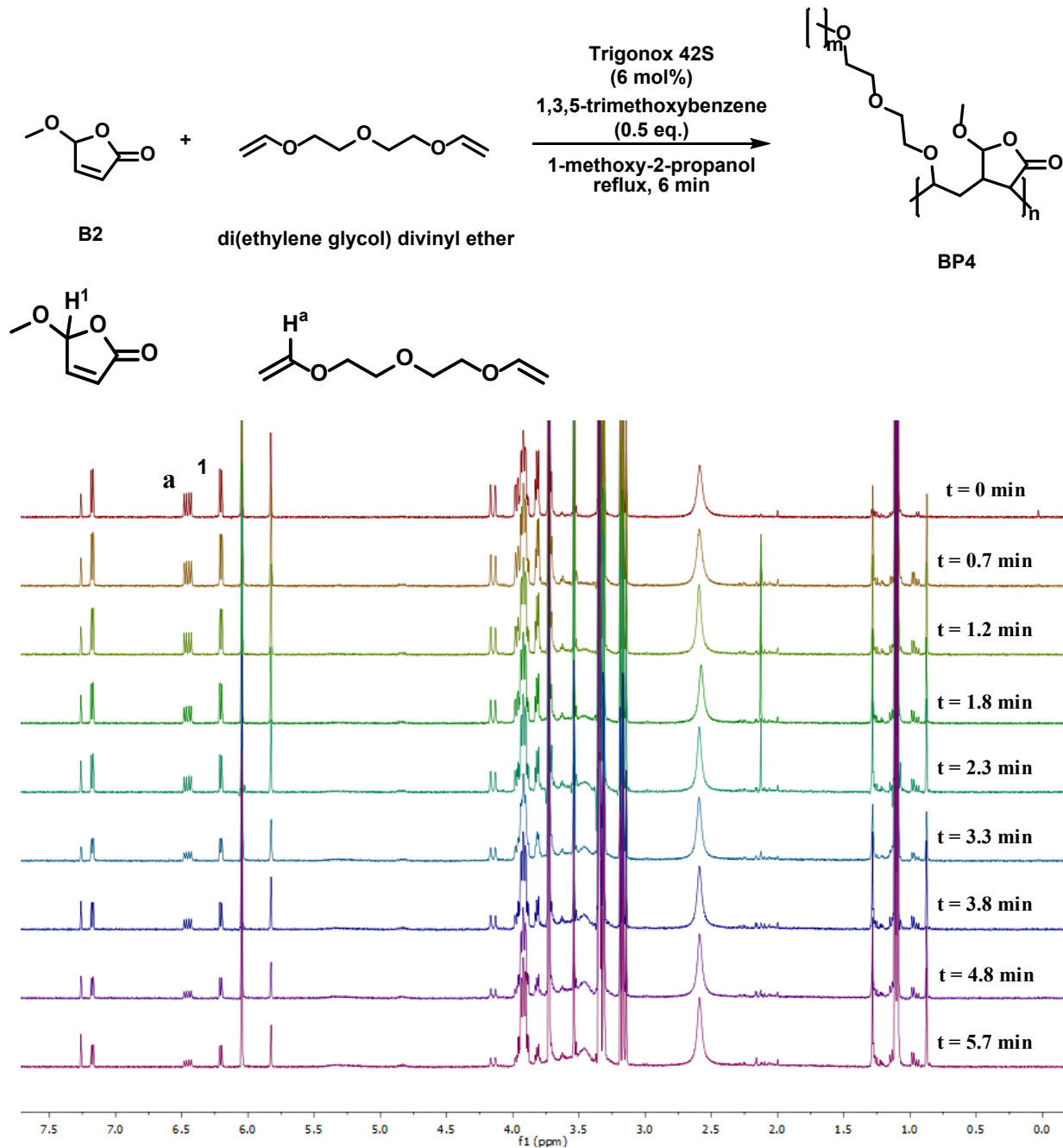
**Fig. S22.** Conversion of polymer **BP3** over time; copolymerization of methoxybutenolide **B2** with dodecyl vinyl ether (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.





**Fig. S23.** Rate of copolymerization of methoxybutenolide **B2** with dodecyl vinyl ether (1:1 ratio) to **BP3** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

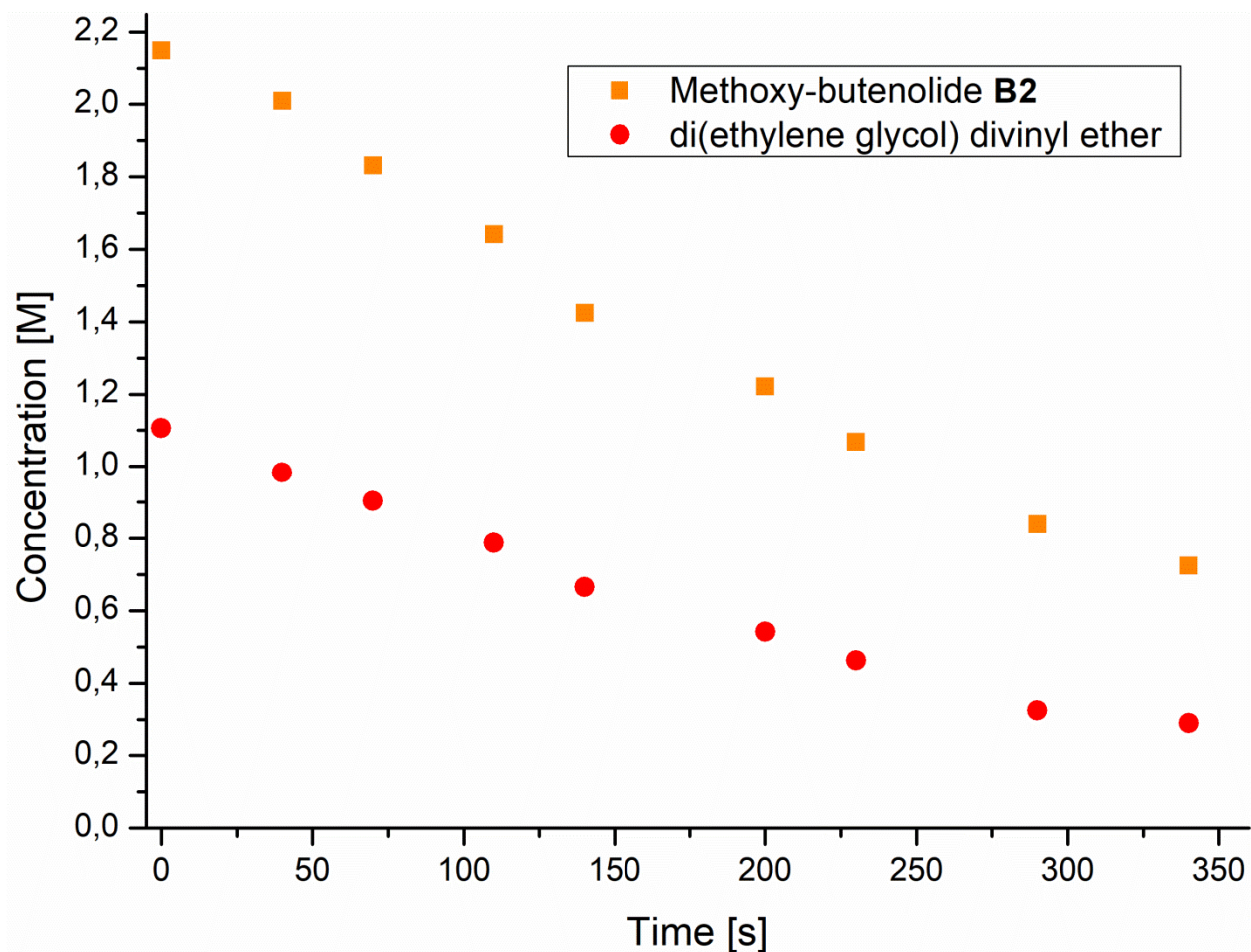
5-methoxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer BP4



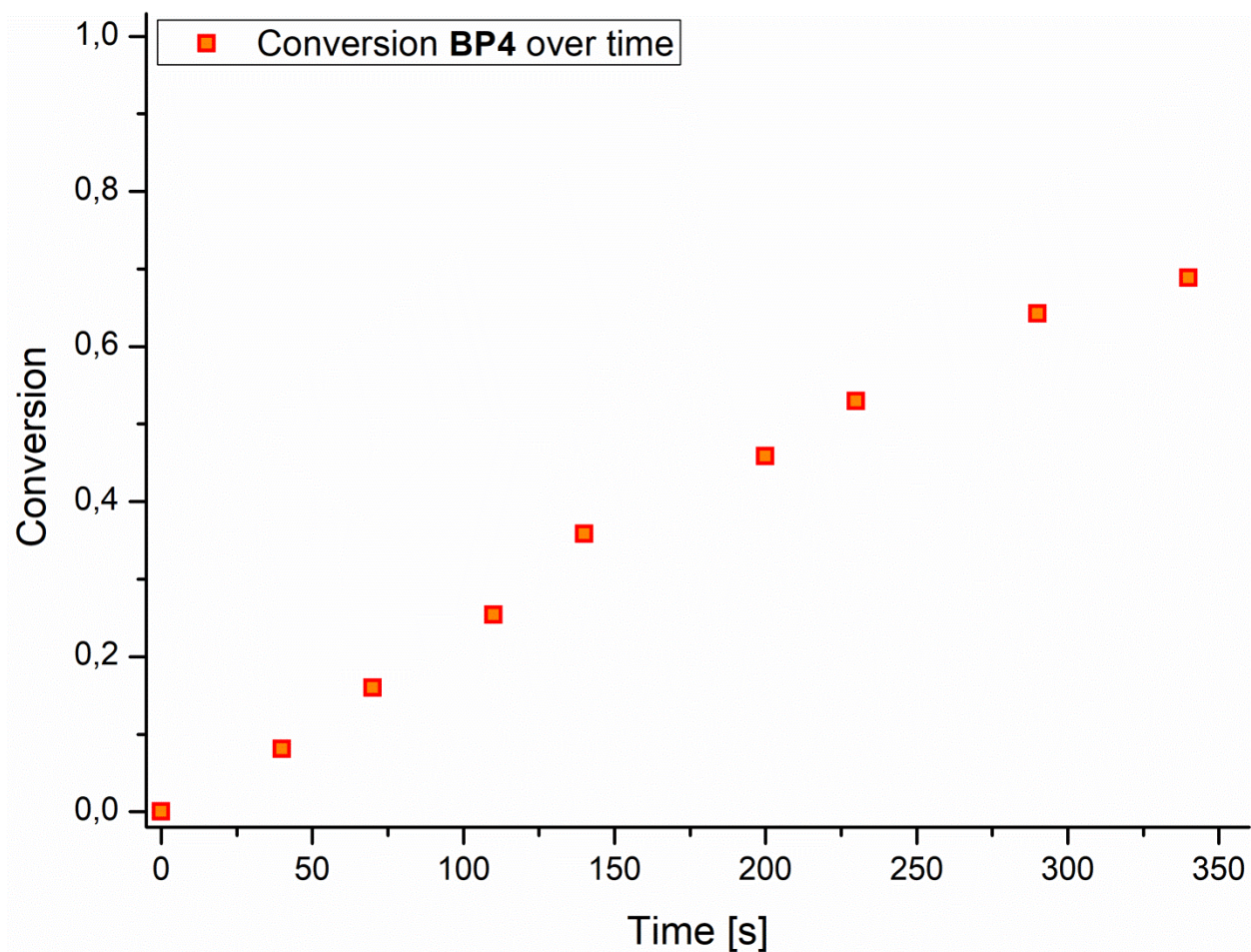
**Fig. S24.** Reaction scheme copolymerization methoxybutenolide **B2** with di(ethylene glycol) divinyl ether (1:0.5 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for di(ethylene glycol) divinyl ether), reflux, 5.7 min (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S8.** Kinetic studies of the copolymerization of methoxybutenolide **B2** with di(ethylene glycol) divinyl ether (1:0.5 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for di(ethylene glycol) divinyl ether), reflux, 5.7 min.

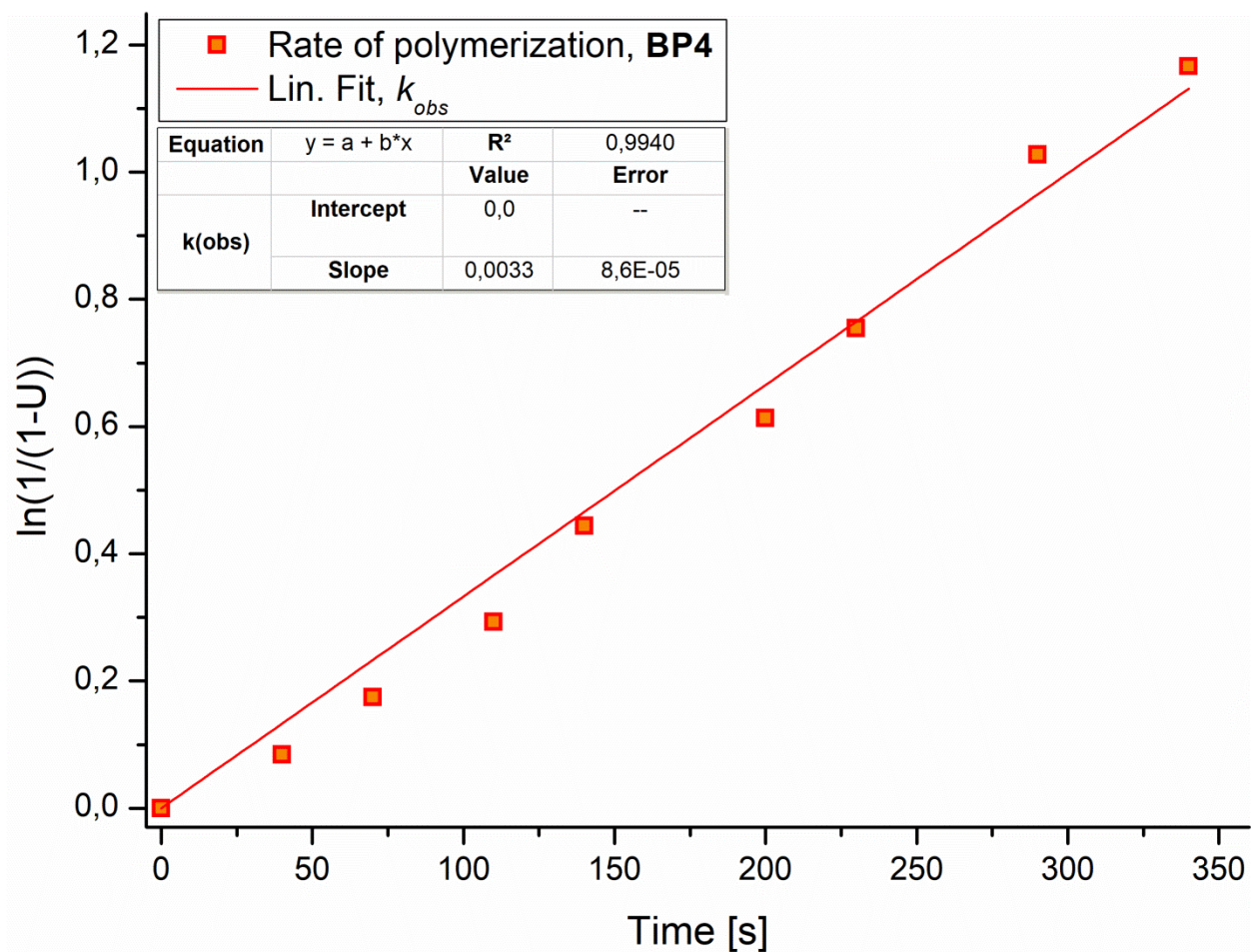
Methoxybutenolide-DVE-copolymer BP4						
	Methoxybutenolide <b>B2</b>		Di(ethylene glycol) divinyl ether		<b>k(obs)</b>	<b>(3.3±0.1)·10<sup>-3</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,85	2,15	1,02	1,13	0,00	0,00
40	0,79	2,01	0,91	1,00	0,08	0,08
70	0,72	1,83	0,83	0,92	0,16	0,17
110	0,65	1,64	0,73	0,80	0,25	0,29
140	0,56	1,42	0,61	0,68	0,36	0,44
200	0,48	1,22	0,50	0,55	0,46	0,61
230	0,42	1,07	0,43	0,47	0,53	0,76
290	0,33	0,84	0,30	0,33	0,64	1,03
340	0,29	0,73	0,27	0,29	0,69	1,17



**Fig. S25.** Concentration of monomers over time of the copolymerization of methoxybutenolide **B2** with di(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 5.7 min.



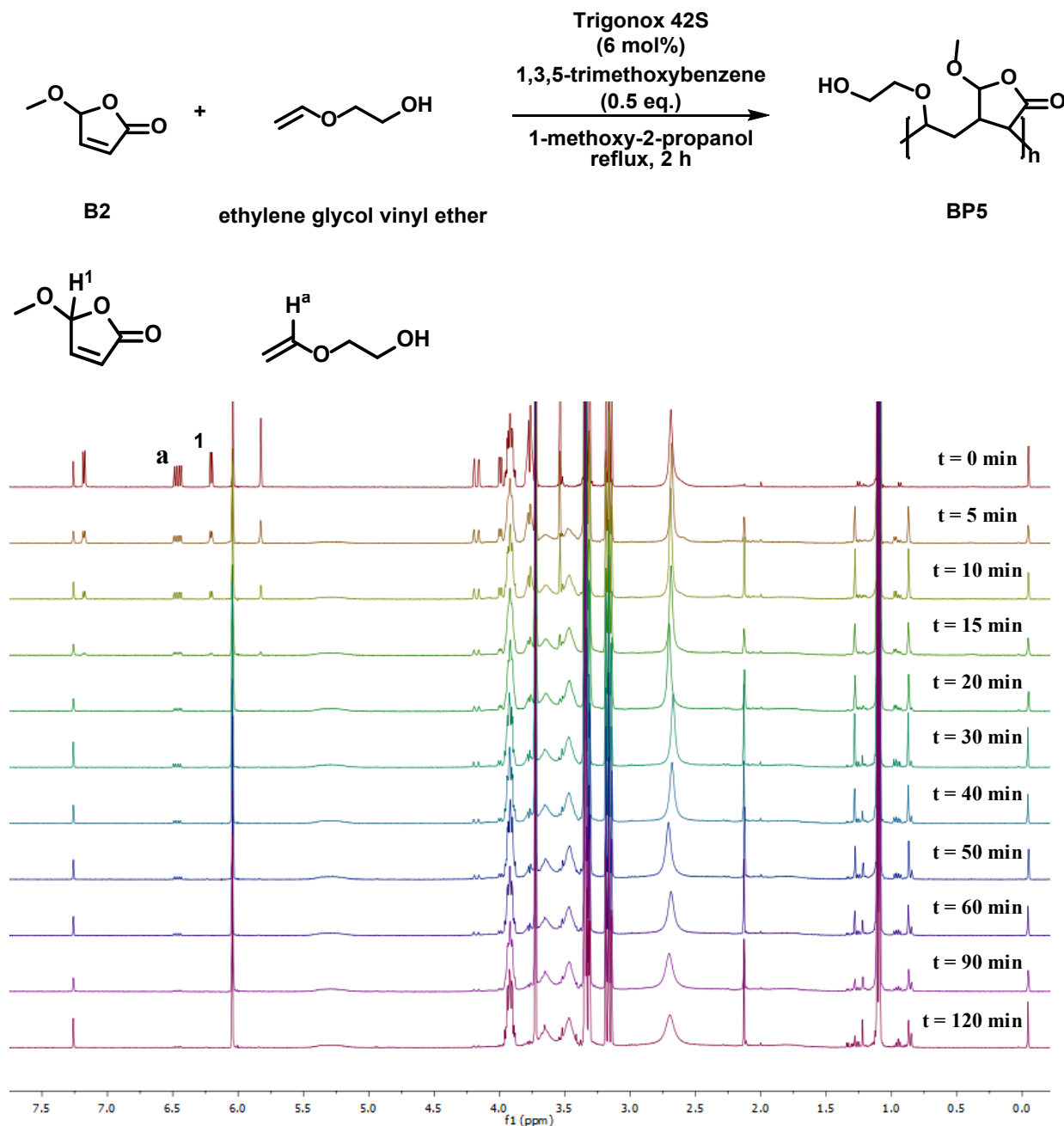
**Fig. S26.** Conversion of polymer **BP4** over time; copolymerization of methoxybutenolide **B2** with di(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 5.7 min.



**Fig. S27.** Rate of copolymerization of methoxybutenolide **B2** with di(ethylene glycol) divinyl ether (1:0.5 ratio) to **BP4** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 5.7 min.



### 5-methoxy-2(5H)-furanone-ethylene-glycol-vinyl-ether BP5

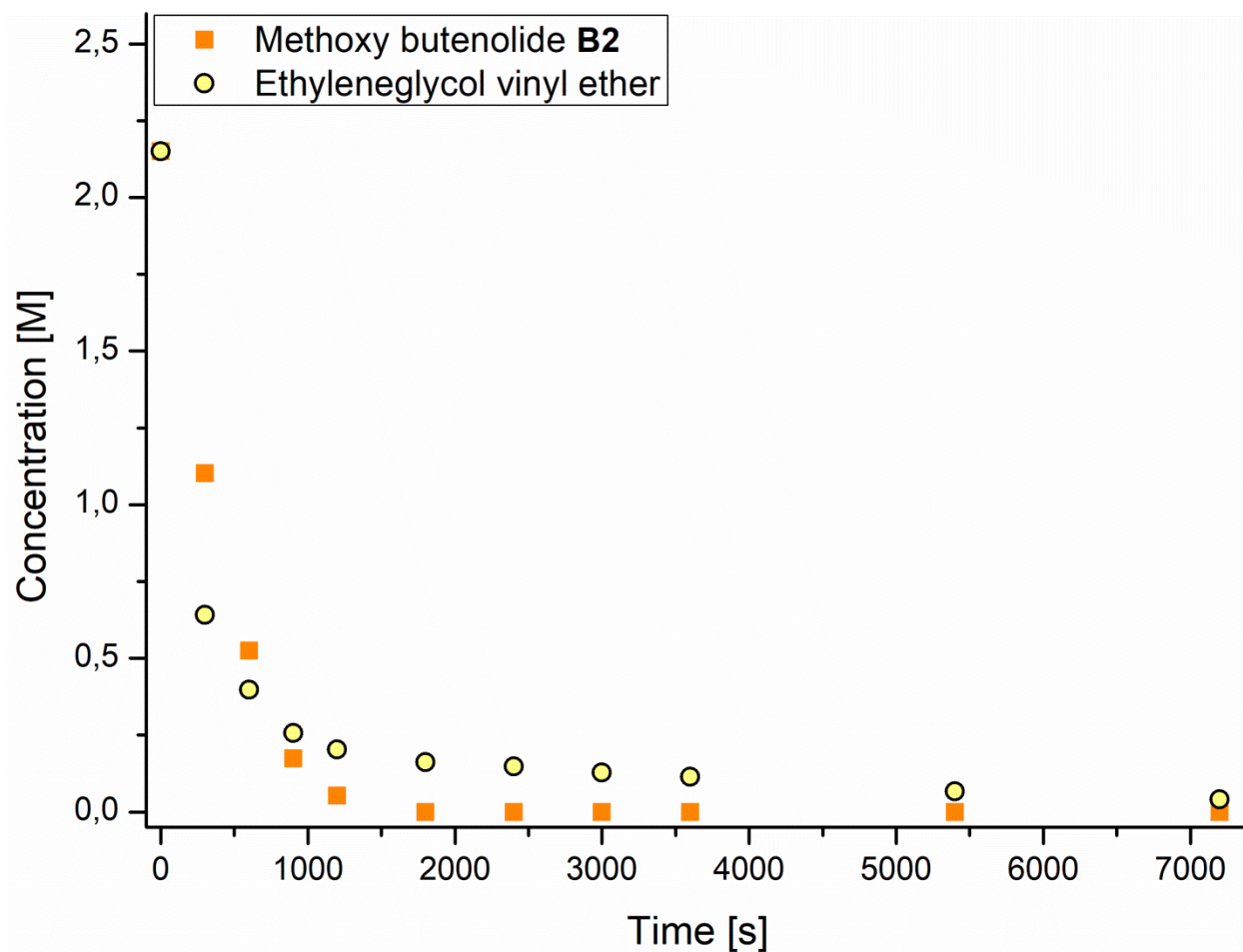


**Fig. S28.** Reaction scheme copolymerization methoxybutenolide **B2** with ethylene glycol vinyl ether (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h (top).  $^1H$  NMR signals over time by taking samples and flash freezing ( $-18^\circ C$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

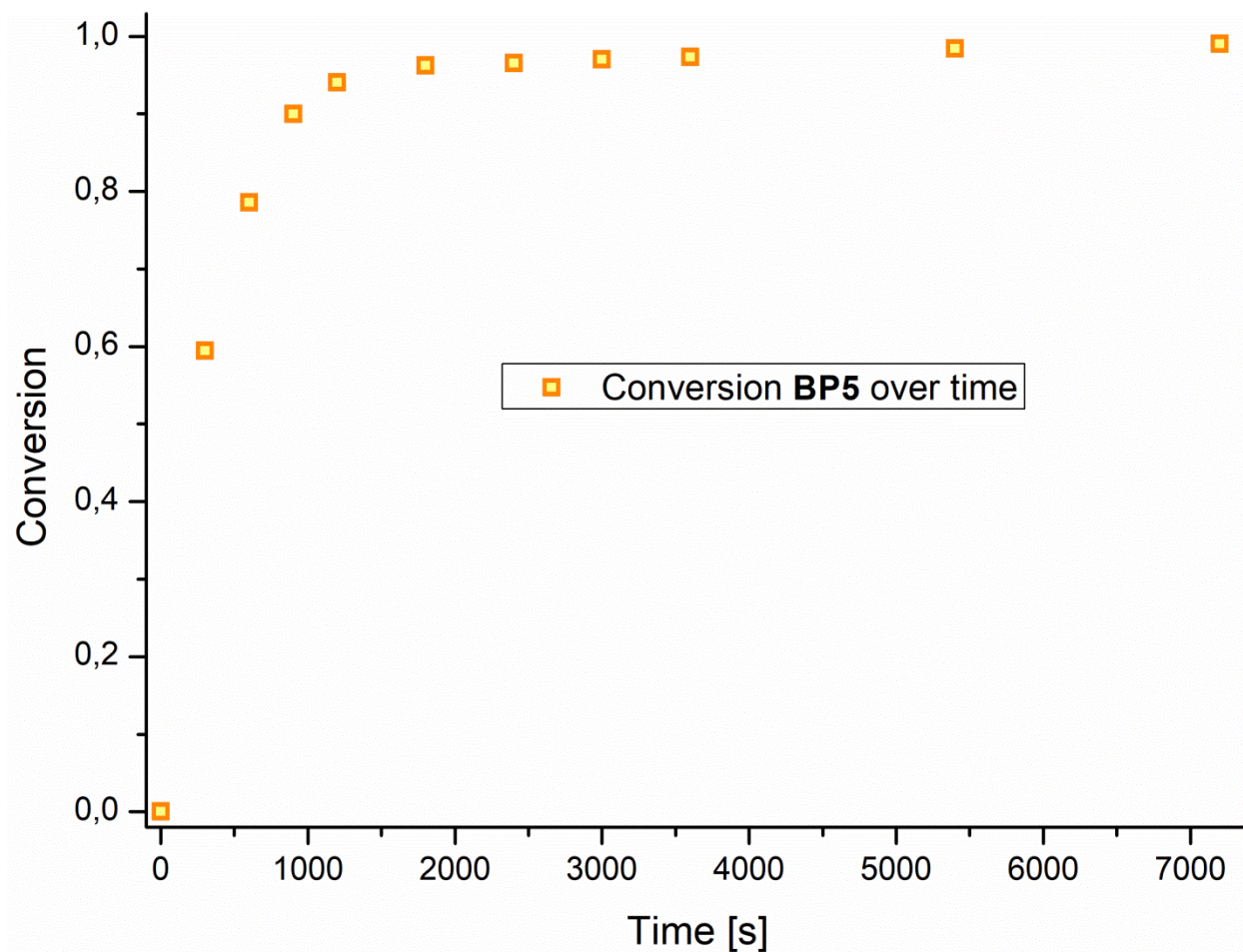
**Table S9.** Kinetic studies of the copolymerization of methoxybutenolide **B2** with ethylene glycol vinyl ether (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

Methoxybutenolide-vinyl-ether-copolymer BP5					k1(obs)	(2.5±0.1)·10 <sup>-3</sup> [s <sup>-1</sup> ]
Methoxybutenolide B2		Ethylene glycol vinyl ether		k2(obs)	(2.6±0.1)·10 <sup>-4</sup> [s <sup>-1</sup> ]	
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,80	2,15	0,80	2,15	0,00	0,00
300	0,41	1,10	0,48	0,64	0,59	0,90
600	0,20	0,52	0,30	0,40	0,79	1,54
900	0,07	0,17	0,19	0,26	0,90	2,30
1200	0,02	0,05	0,15	0,20	0,94	2,82
1800	0,00	0,00	0,12	0,16	0,96	3,28
2400	0,00	0,00	0,11	0,15	0,97	3,37
3000	0,00	0,00	0,10	0,13	0,97	3,51
3600	0,00	0,00	0,09	0,11	0,97	3,62
5400	0,00	0,00	0,05	0,07	0,98	4,15
7200	0,00	0,00	0,03	0,04	0,99	4,67

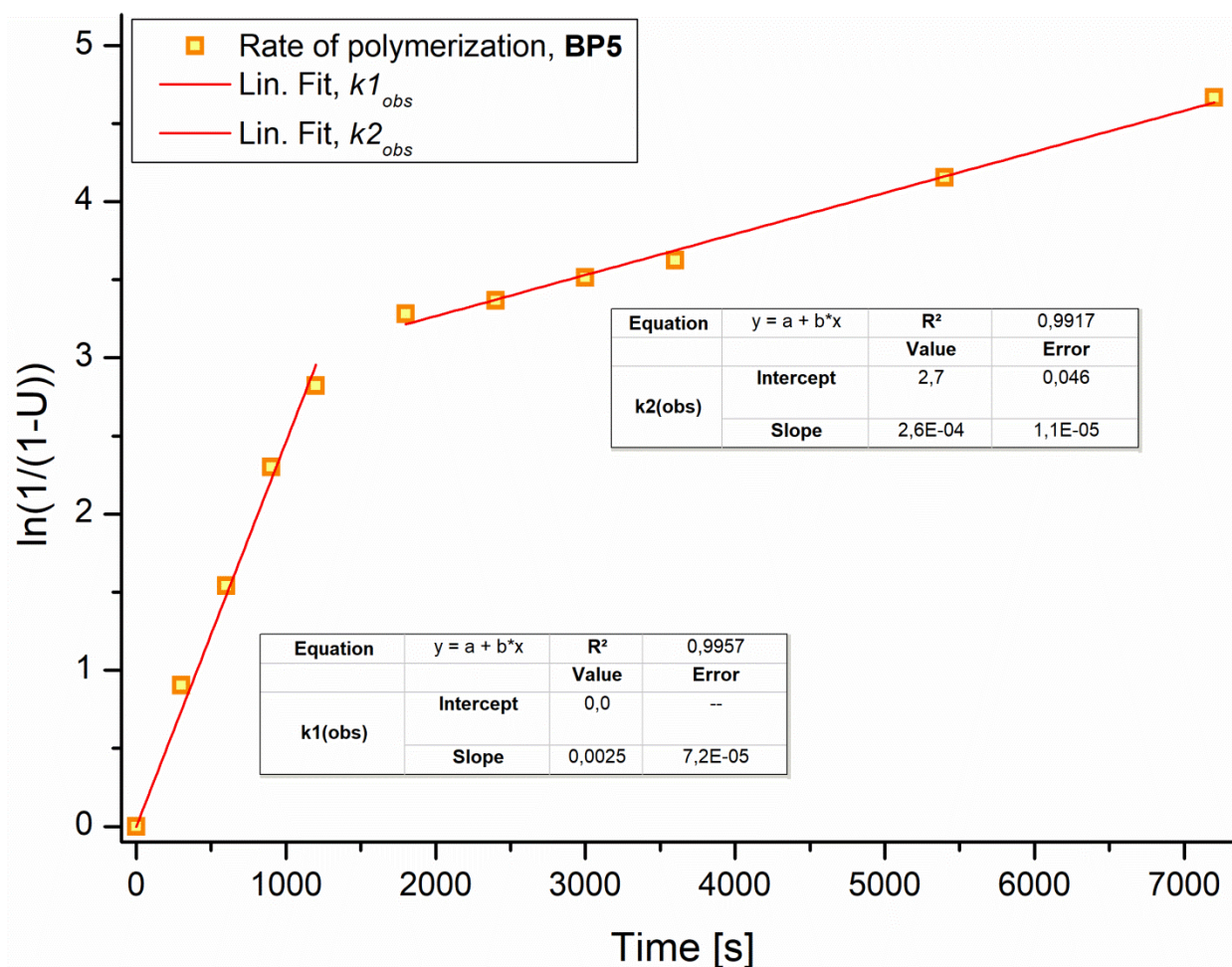




**Fig. S29.** Concentration of monomers over time of the copolymerization of methoxybutenolide **B2** with ethylene glycol vinyl ether (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

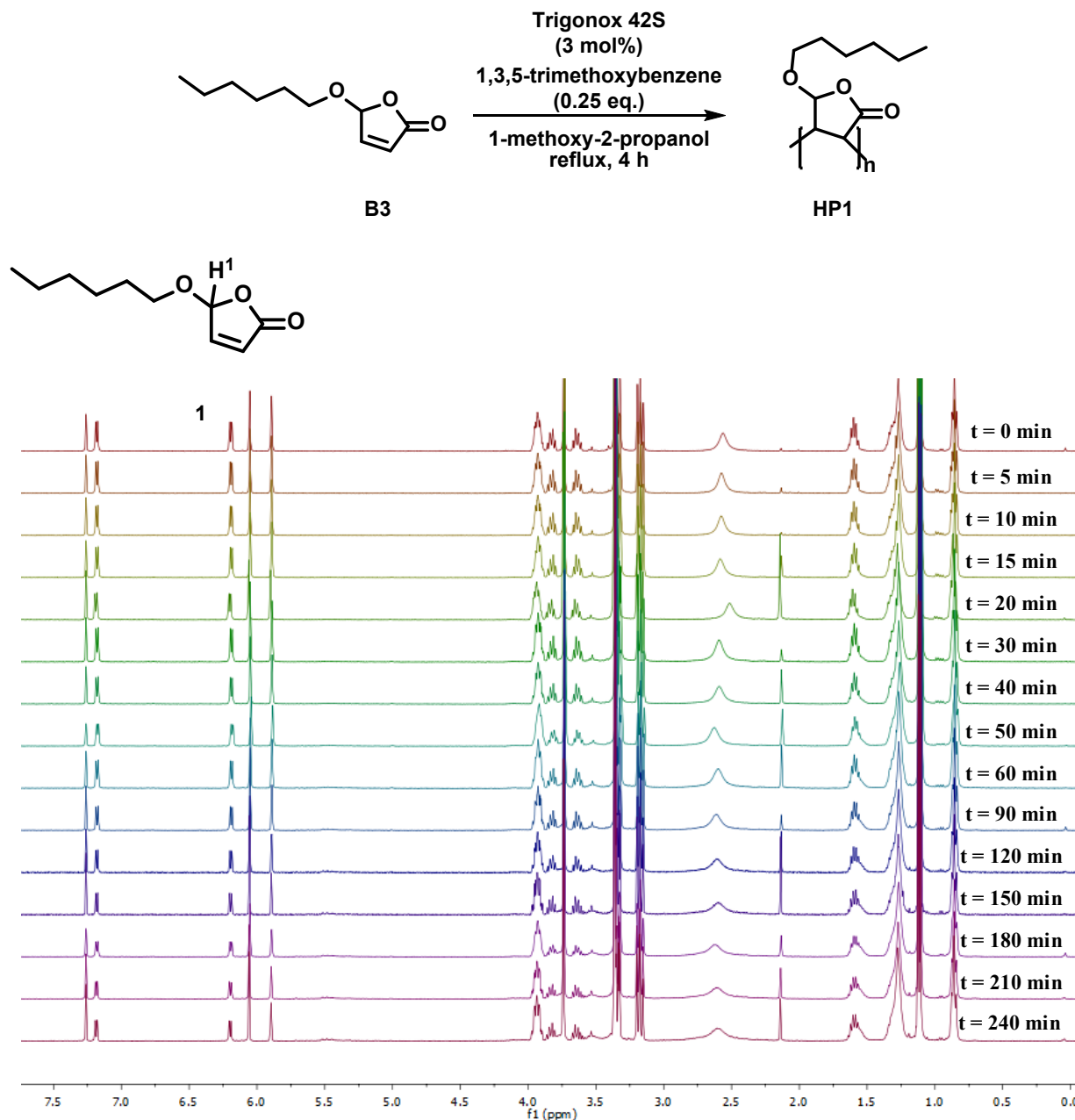


**Fig. S30.** Conversion of polymer **BP5** over time; copolymerization of methoxybutenolide **B2** with ethylene glycol vinyl ether (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.



**Fig. S31.** Rate of copolymerization of methoxybutenolide **B2** with ethylene glycol vinyl ether (1:1 ratio) to **BP5** over time; followed by  $^1\text{H NMR}$  signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

poly-5-hexyloxy-2(5H)-furanone HP1

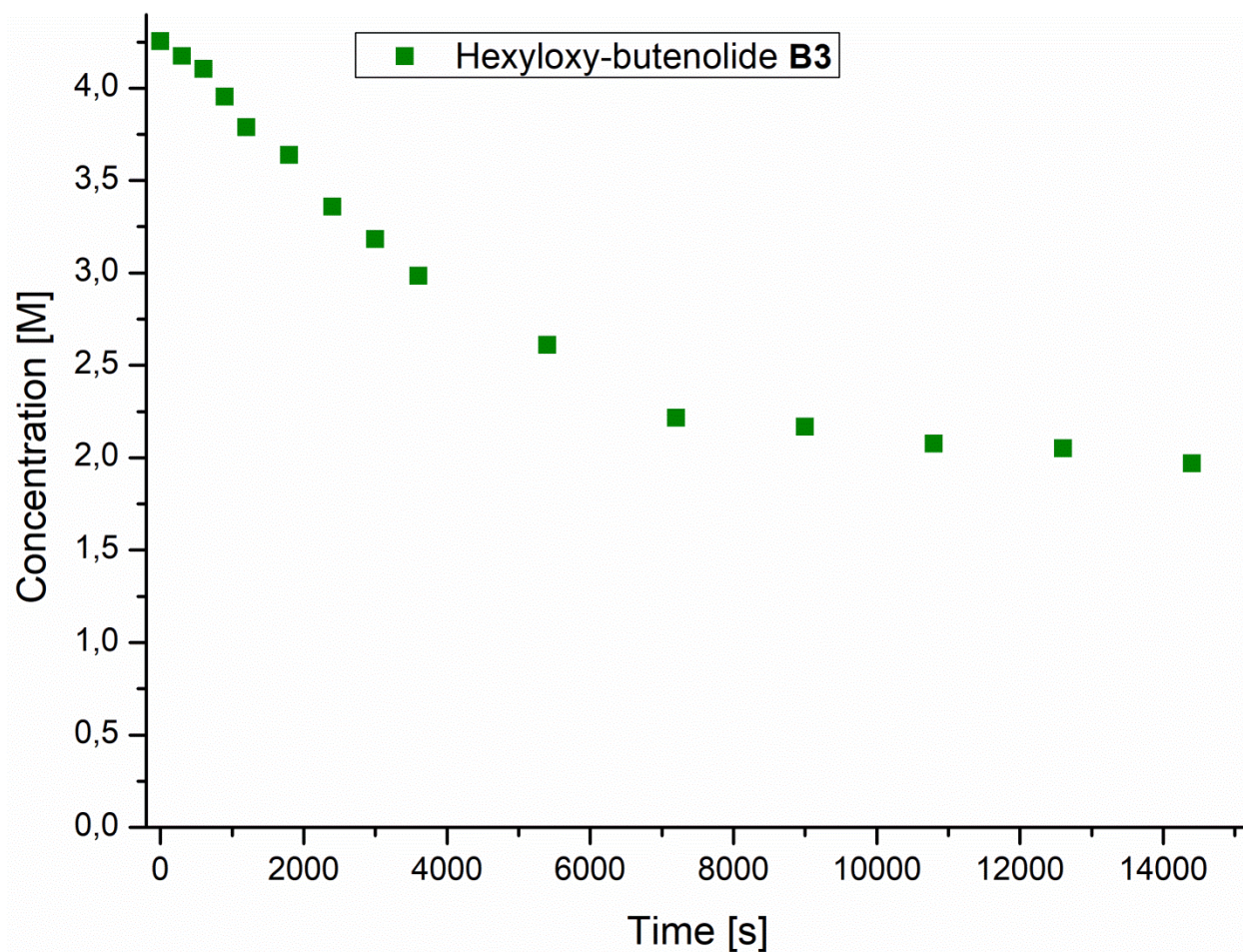


**Fig. S32.** Reaction scheme homopolymerization hexyloxybutenolide **B3** (2 eq.), reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 4 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard (bottom).

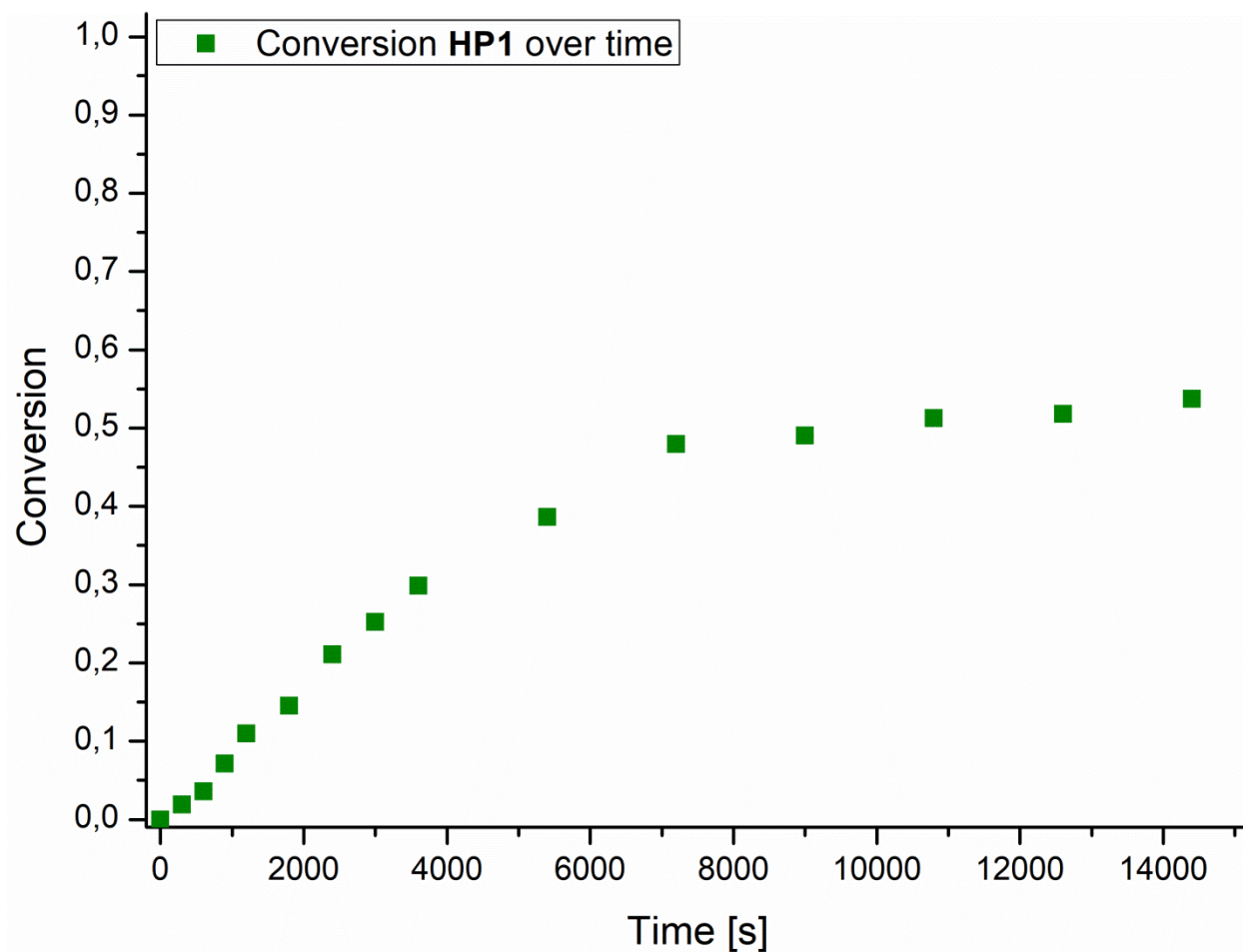
**Table S10.** Kinetic studies of the homopolymerization of hexyloxybutenolide **B3** (2 eq.), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.25 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 4 h.

Hexyloxybutenolide-polymer HP1			k1(obs)	(9.2±0.1)·10 <sup>-5</sup> [s <sup>-1</sup> ]
Hexyloxybutenolide B3			k2(obs)	(1.6±0.1)·10 <sup>-5</sup> [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,92	4,26	0,00	0,00
300	0,90	4,17	0,02	0,02
600	0,89	4,10	0,04	0,04
900	0,85	3,95	0,07	0,07
1200	0,82	3,79	0,11	0,12
1800	0,78	3,64	0,15	0,16
2400	0,72	3,36	0,21	0,24
3000	0,69	3,18	0,25	0,29
3600	0,64	2,98	0,30	0,35
5400	0,56	2,61	0,39	0,49
7200	0,48	2,21	0,48	0,65
9000	0,47	2,17	0,49	0,67
10800	0,45	2,08	0,51	0,72
12600	0,44	2,05	0,52	0,73
14400	0,43	1,97	0,54	0,77

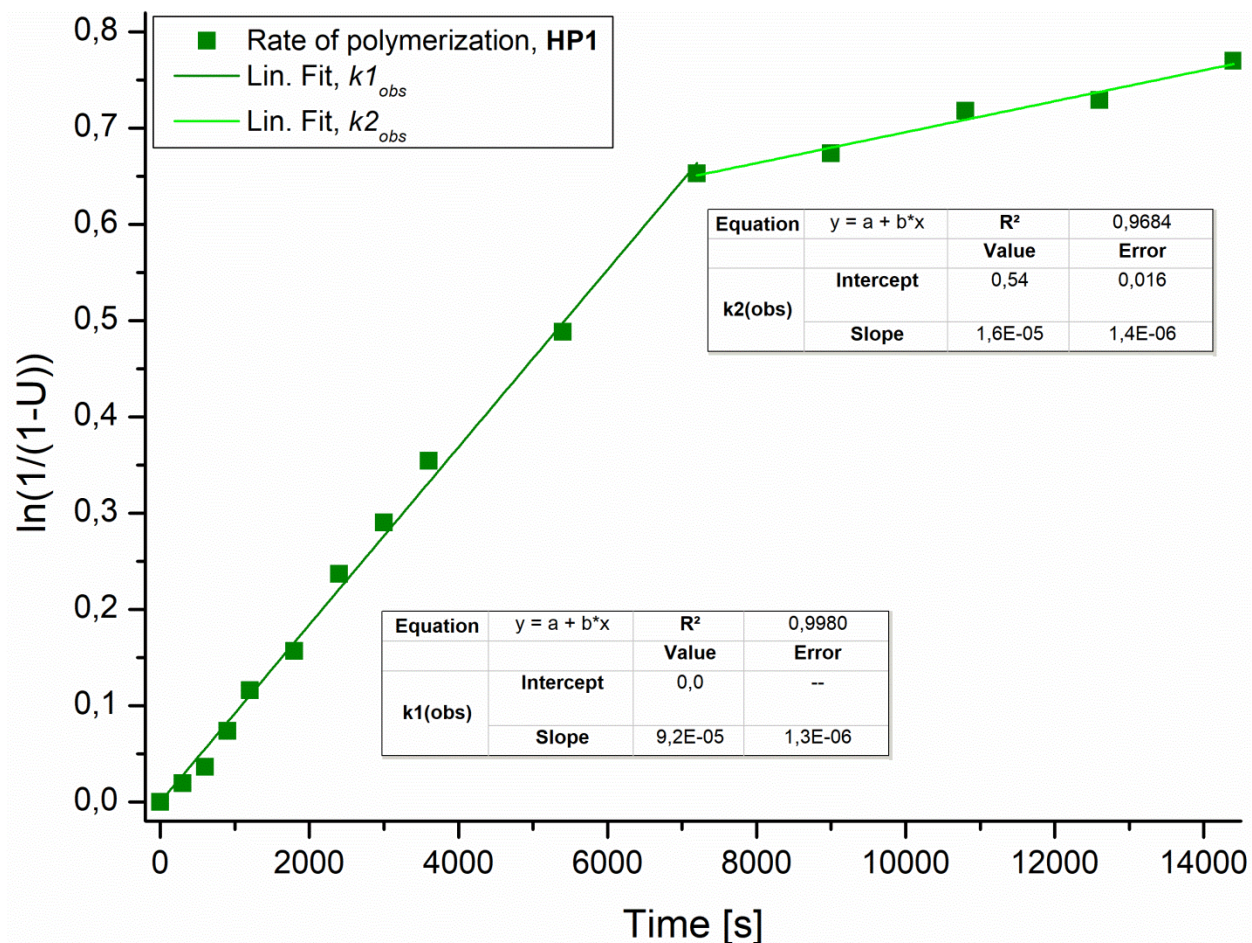




**Fig. S33.** Concentration of the monomer hexyloxybutenolide **B3** over time followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 4 h.



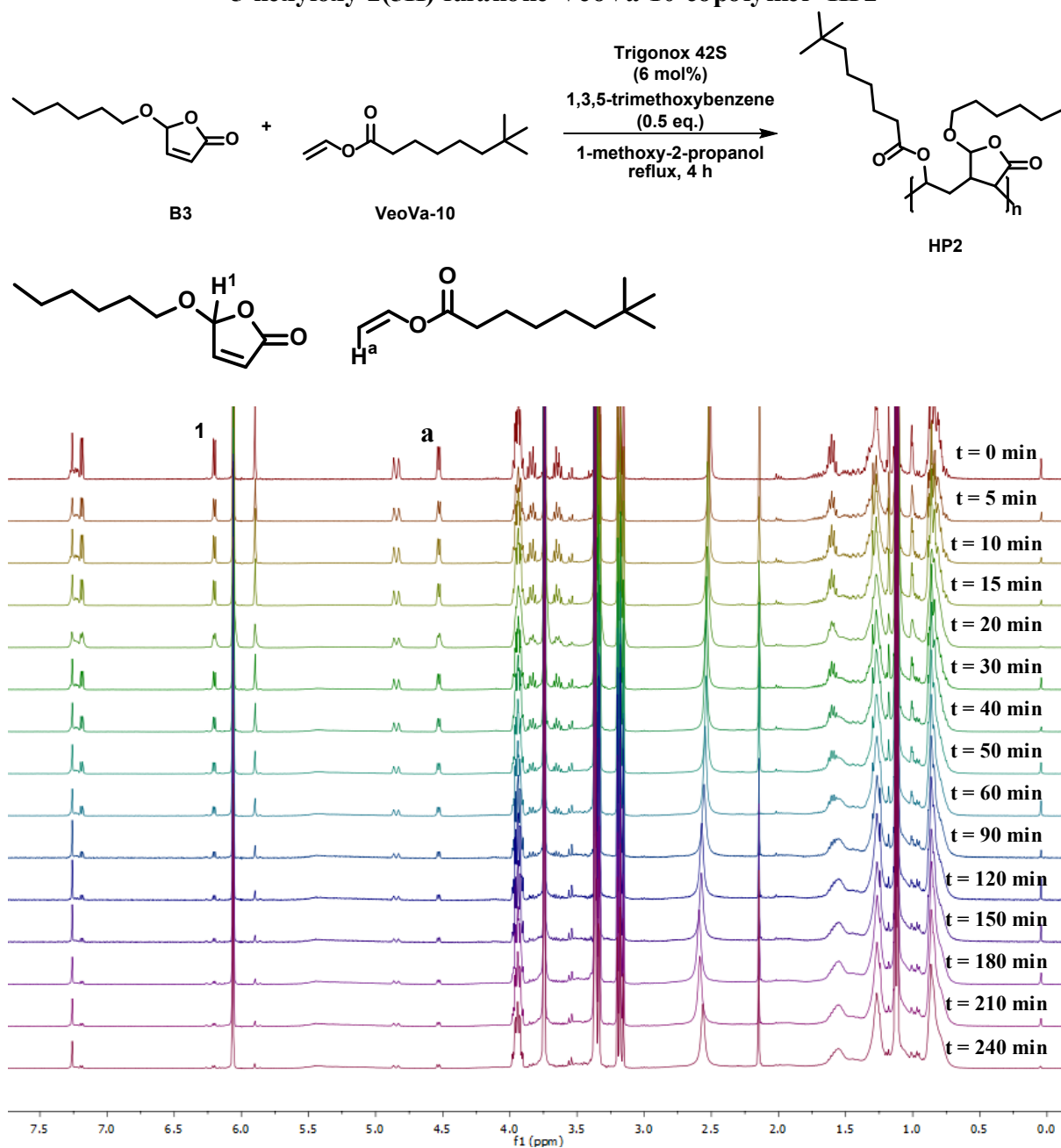
**Fig. S34.** Conversion of polymer **HP1** over time; homo-polymerization of hexyloxybutenolide **B3** followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 4 h.



**Fig. S35.** Rate of homo-polymerization of hexyloxybutenolide **B3** to **HP1** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 4 h.



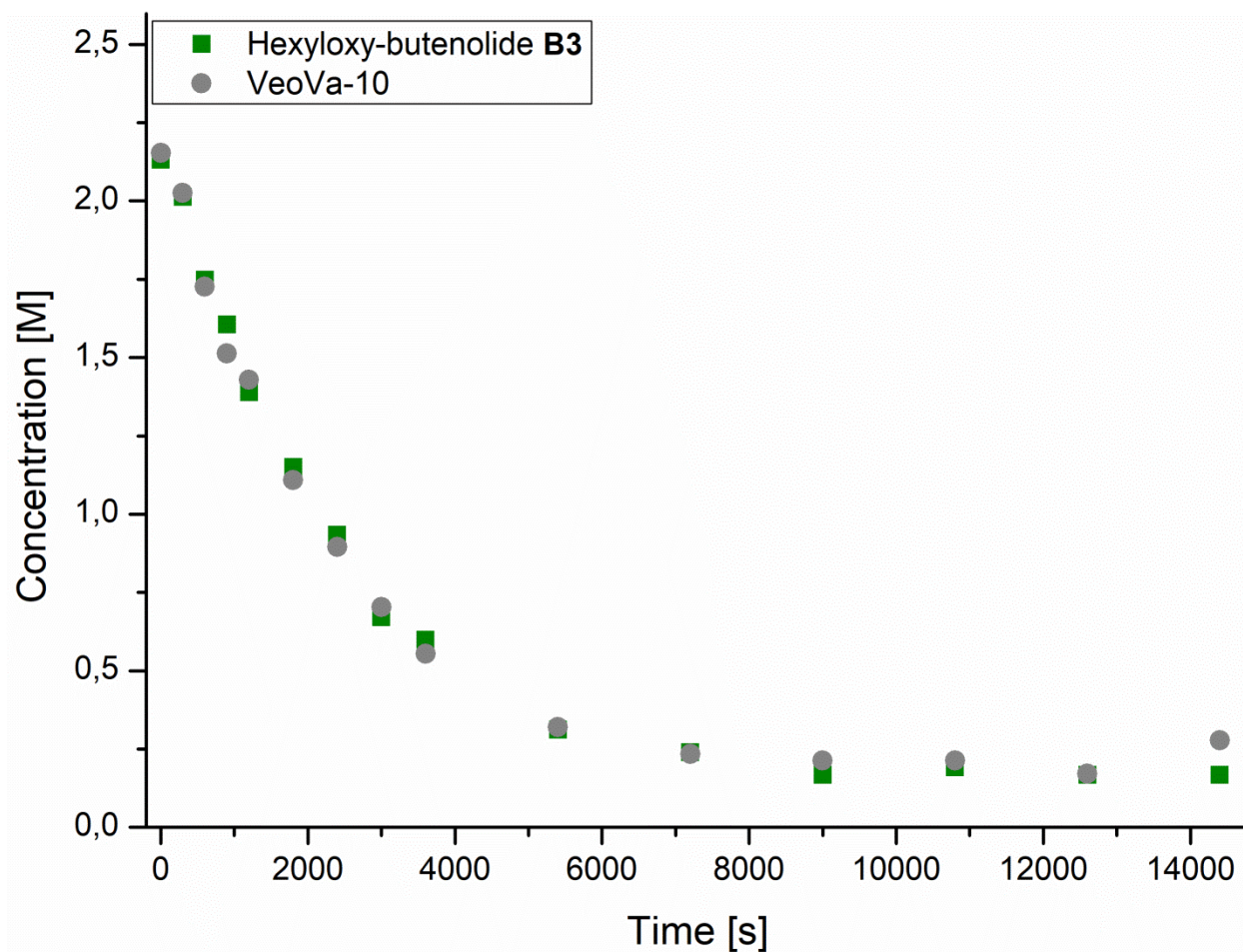
### 5-hexyloxy-2(5H)-furanone-VeoVa-10-copolymer HP2



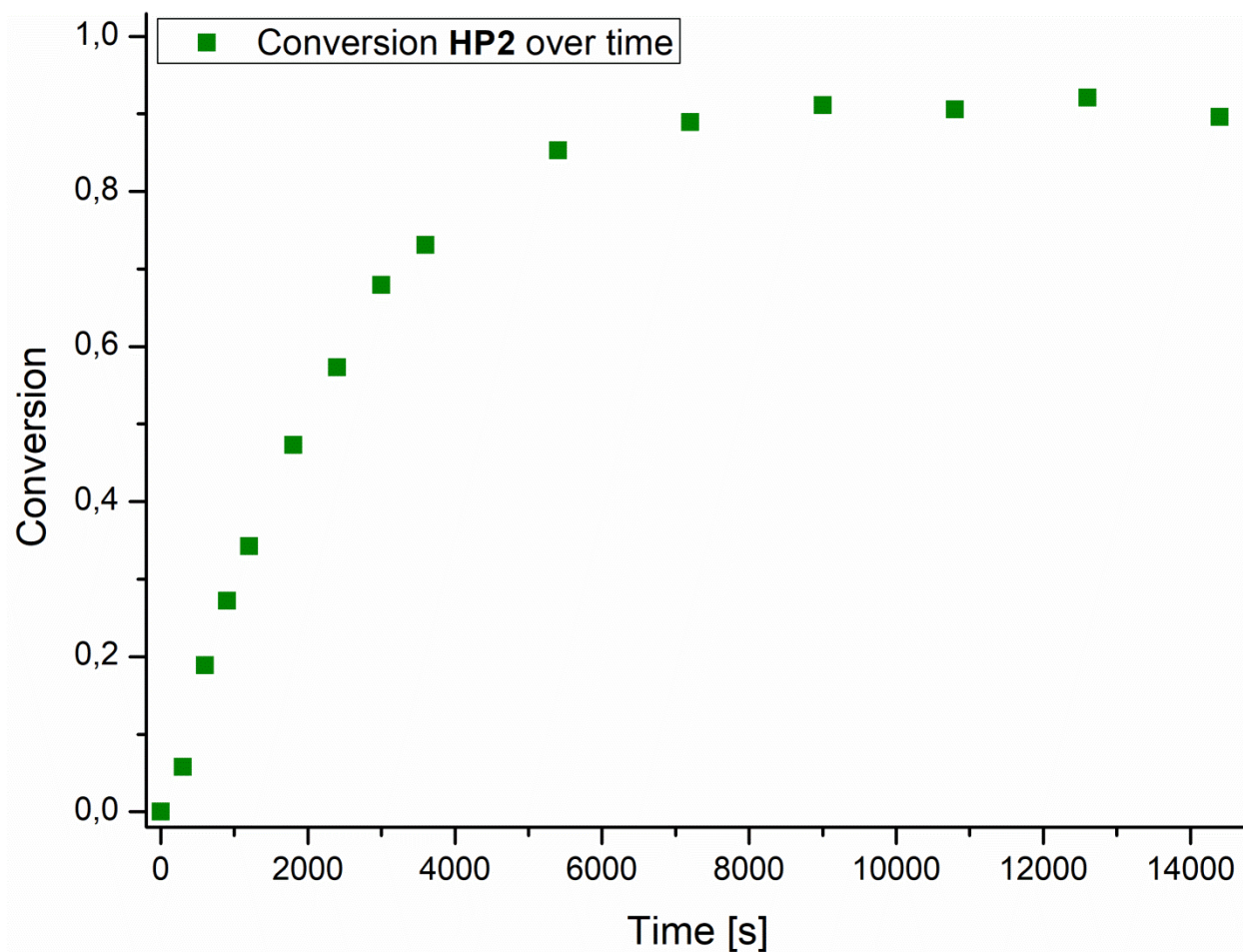
**Fig. S36.** Reaction scheme copolymerization hexyloxybutenolide **B3** with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S11.** Kinetic studies of the copolymerization of hexyloxybutenolide **B3** with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.

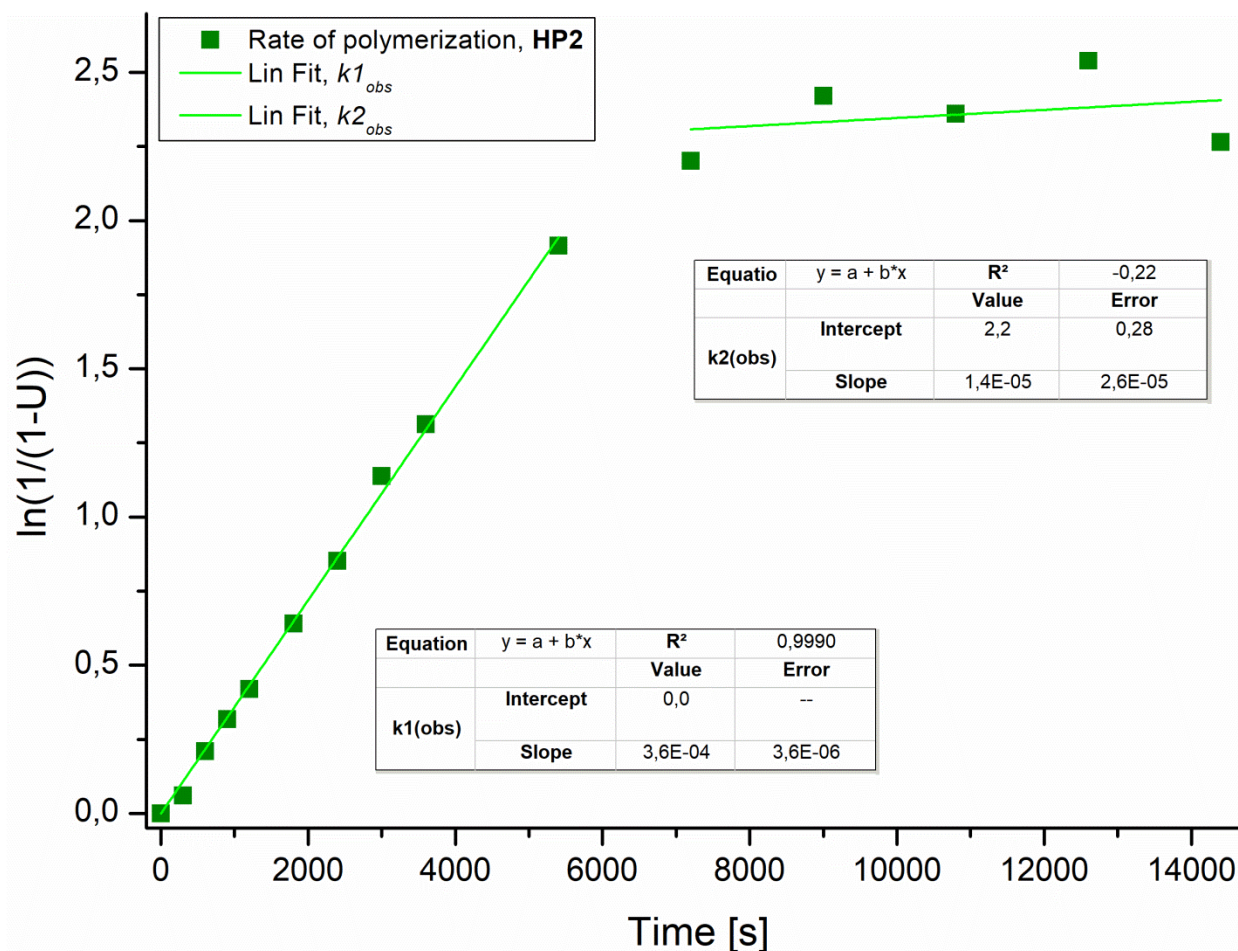
Hexyloxybutenolide-VeoVa-10-copolymer HP2					k1(obs)	(3.6±0.1)·10 <sup>-4</sup> [s <sup>-1</sup> ]
Hexyloxybutenolide <b>B3</b>		VeoVa-10			k2(obs)	(1.4±2.6)·10 <sup>-5</sup> [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,91	2,13	1,02	2,15	0,00	0,00
300	0,85	2,01	0,96	2,03	0,06	0,06
600	0,74	1,75	0,82	1,73	0,19	0,21
900	0,68	1,61	0,71	1,51	0,27	0,32
1200	0,59	1,39	0,67	1,43	0,34	0,42
1800	0,49	1,15	0,52	1,11	0,47	0,64
2400	0,40	0,93	0,42	0,90	0,57	0,85
3000	0,28	0,67	0,33	0,70	0,68	1,14
3600	0,25	0,60	0,26	0,55	0,73	1,31
5400	0,13	0,31	0,15	0,32	0,85	1,92
7200	0,10	0,24	0,11	0,23	0,89	2,20
9000	0,07	0,17	0,10	0,21	0,91	2,42
10800	0,08	0,19	0,10	0,21	0,91	2,36
12600	0,07	0,17	0,08	0,17	0,92	2,54
14400	0,07	0,17	0,13	0,28	0,90	2,27



**Fig. S37.** Concentration of monomers over time of the copolymerization of hexyloxybutenolide **B3** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.

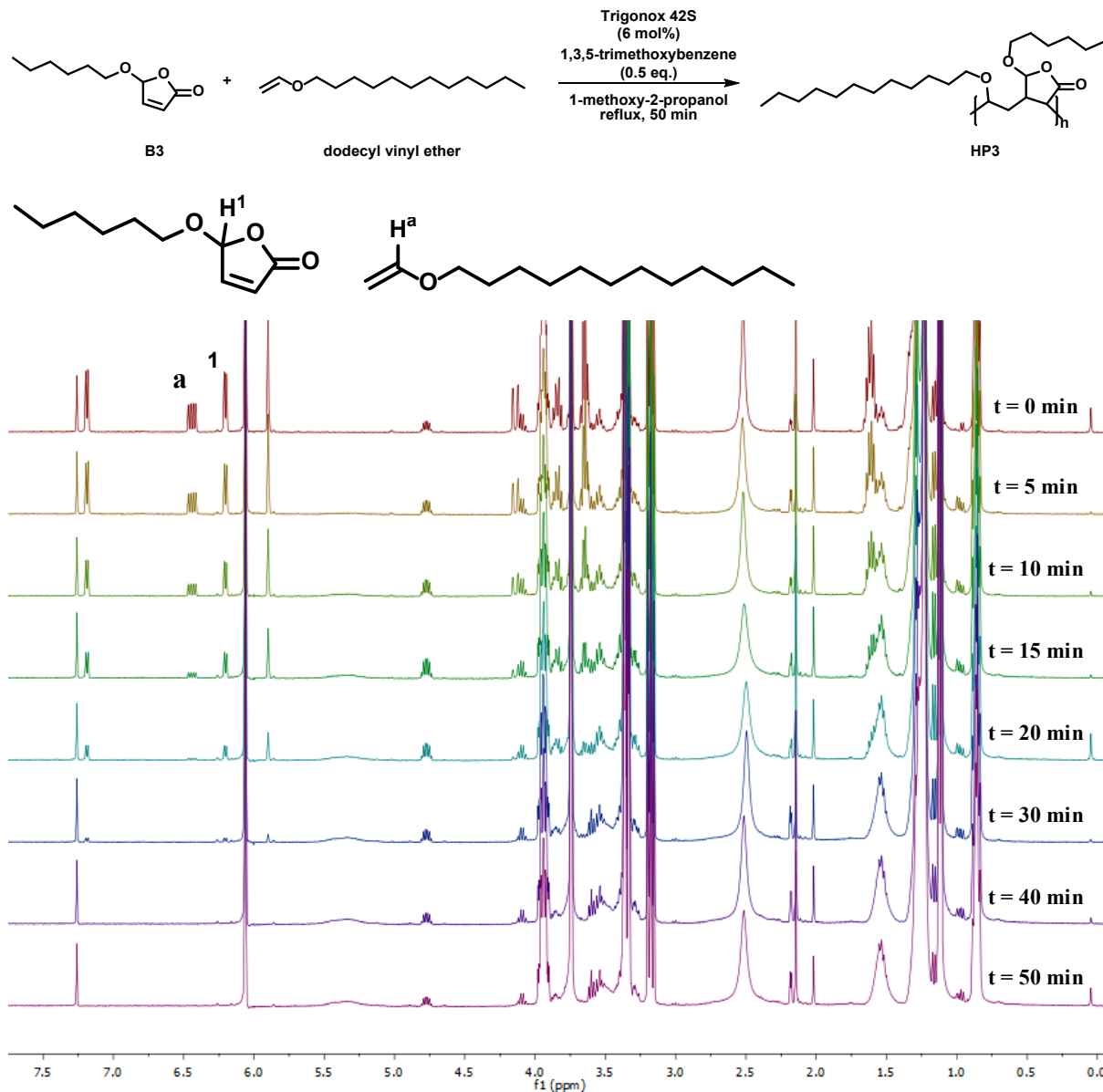


**Fig. S38.** Conversion of polymer **HP2** over time; copolymerization of hexyloxybutenolide **B3** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.



**Fig. S39.** Rate of copolymerization of hexyloxybutenolide **B3** with VeoVa-10 (1:1 ratio) to **HP2** over time; followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.

### 5-hexyloxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer HP3

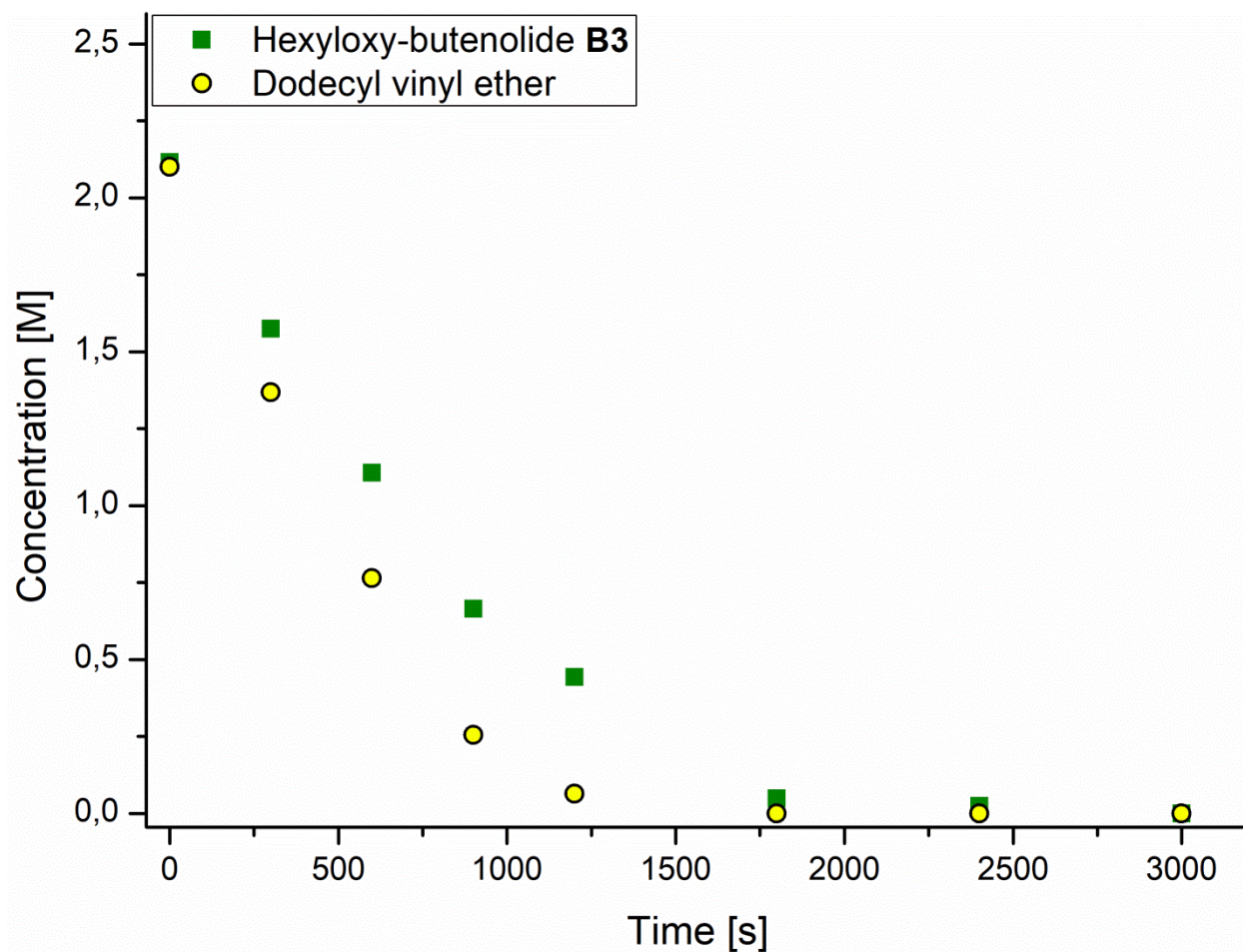


**Fig. S40.** Reaction scheme copolymerization hexyloxybutenolide **B3** with dodecyl vinyl ether (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S12.** Kinetic studies of the copolymerization of hexyloxybutenolide **B3** with dodecyl vinyl ether (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.

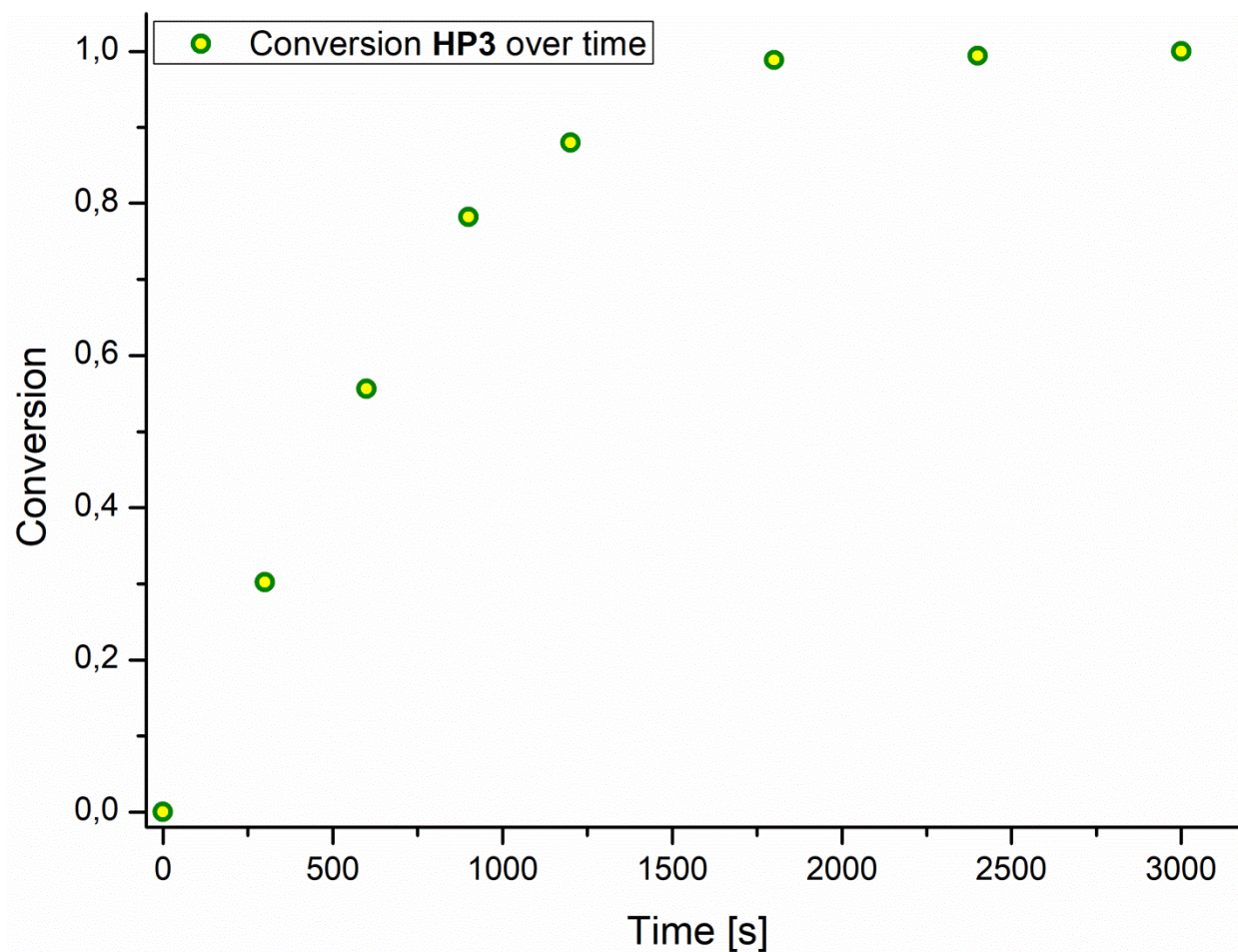
<b>Hexyloxybutenolide-dodecyl-vinyl-ether-copolymer HP3</b>						
	Hexyloxybutenolide <b>B3</b>		Dodecyl vinyl ether		<b>k(obs)</b>	<b>(2.1±0.1)·10<sup>-3</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,87	2,12	0,68	2,10	0,00	0,00
300	0,65	1,57	0,44	1,37	0,30	0,36
600	0,46	1,11	0,25	0,76	0,56	0,81
900	0,27	0,66	0,08	0,25	0,78	1,52
1200	0,18	0,44	0,02	0,06	0,88	2,12
1800	0,02	0,05	0,00	0,00	0,99	4,45
2400	0,01	0,02	0,00	0,00	0,99	5,14
3000	0,00	0,00	0,00	0,00	1,00	-



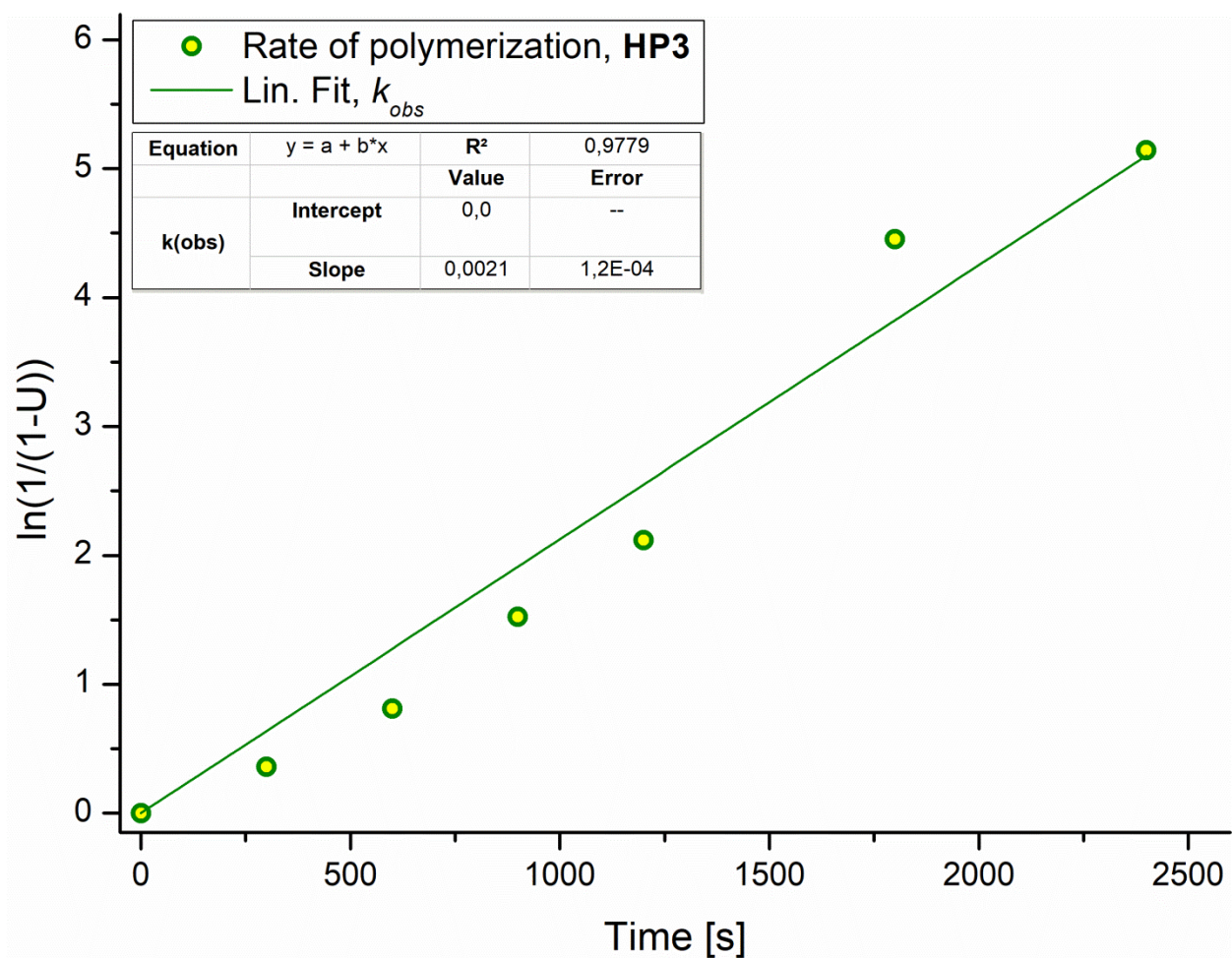


**Fig. S41.** Concentration of monomers over time of the copolymerization of hexyloxybutenolide **B3** with dodecyl vinyl ether (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.



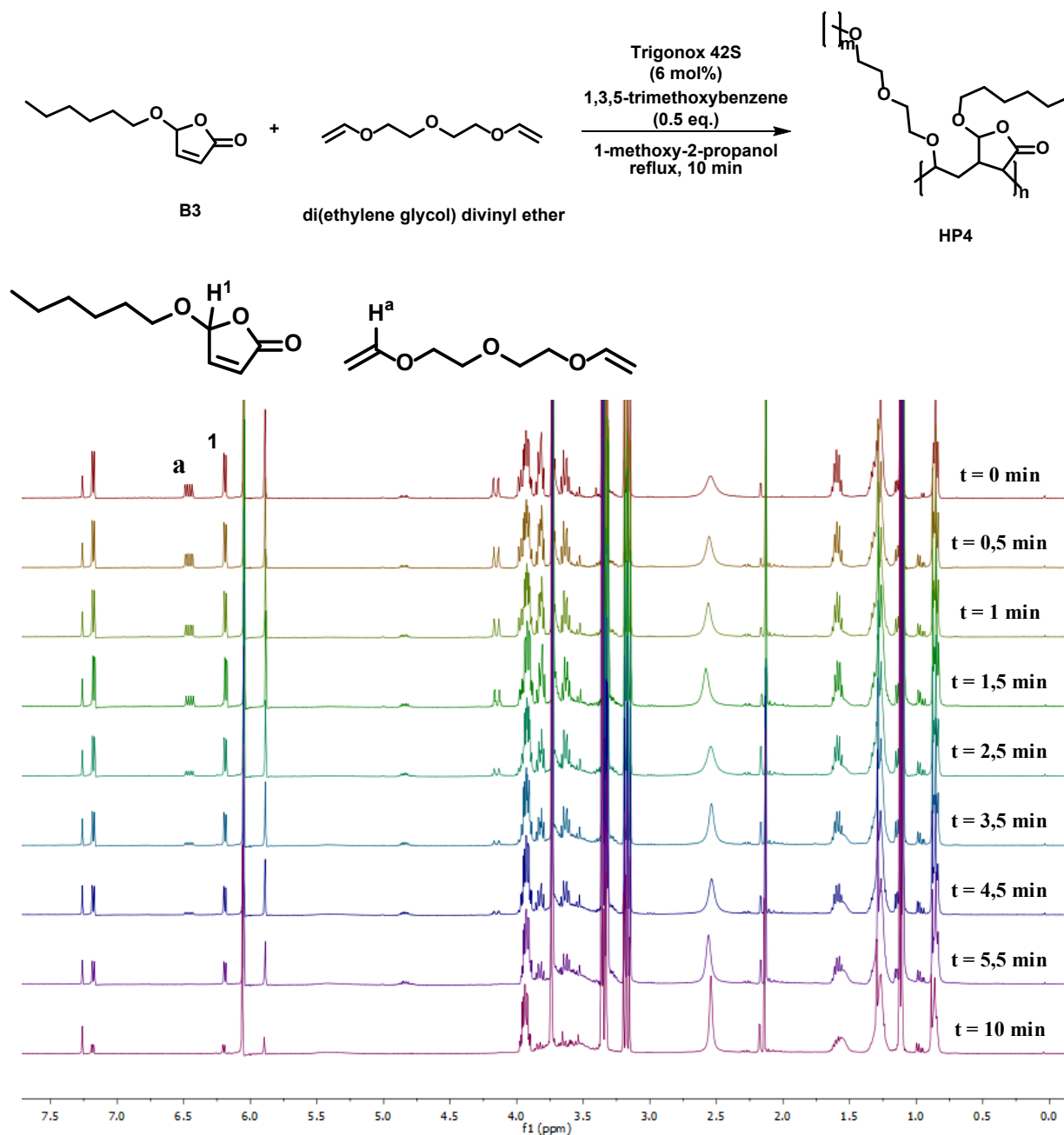


**Fig. S42.** Conversion of polymer **HP3** over time; copolymerization of hexyloxybutenolide **B3** with dodecyl vinyl ether (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.



**Fig. S43.** Rate of copolymerization of hexyloxybutenolide **B3** with dodecyl vinyl ether (1:1 ratio) to **HP3** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.

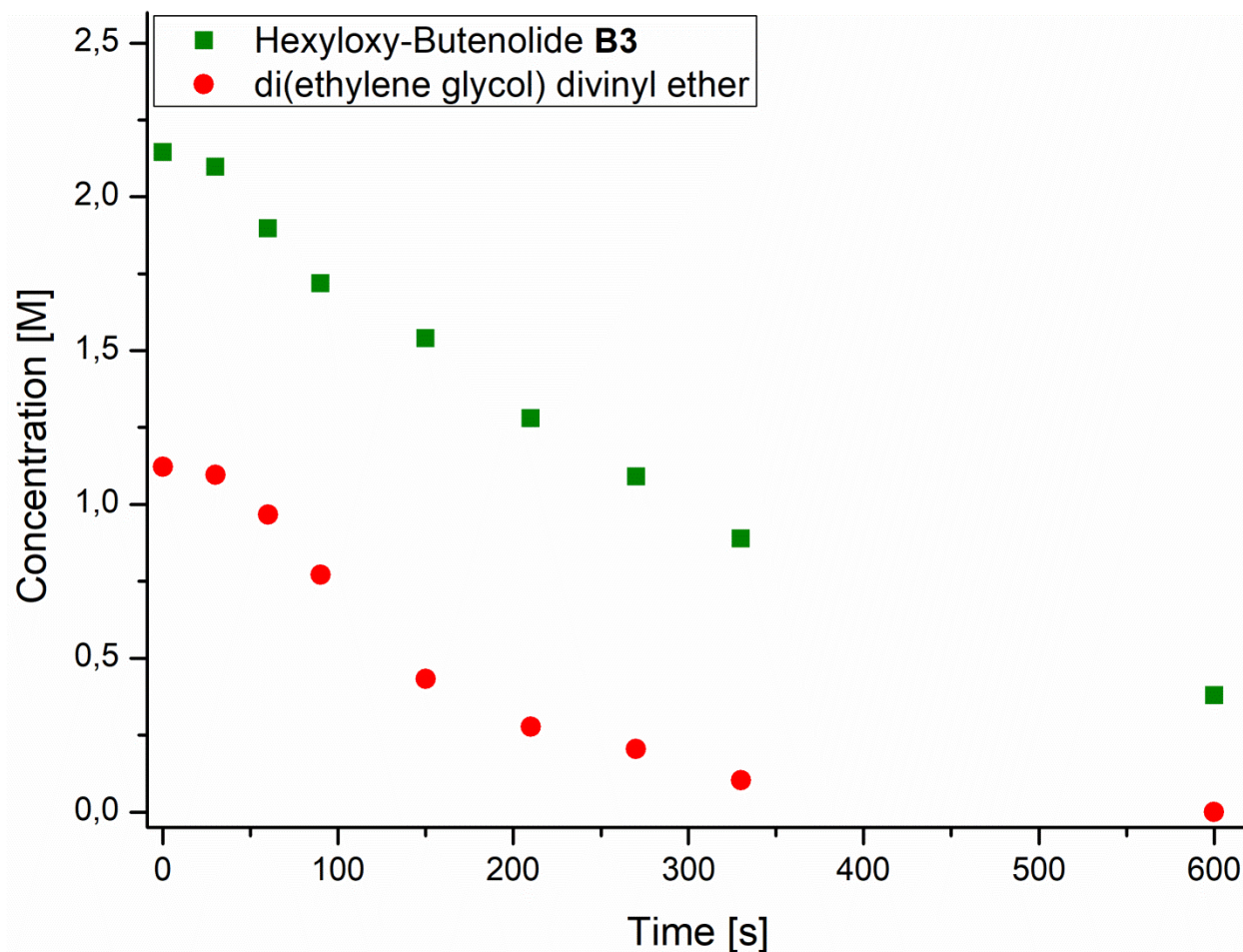
### 5-hexyloxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer HP4



**Fig. S44.** Reaction scheme copolymerization hexyloxybutenolide **B3** with di(ethylene glycol) divinyl ether (1:0.5 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for di(ethylene glycol) divinyl ether), reflux, 10 min (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

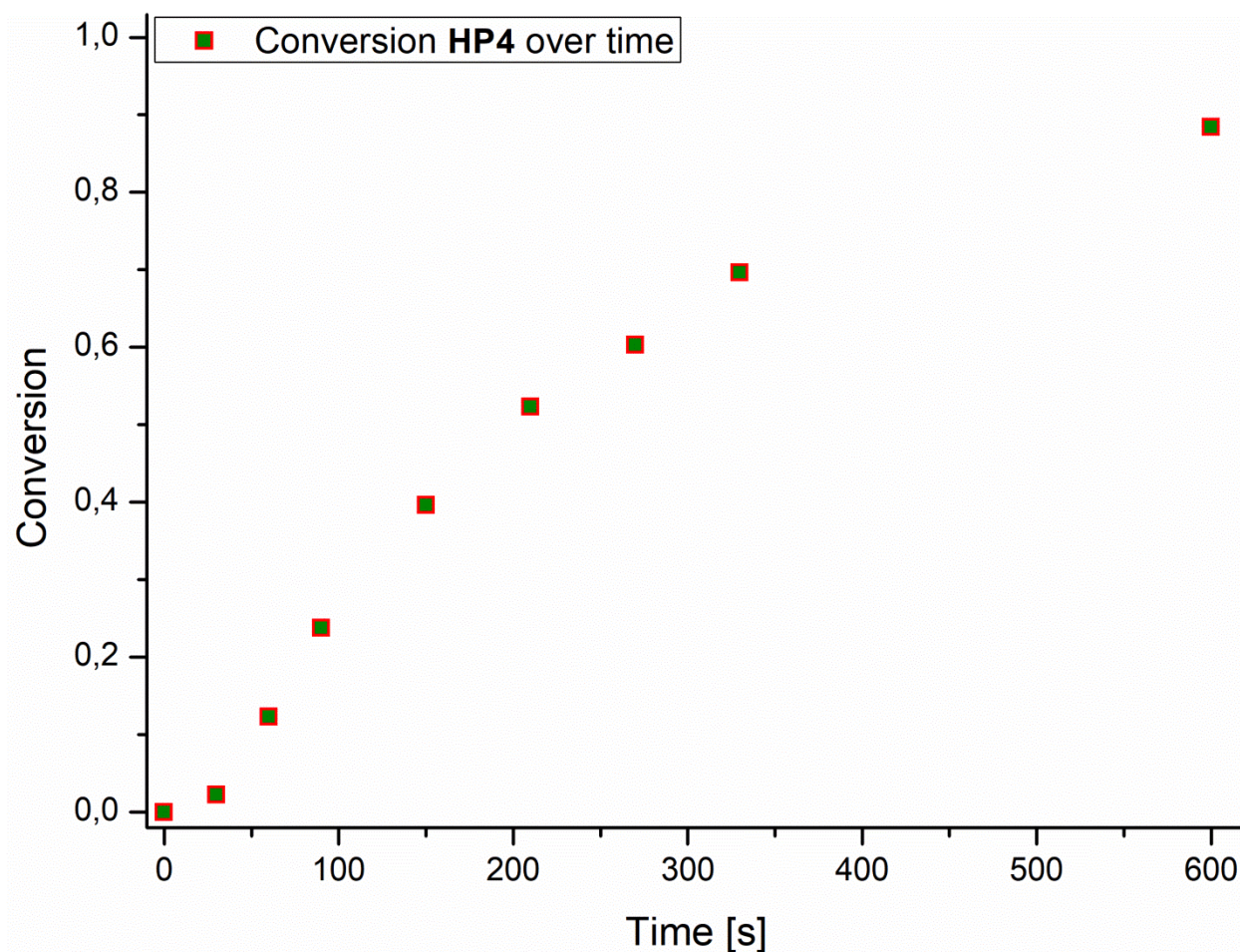
**Table S13.** Kinetic studies of the copolymerization of hexyloxybutenolide **B3** with di(ethylene glycol) divinyl ether (1:0.5 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for di(ethylene glycol) divinyl ether), reflux, 10 min.

Hexyloxybutenolide-DVE-copolymer HP4						
	Hexyloxybutenolide B3		Di(ethylene glycol) divinyl ether		k(obs)	(3.5±0.1)·10 <sup>-3</sup> [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,91	2,15	0,73	1,12	0,00	0,00
30	0,89	2,10	0,71	1,10	0,02	0,02
60	0,80	1,90	0,63	0,97	0,12	0,13
90	0,73	1,72	0,50	0,77	0,24	0,27
150	0,65	1,54	0,28	0,43	0,40	0,50
210	0,54	1,28	0,18	0,28	0,52	0,74
270	0,46	1,09	0,13	0,21	0,60	0,92
330	0,38	0,89	0,07	0,10	0,70	1,19
600	0,16	0,38	0,00	0,00	0,88	2,15

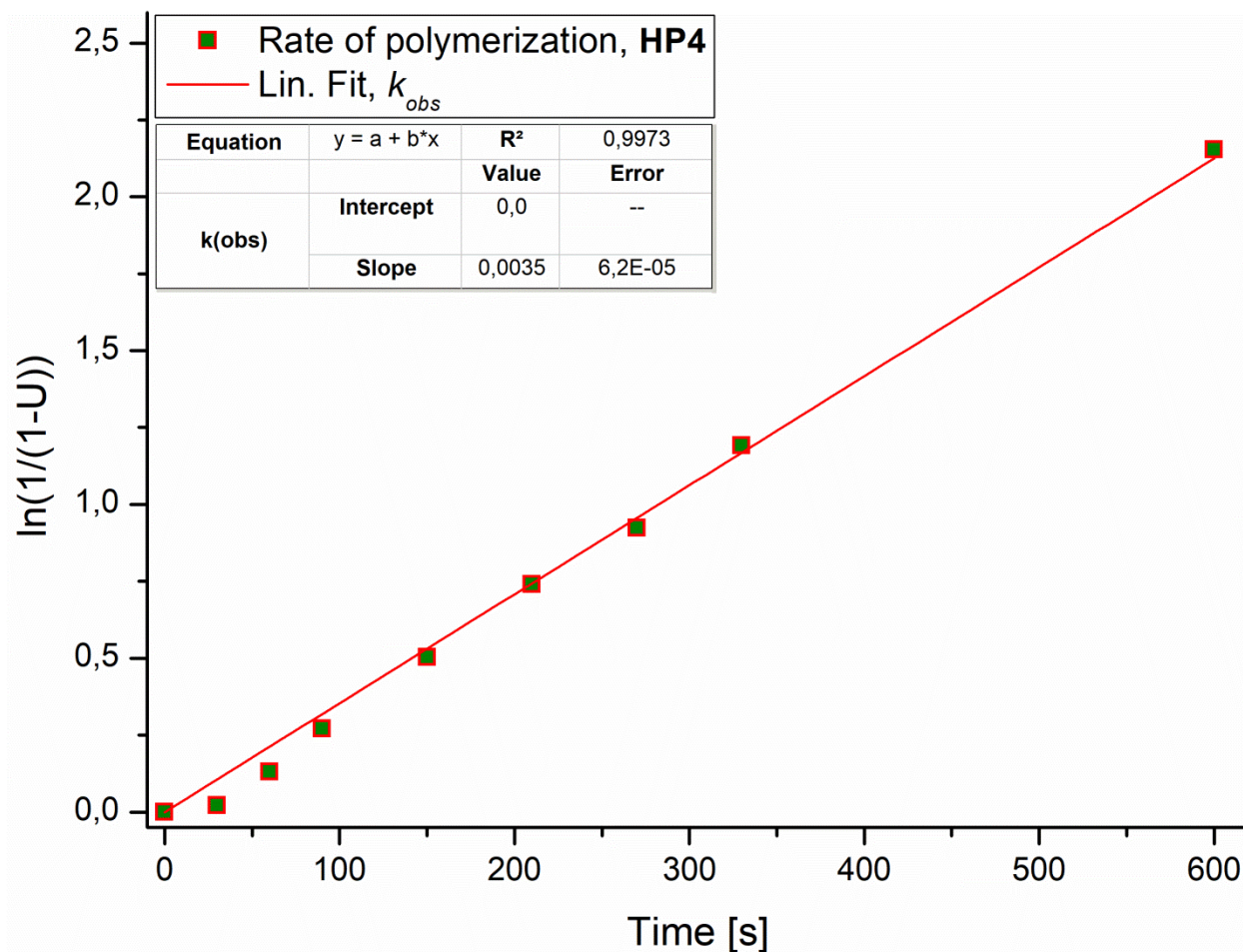


**Fig. S45.** Concentration of monomers over time of the copolymerization of hexyloxybutenolide **B3** with di(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 10 min.



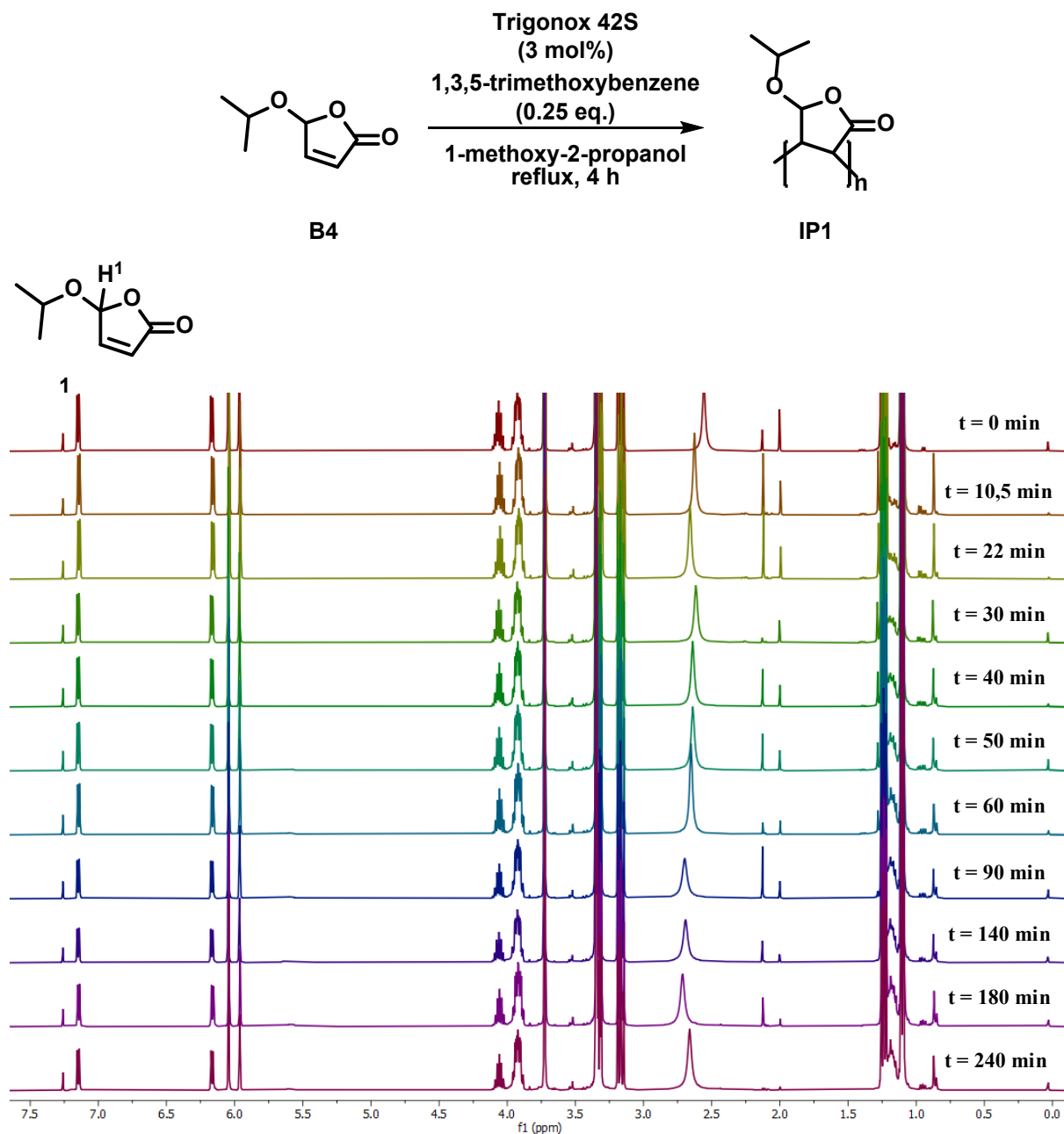


**Fig. S46.** Conversion of polymer **HP4** over time; copolymerization of hexyloxybutenolide **B3** with di(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 10 min.



**Fig. S47.** Rate of copolymerization of hexyloxybutenolide **B3** with di(ethylene glycol) divinyl ether (1:0.5 ratio) to **HP4** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 10 min.

poly-5-isopropoxy-2(5H)-furanone IP1

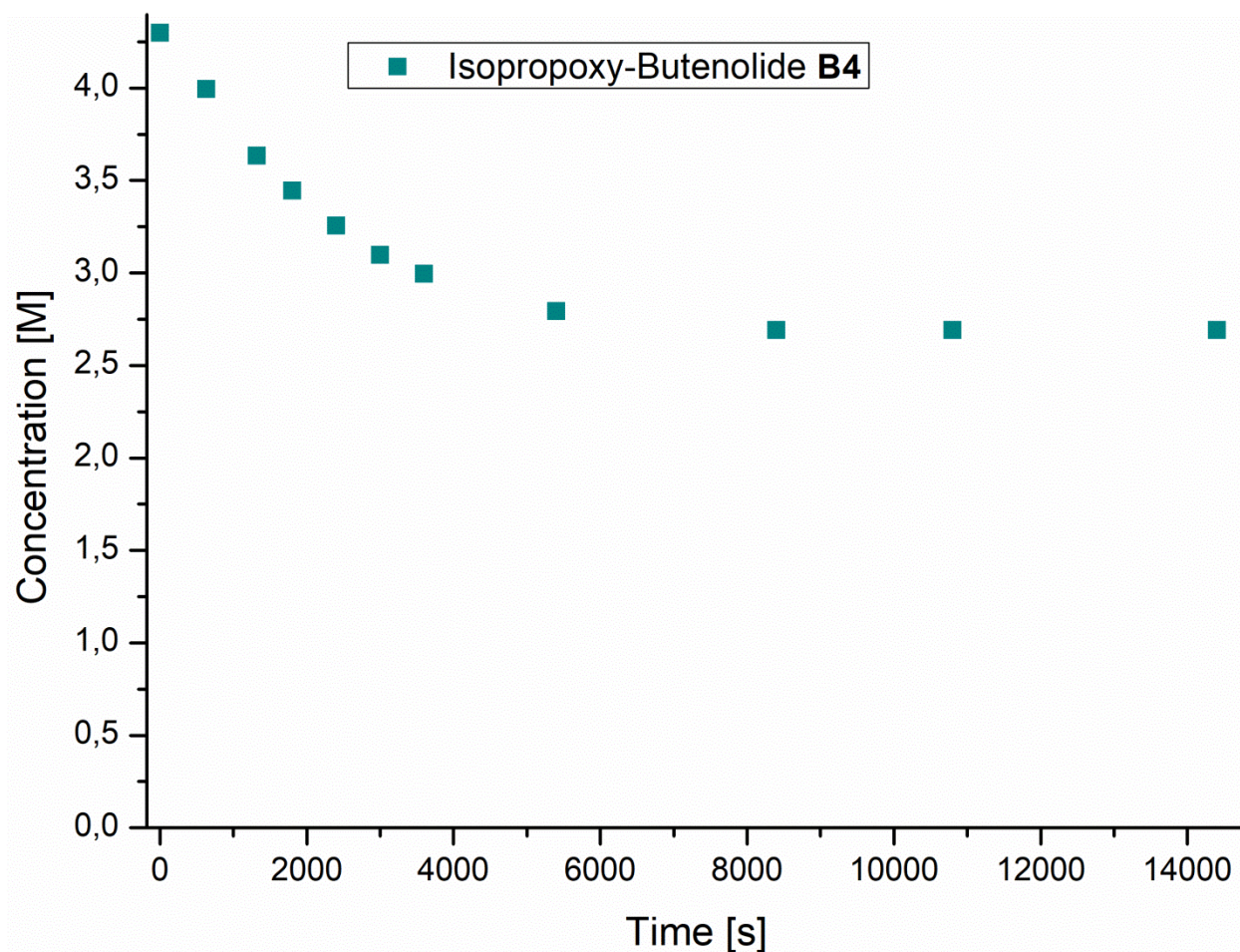


**Fig. S48.** Reaction scheme homopolymerization isopropoxybutenolide **B4** (2 eq.), reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 4 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard (bottom).

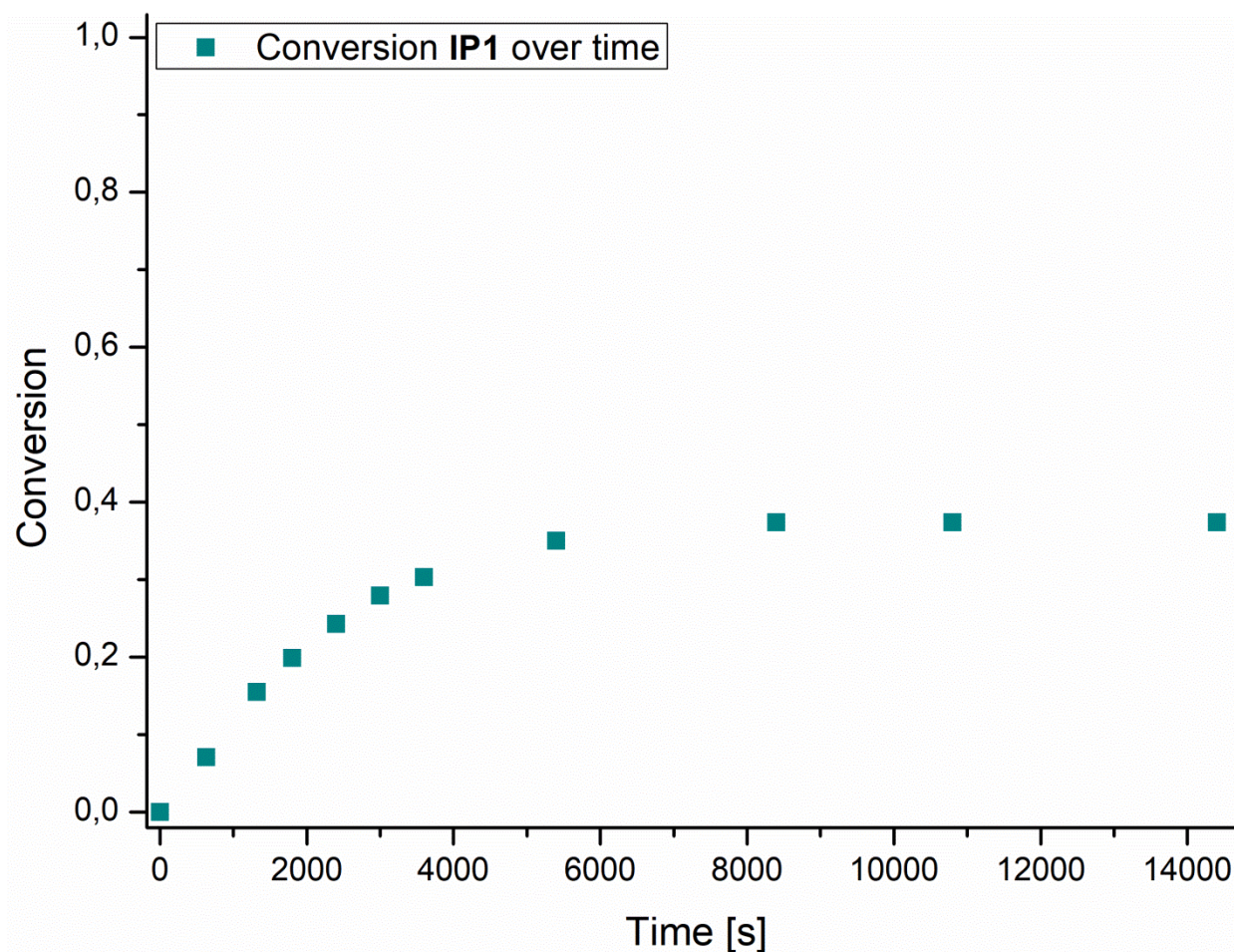


**Table S14.** Kinetic studies of the homopolymerization of isopropoxybutenolide **B4** (2 eq.), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.25 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 4 h.

Isopropoxybutenolide-polymer IP1			k1(obs)	(1.1±0.1)·10 <sup>-4</sup> [s <sup>-1</sup> ]
Isopropoxybutenolide B4			k2(obs)	(3.7±0.2)·10 <sup>-5</sup> [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,74	4,30	0,00	0,00
630	0,69	4,00	0,07	0,07
1320	0,63	3,63	0,16	0,17
1800	0,60	3,45	0,20	0,22
2400	0,56	3,26	0,24	0,28
3000	0,54	3,10	0,28	0,33
3600	0,52	3,00	0,30	0,36
5400	0,48	2,79	0,35	0,43
8400	0,47	2,69	0,37	0,47
10800	0,47	2,69	0,37	0,47
14400	0,47	2,69	0,37	0,47

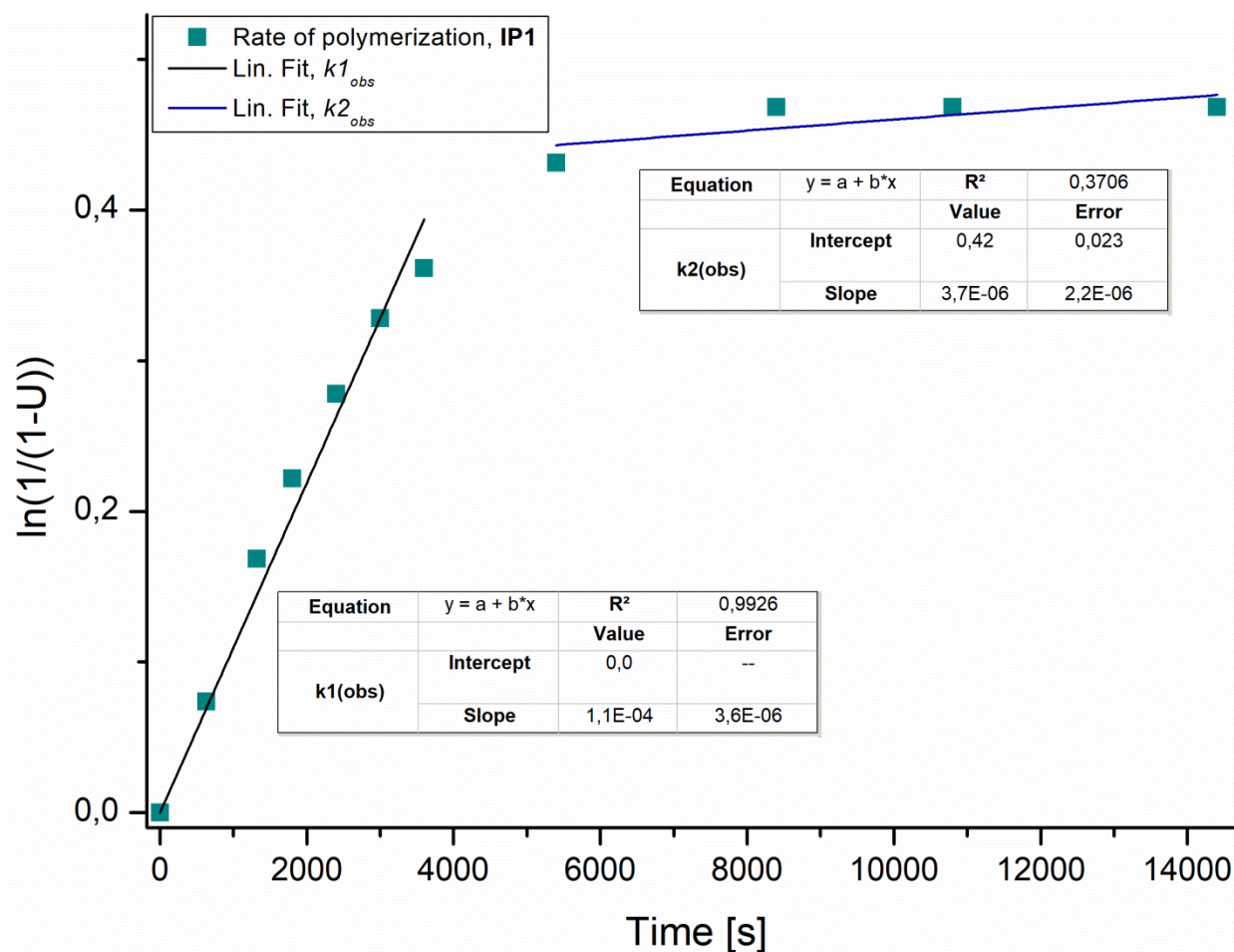


**Fig. S49.** Concentration of the monomer isopropoxybutenolide **B4** over time followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 4 h.



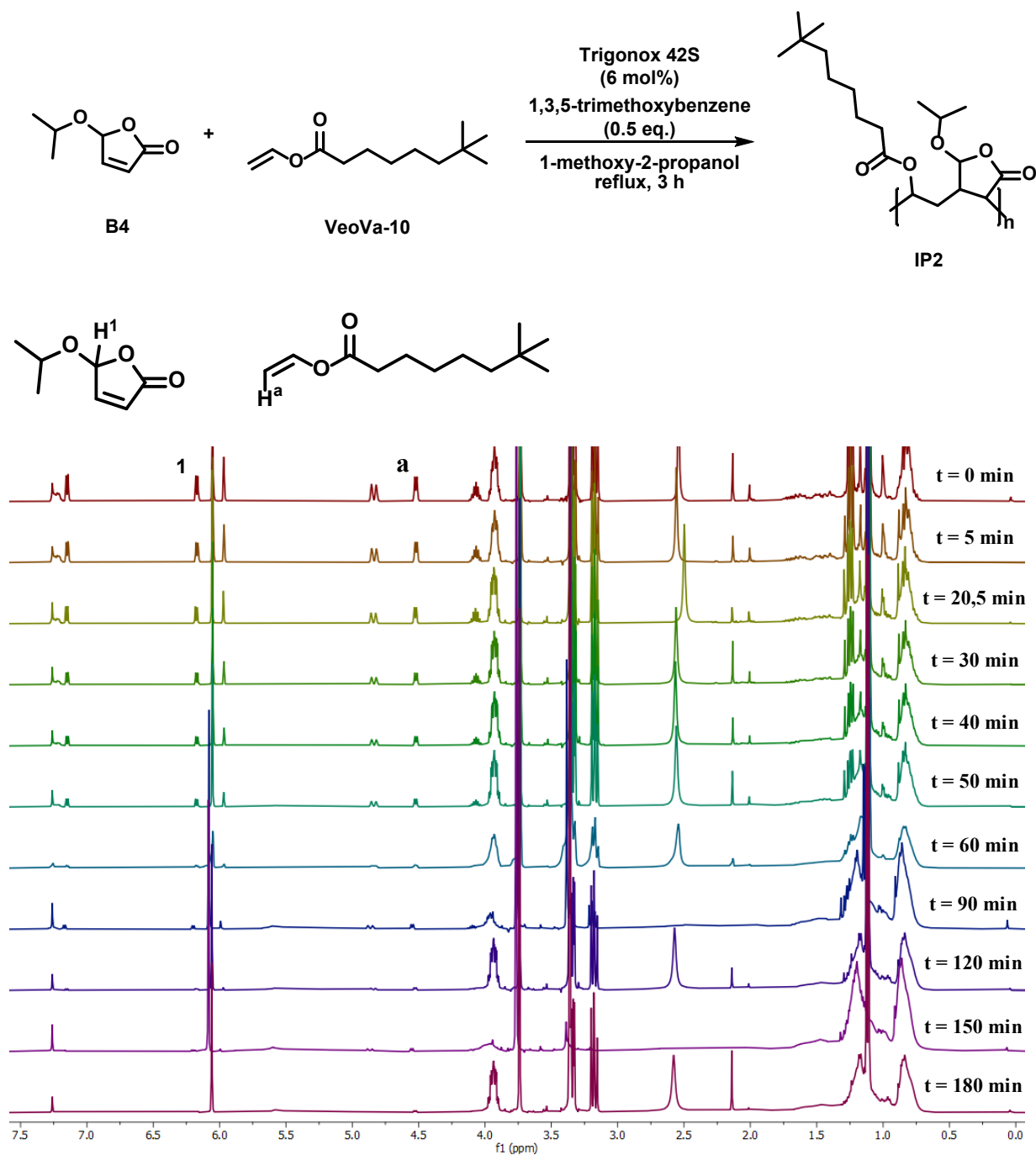
**Fig. S50.** Conversion of polymer **IP1** over time; homo-polymerization of isopropoxybutenolide **B4** followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 4 h.





**Fig. S51.** Rate of homo-polymerization of isopropoxybutenolide **B4** to **IP1** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 4 h.

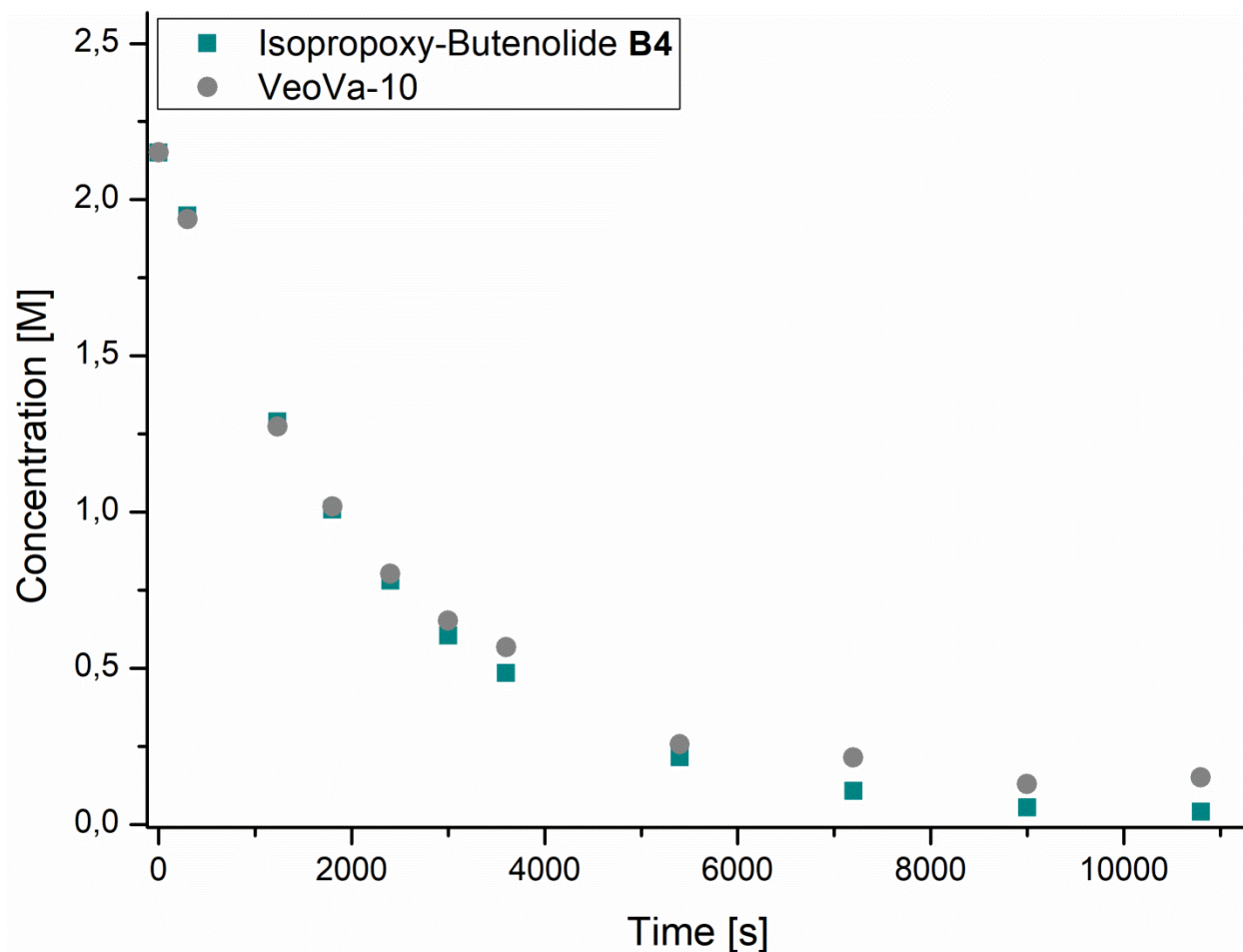
5-isopropoxy-2(5H)-furanone-VeoVa-10-copolymer IP2



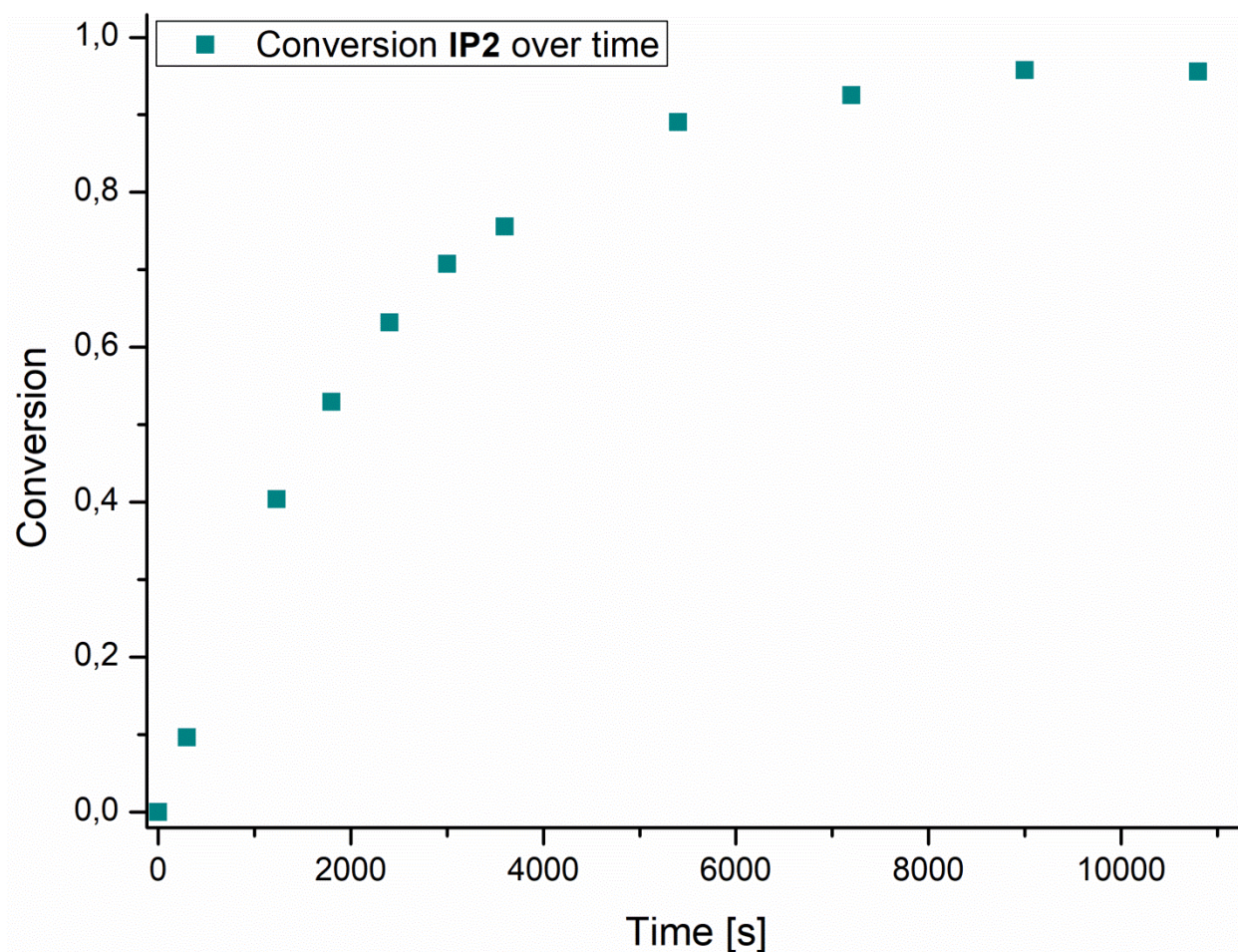
**Fig. S52.** Reaction scheme copolymerization isopropoxybutenolide **B4** with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 3 h (top).  $^1H$ NMR signals over time by taking samples and flash freezing ( $-18^\circ C$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S15.** Kinetic studies of the copolymerization of isopropoxybutenolide **B4** with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 3 h.

Isopropoxybutenolide-VeoVa-10-copolymer IP2						
	Isopropoxybutenolide <b>B4</b>		VeoVa-10		<b>k(obs)</b>	<b>(3.7±0.1)·10<sup>-4</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,80	2,15	1,01	2,15	0,00	0,00
300	0,73	1,95	0,91	1,94	0,10	0,10
1230	0,48	1,29	0,60	1,27	0,40	0,52
1800	0,38	1,01	0,48	1,02	0,53	0,75
2400	0,29	0,78	0,38	0,80	0,63	1,00
3000	0,23	0,60	0,31	0,65	0,71	1,23
3600	0,18	0,48	0,27	0,57	0,76	1,41
5400	0,08	0,22	0,12	0,26	0,89	2,21
7200	0,04	0,11	0,10	0,21	0,93	2,59
9000	0,02	0,05	0,06	0,13	0,96	3,16
10800	0,02	0,04	0,07	0,15	0,96	3,12

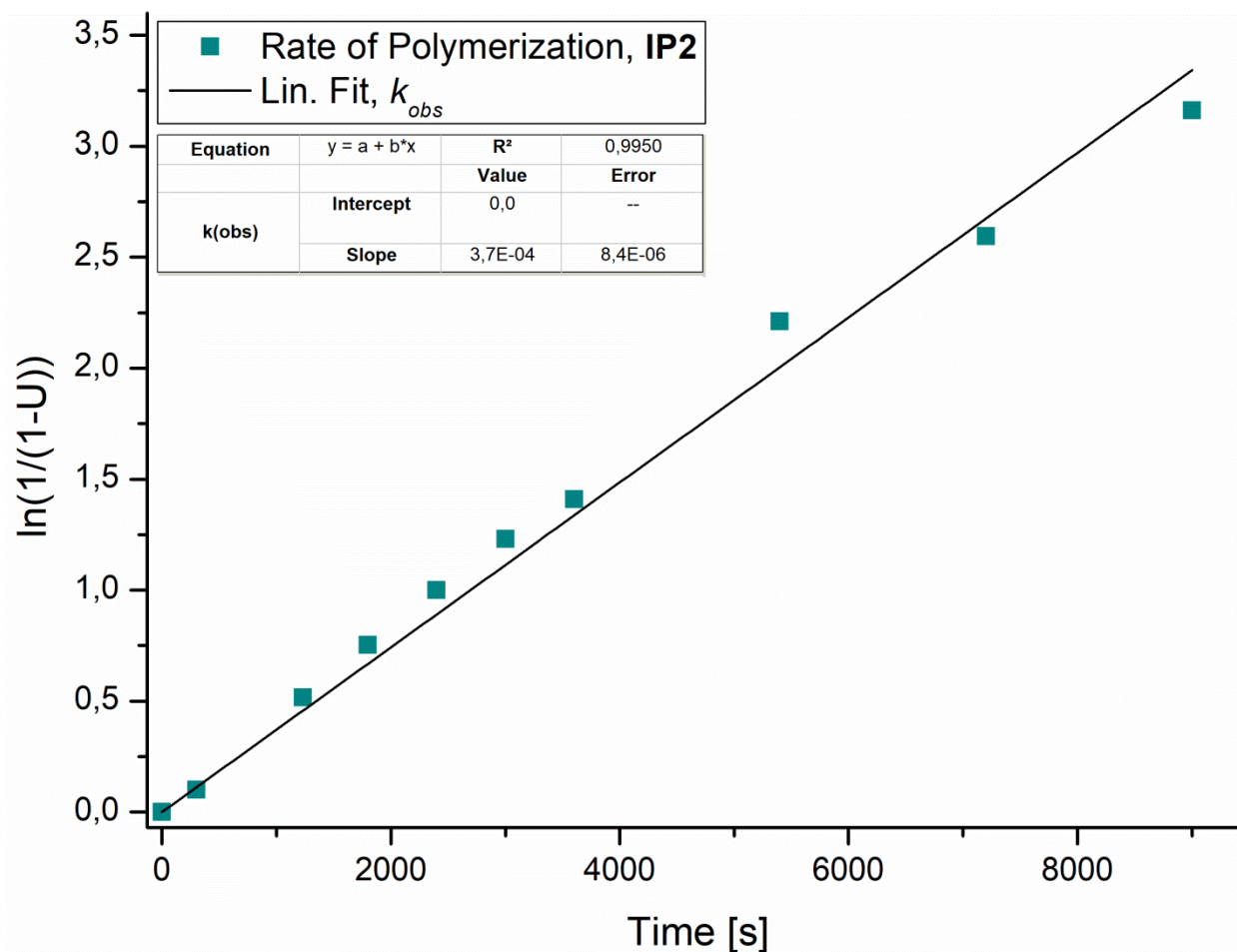


**Fig. S53.** Concentration of monomers over time of the copolymerization of isopropoxybutenolide **B4** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 3 h.



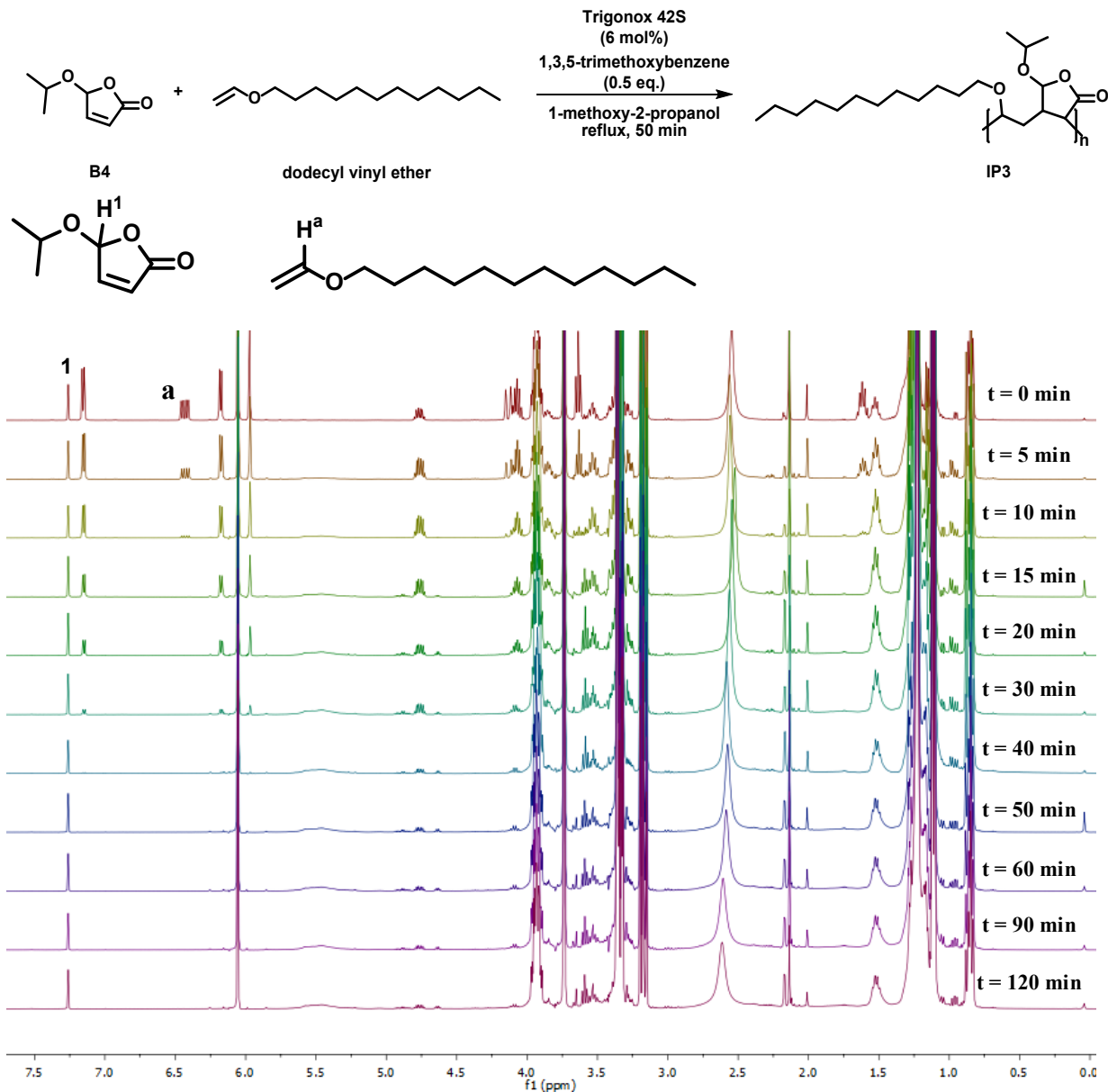
**Fig. S54.** Conversion of polymer **IP2** over time; copolymerization of isopropoxybutenolide **B4** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 3 h.





**Fig. S55.** Rate of copolymerization of isopropoxybutenolide **B4** with VeoVa-10 (1:1 ratio) to **IP2** over time; followed by <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 3 h.

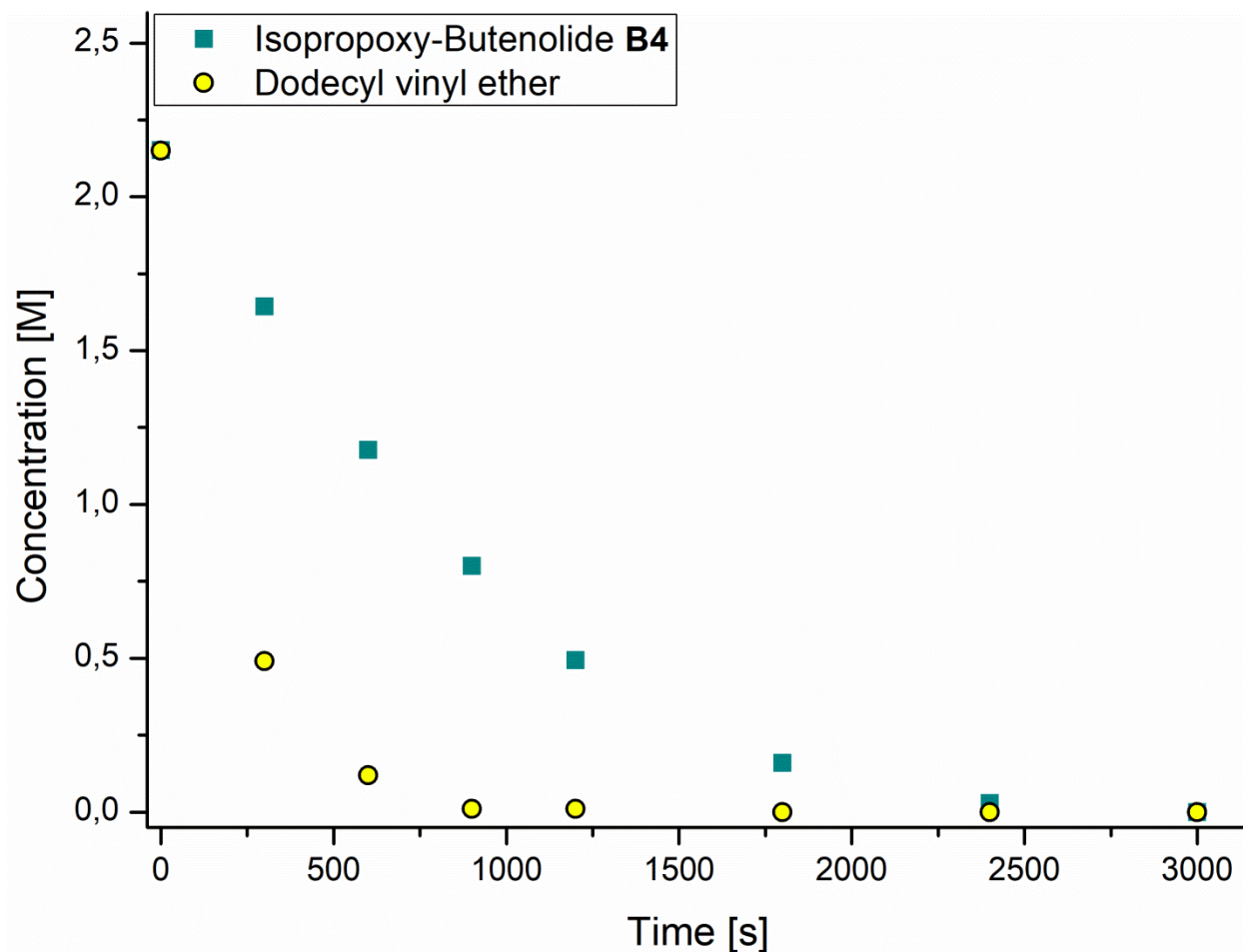
### 5-isopropoxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer IP3



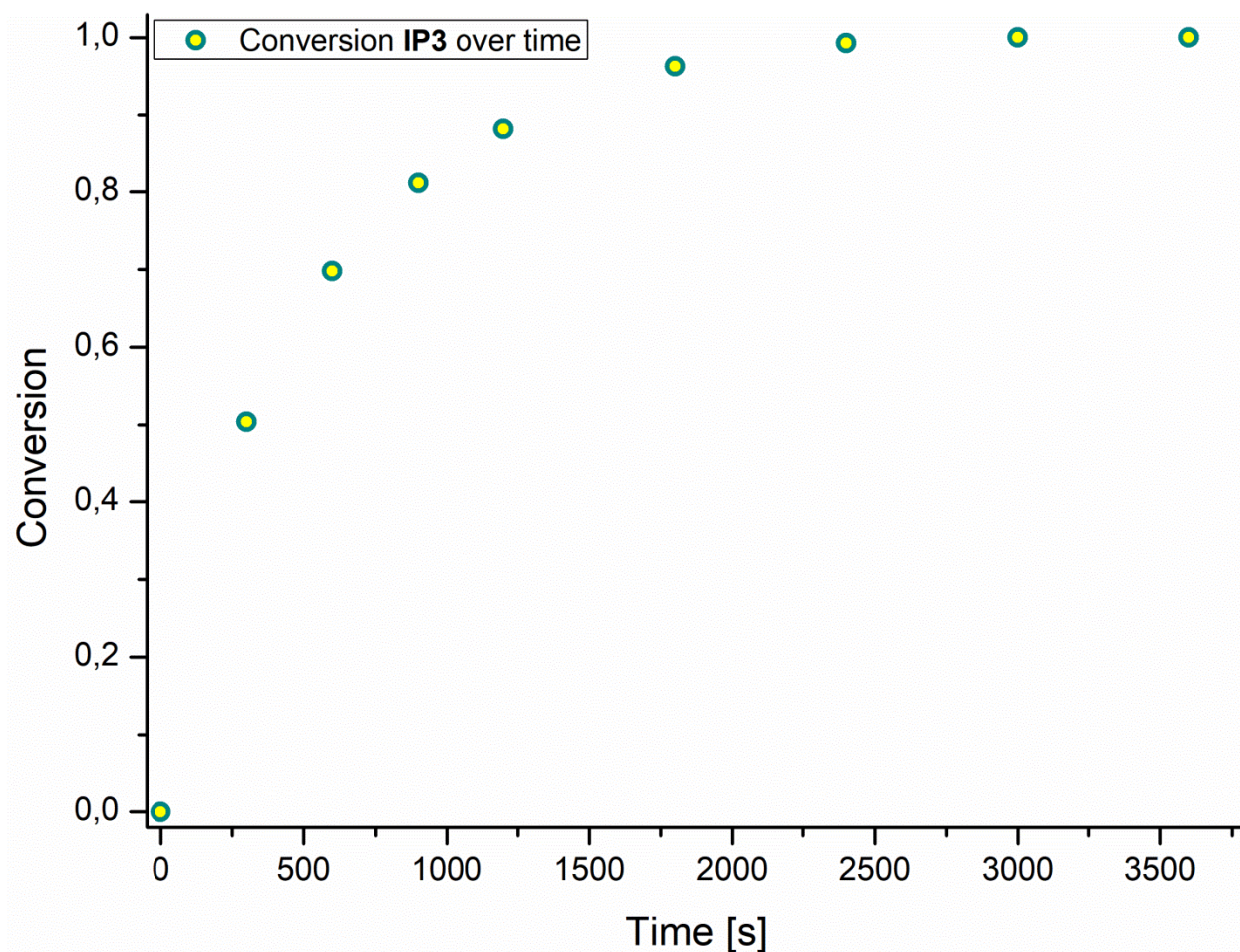
**Fig. S56.** Reaction scheme copolymerization isopropoxybutenolide **B4** with dodecyl vinyl ether (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S16.** Kinetic studies of the copolymerization of isopropoxybutenolide **B4** with dodecyl vinyl ether (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.

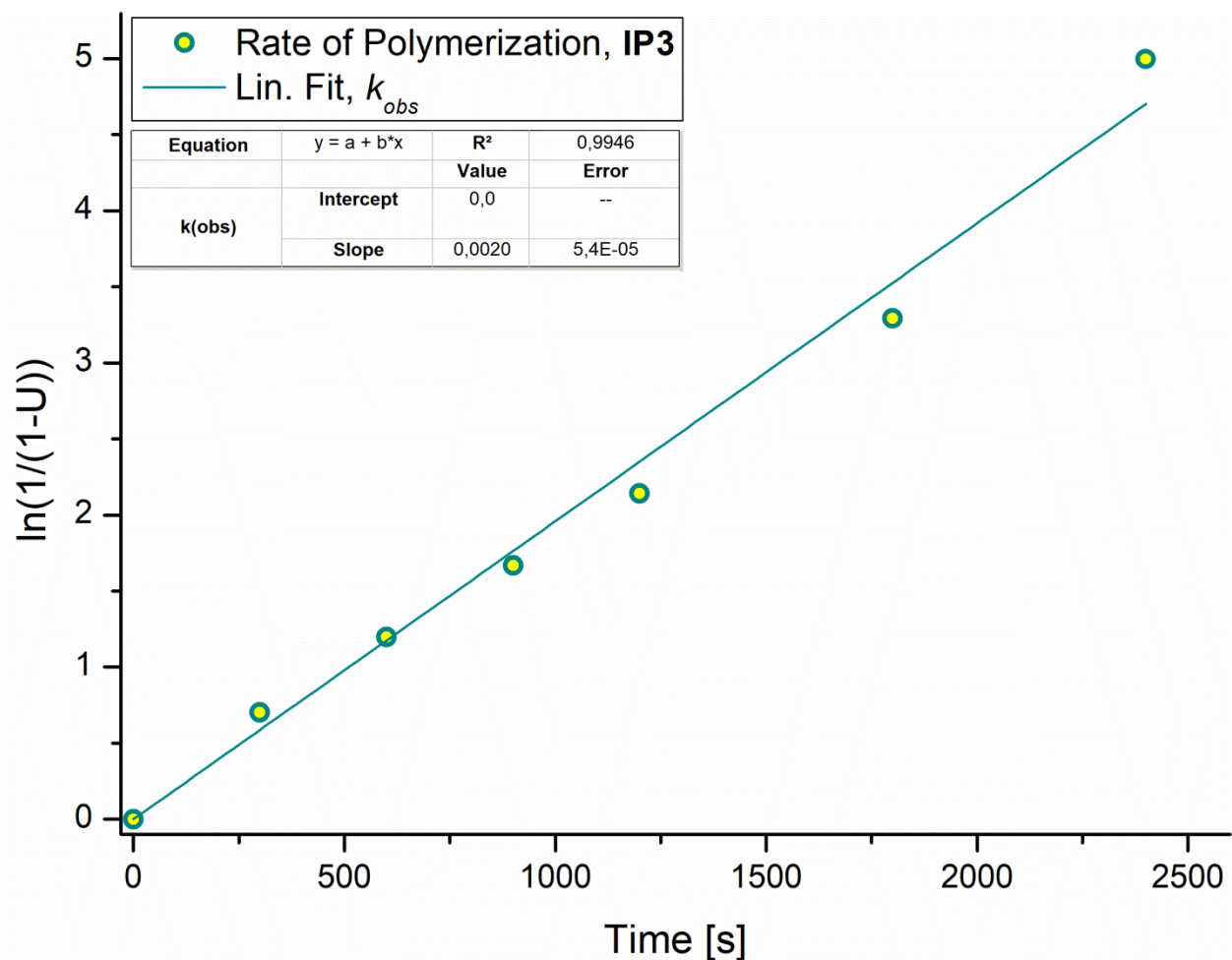
Isopropoxybutenolide-vinyl-copolymer IP3						
	Isopropoxybutenolide B4		Dodecyl vinyl ether		k(obs)	$(2.0 \pm 0.1) \cdot 10^{-3}$ [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	0,74	2,15	0,50	2,15	0,00	0,00
300	0,57	1,64	0,23	0,49	0,50	0,70
600	0,41	1,18	0,06	0,12	0,70	1,20
900	0,28	0,80	0,01	0,01	0,81	1,67
1200	0,17	0,49	0,01	0,01	0,88	2,14
1800	0,06	0,16	0,00	0,00	0,96	3,29
2400	0,01	0,03	0,00	0,00	0,99	5,00
3000	0,00	0,00	0,00	0,00	1,00	-



**Fig. S57.** Concentration of monomers over time of the copolymerization of isopropoxybutenolide **B4** with dodecyl vinyl ether (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.



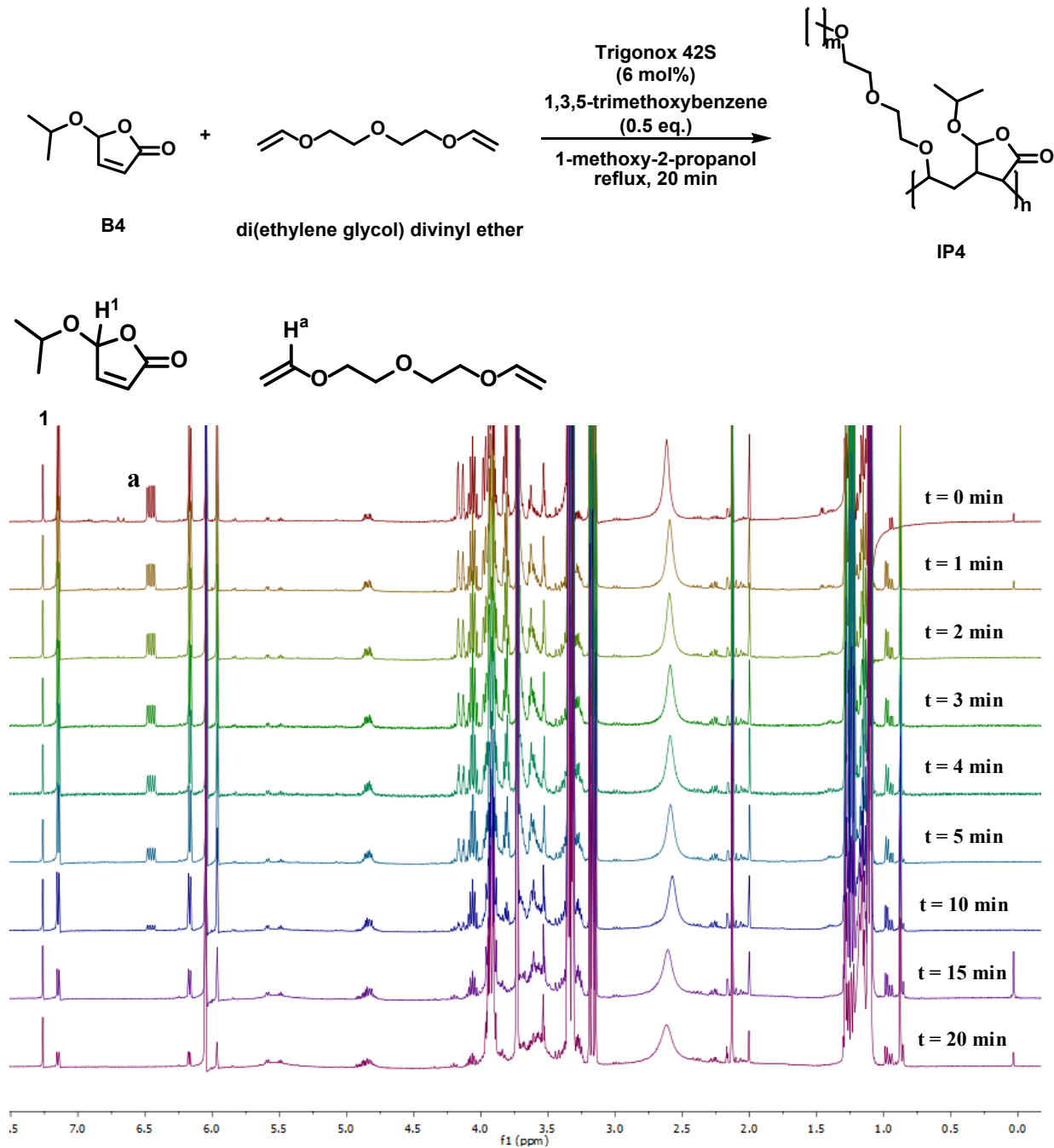
**Fig. S58.** Conversion of polymer **IP3** over time; copolymerization of isopropoxybutenolide **B4** with dodecyl vinyl ether (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.



**Fig. S59.** Rate of copolymerization of isopropoxybutenolide **B4** with dodecyl vinyl ether (1:1 ratio) to **IP3** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.



5-isopropoxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer IP4

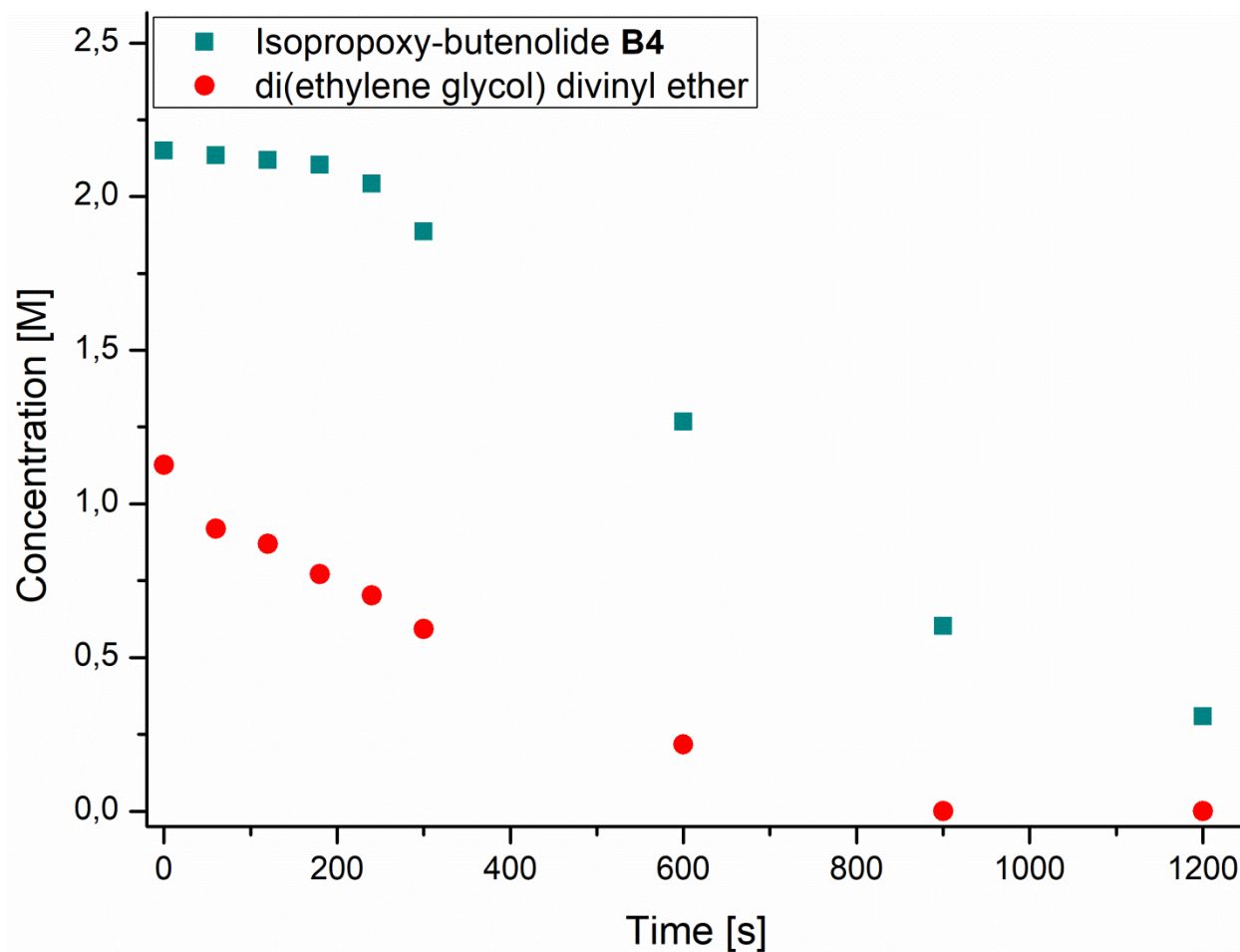


**Fig. S60.** Reaction scheme copolymerization isopropoxybutenolide **B4** with di(ethylene glycol) divinyl ether (1:0.5 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for di(ethylene glycol) divinyl ether), reflux, 10 min (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

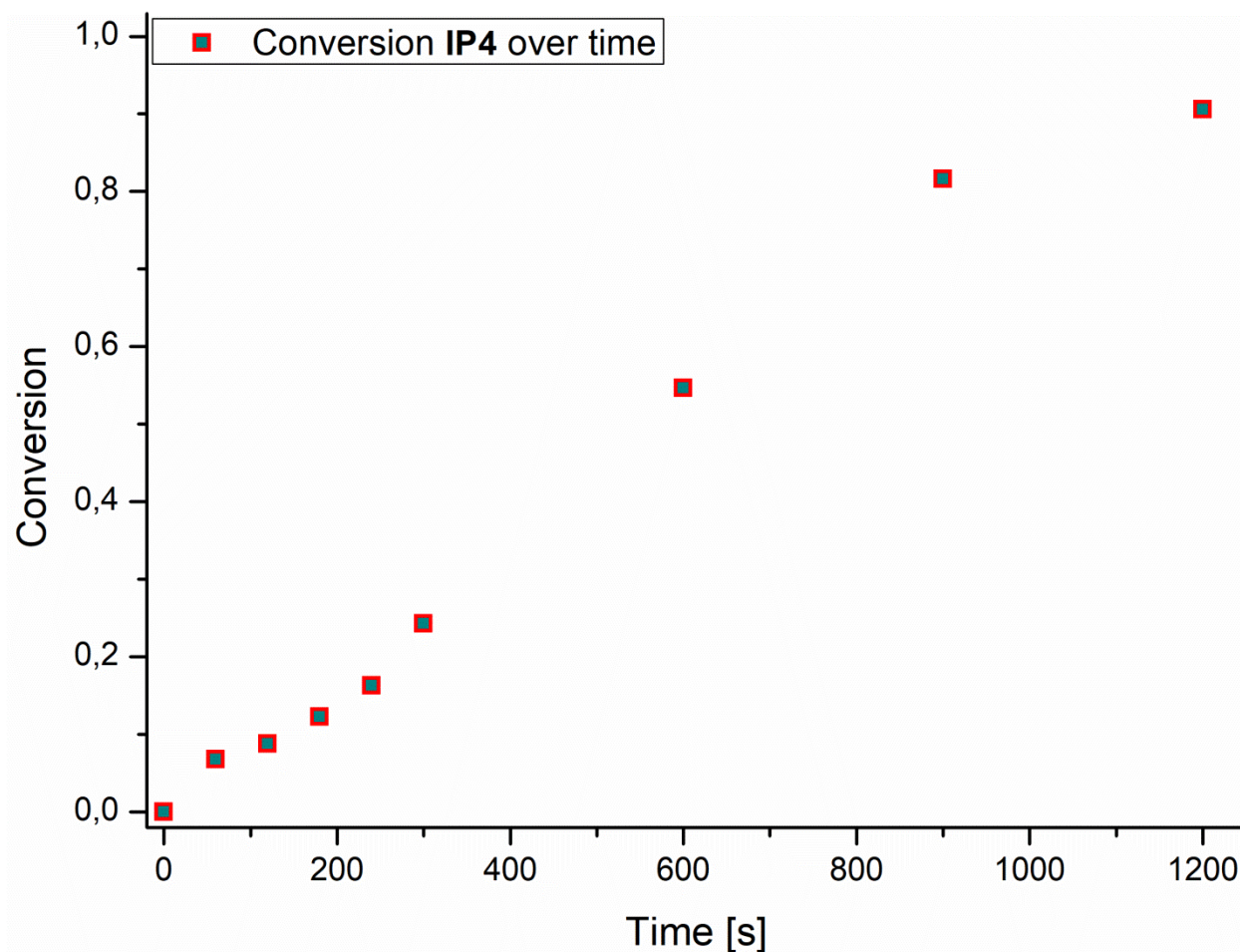
**Table S17.** Kinetic studies of the copolymerization of isopropoxybutenolide **B4** with di(ethylene glycol) divinyl ether (1:0.5 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for di(ethylene glycol) divinyl ether), reflux, 10 min.

Isopropoxybutenolide-crosslink-copolymer IP4						
	Isopropoxybutenolide B4		Di(ethylene glycol) divinyl ether		k(obs)	$(1.8 \pm 0.1) \cdot 10^{-3}$ [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	0,70	2,15	0,57	1,13	0,00	0,00
60	0,69	2,13	0,47	0,92	0,07	0,07
120	0,69	2,12	0,44	0,87	0,09	0,09
180	0,68	2,10	0,39	0,77	0,12	0,13
240	0,66	2,04	0,36	0,70	0,16	0,18
300	0,61	1,89	0,30	0,59	0,24	0,28
600	0,41	1,27	0,11	0,22	0,55	0,79
900	0,20	0,60	0,00	0,00	0,82	1,69
1200	0,10	0,31	0,00	0,00	0,91	2,36

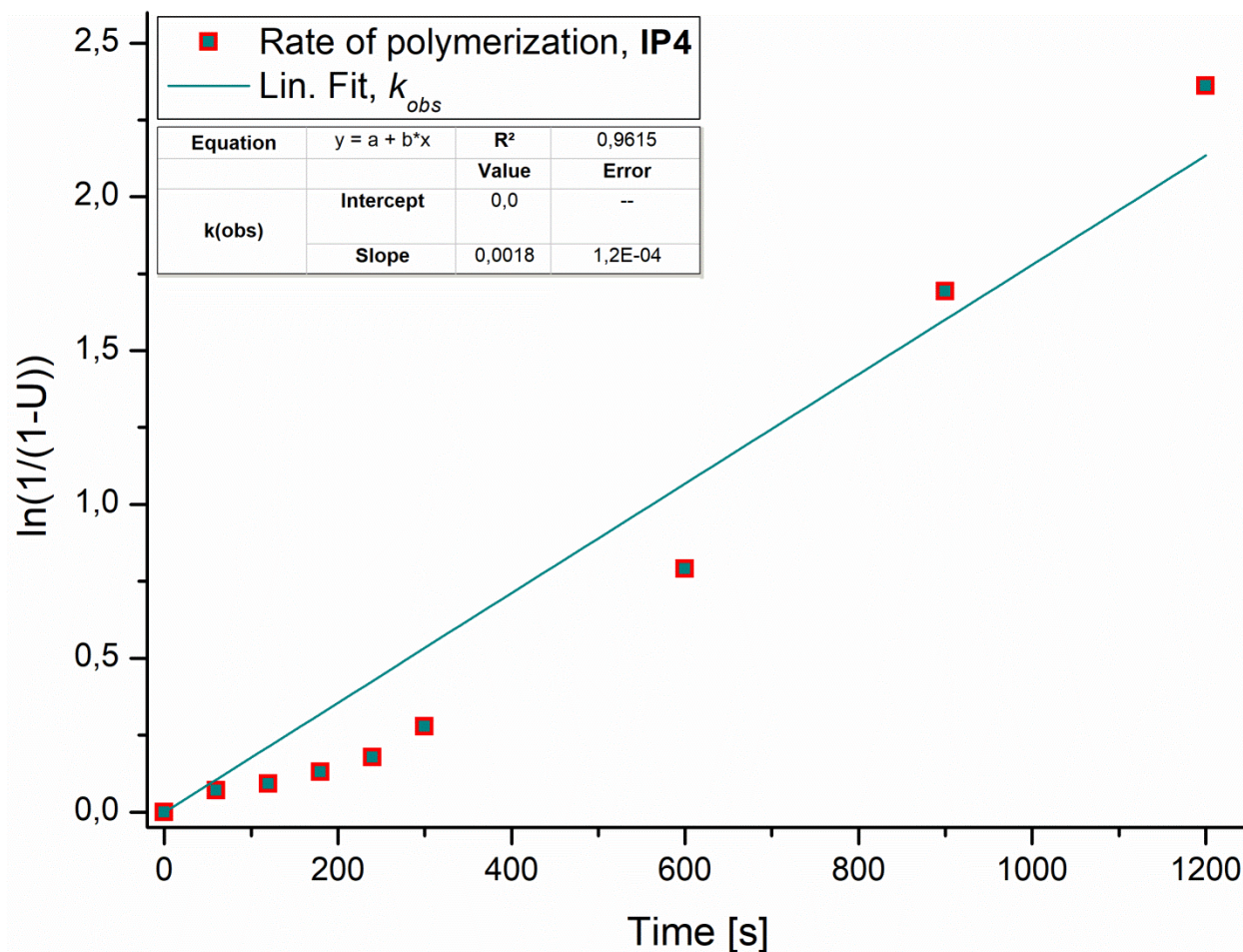




**Fig. S61.** Concentration of monomers over time of the copolymerization of isopropoxybutenolide **B4** with di(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 20 min.

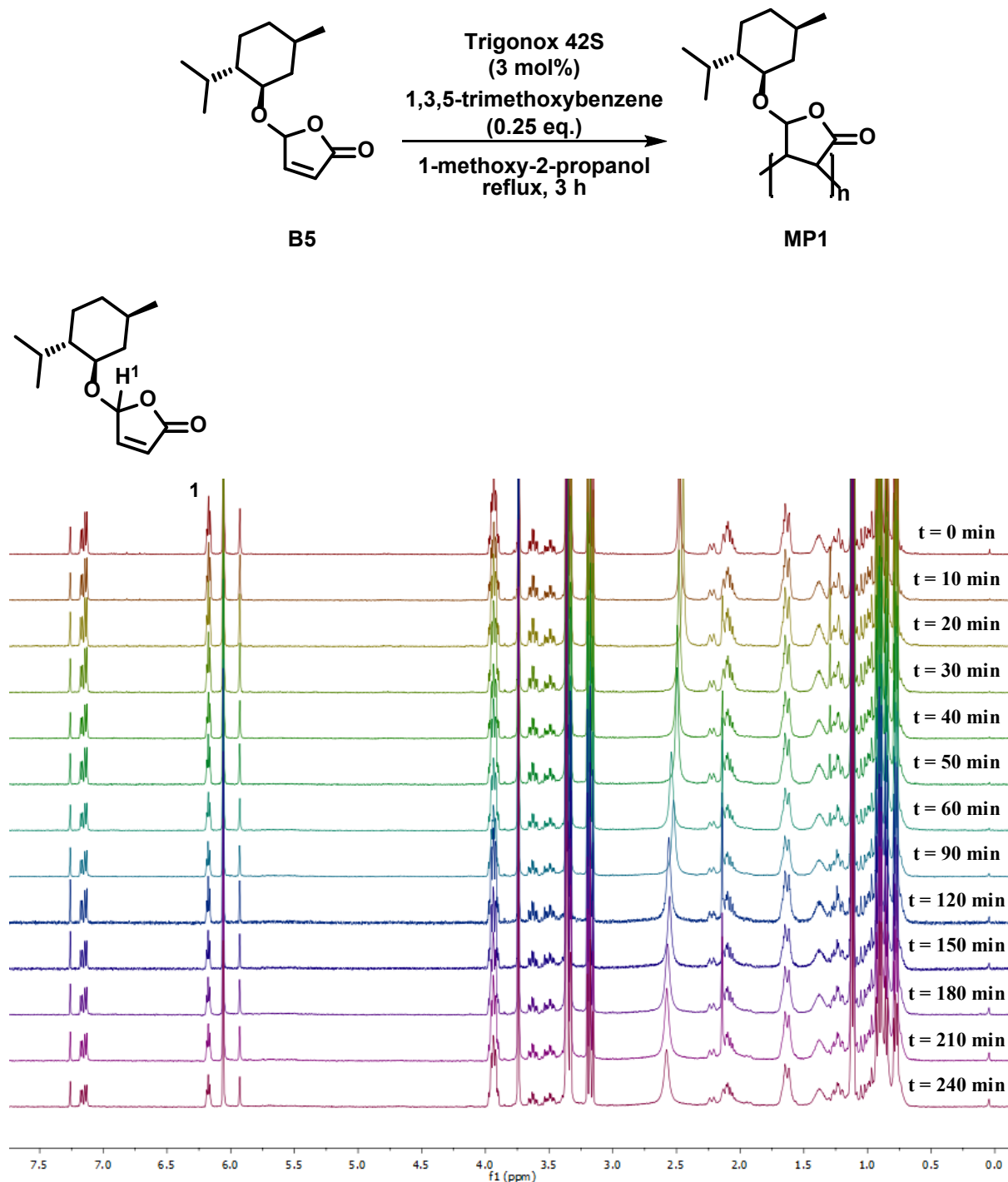


**Fig. S62.** Conversion of polymer **IP4** over time; copolymerization of isopropoxybutenolide **B4** with di(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 20 min.



**Fig. S63.** Rate of copolymerization of isopropoxybutenolide **B4** with di(ethylene glycol) divinyl ether (1:0.5 ratio) to **IP4** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 20 min.

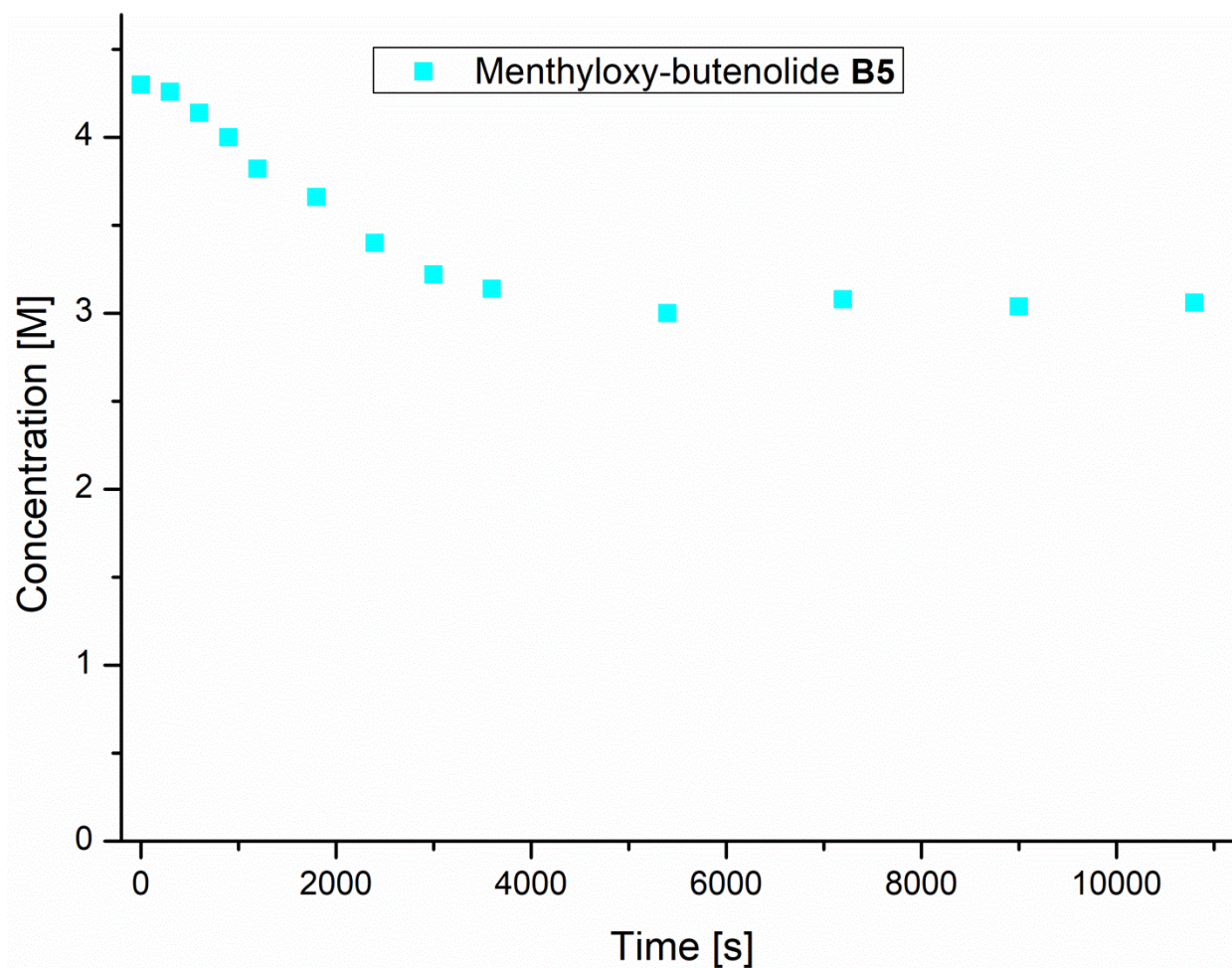
poly-5-menthyloxy-2(5H)-furanone MP1



**Fig. S64.** Reaction scheme homopolymerization menthyloxybutenolide **B5** (2 eq.), reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 3 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard (bottom).

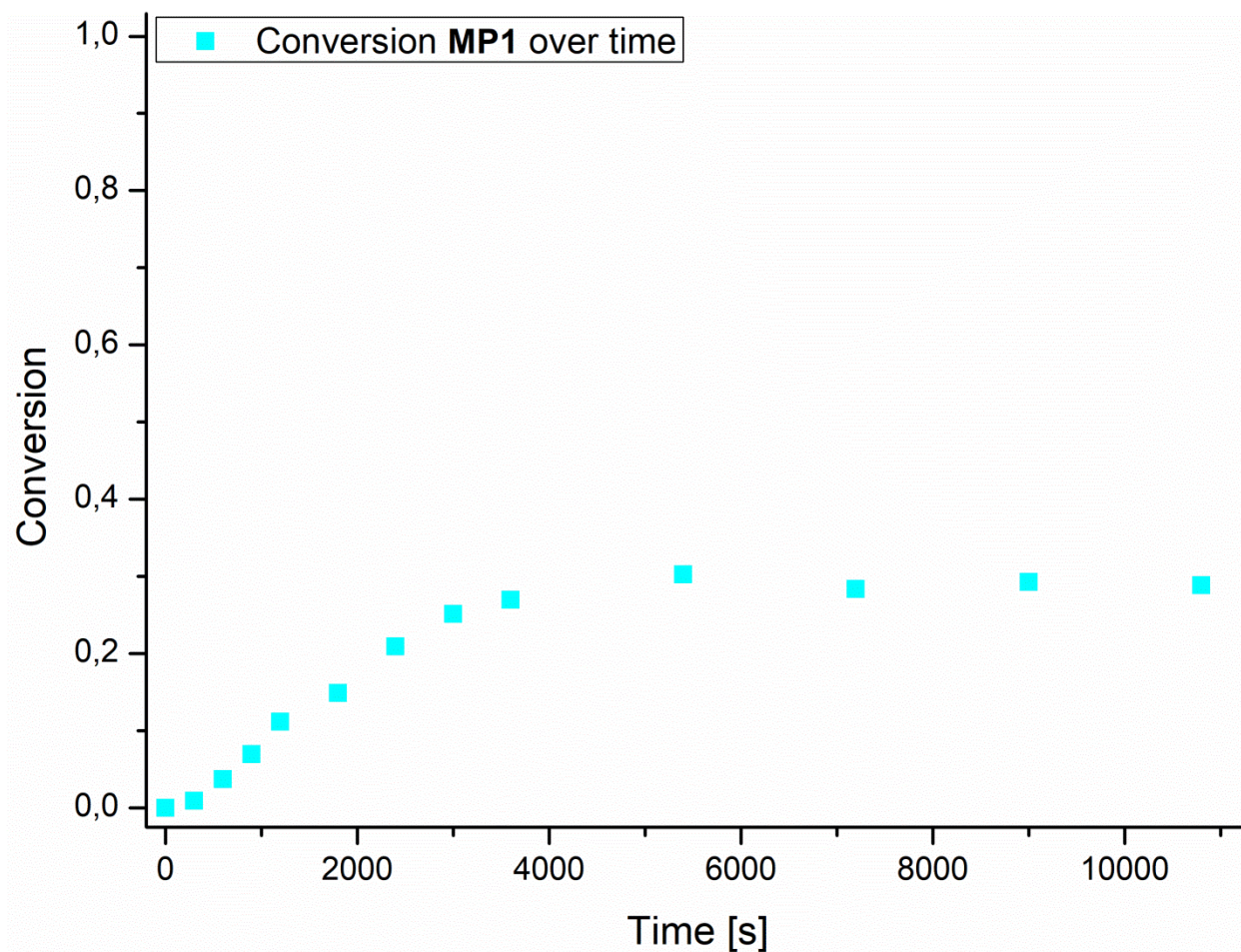
**Table S18.** Kinetic studies of the homopolymerization of menthyloxybutenolide **B5** (2 eq.), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.25 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 3 h.

<b>Menthyloxybutenolide-homo-polymer MP1</b>				
	<b>Menthyloxybutenolide B5</b>		<b>k(obs)</b>	<b>(9.2±0.2)·10<sup>-5</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,53	4,30	0,00	0,00
300	0,53	4,26	0,01	0,01
600	0,51	4,14	0,04	0,04
900	0,49	4,00	0,07	0,07
1200	0,47	3,82	0,11	0,12
1800	0,45	3,66	0,15	0,16
2400	0,42	3,40	0,21	0,23
3000	0,40	3,22	0,25	0,29
3600	0,39	3,14	0,27	0,31
5400	0,37	3,00	0,30	0,36
7200	0,38	3,08	0,28	0,33
9000	0,38	3,04	0,29	0,35
10800	0,38	3,06	0,29	0,34

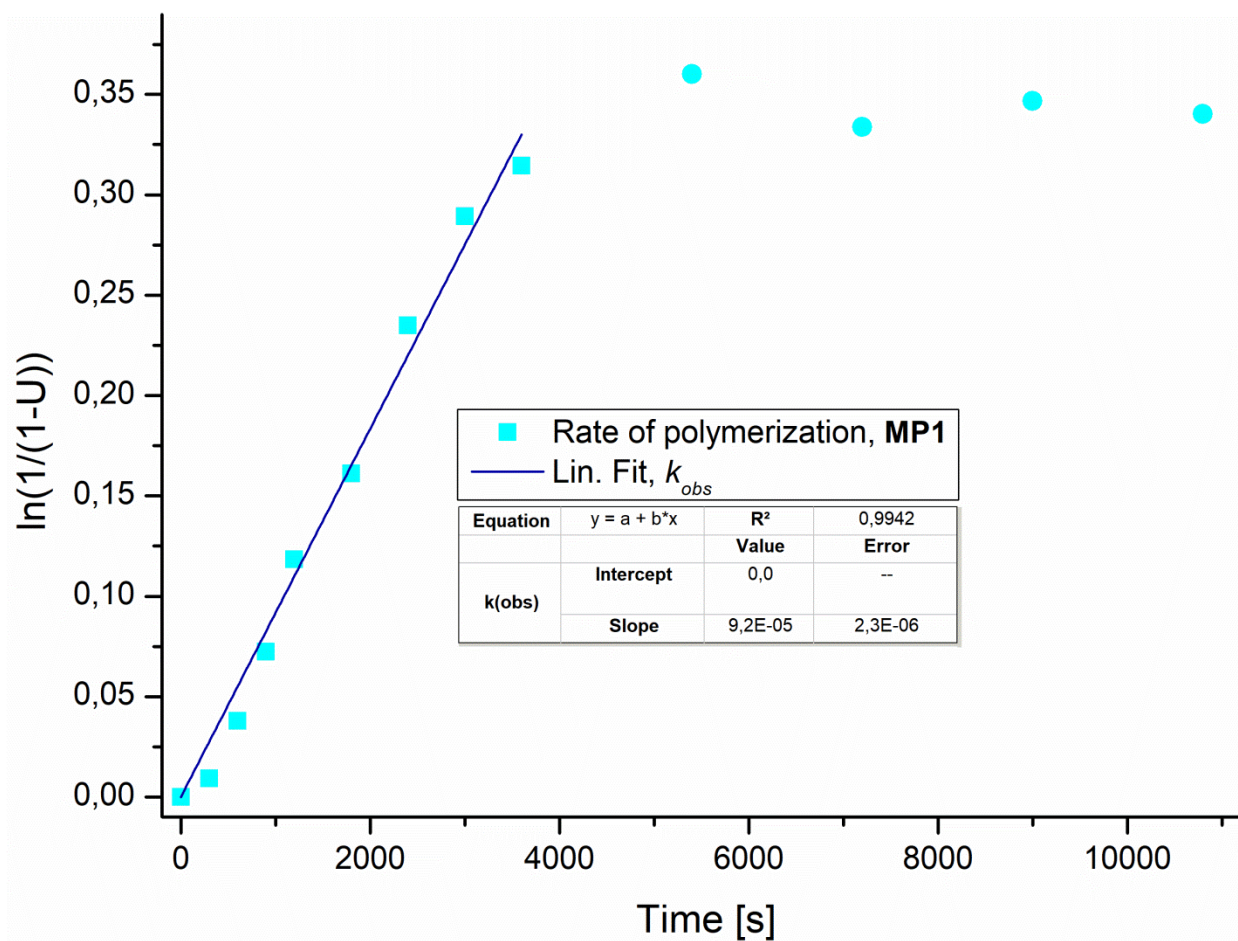


**Fig. S65.** Concentration of the monomer menthyloxybutenolide **B5** over time followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 3 h.





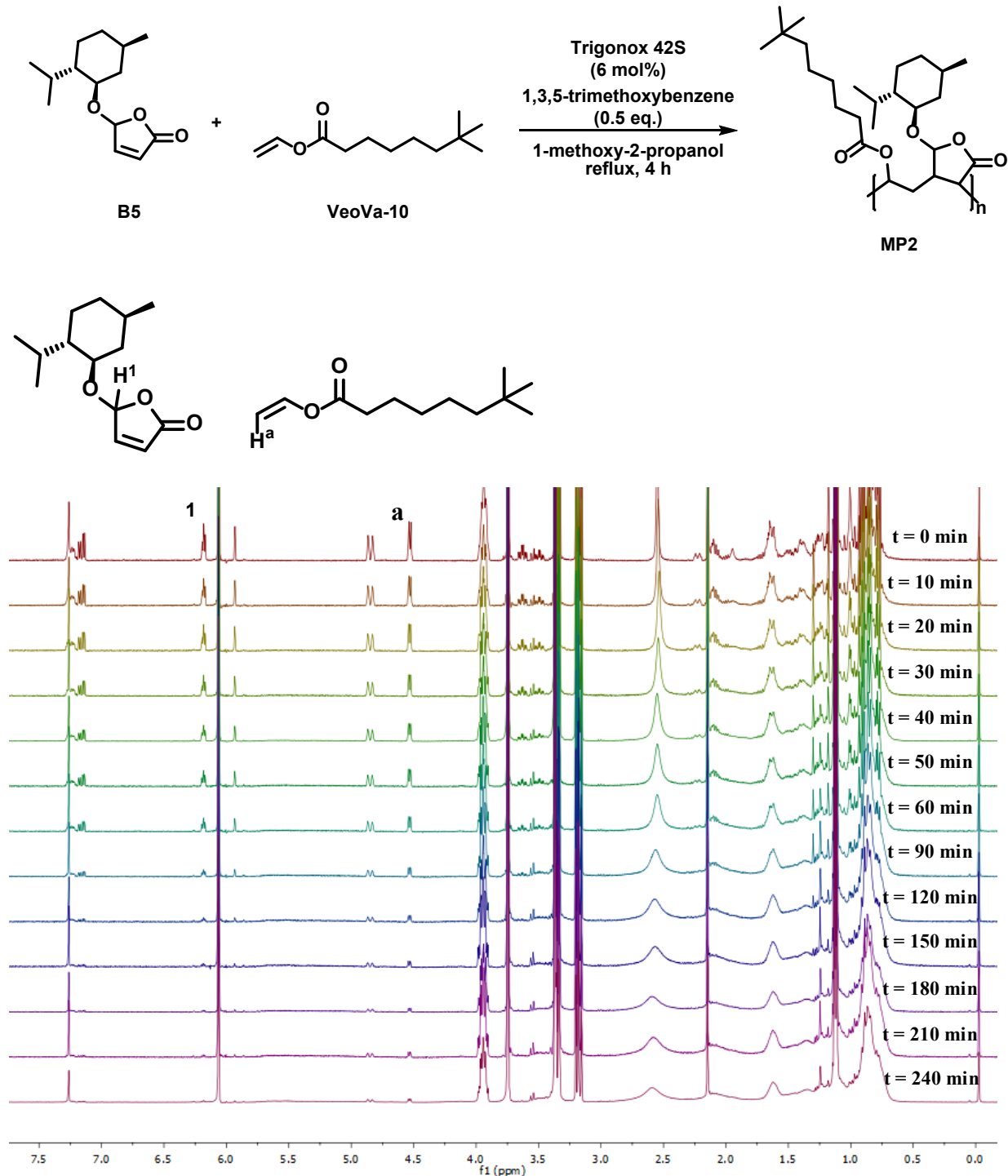
**Fig. S66.** Conversion of polymer **MP1** over time; homo-polymerization of menthyloxybutenolide **B5** followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 3 h.



**Fig. S67.** Rate of homo-polymerization of menthylxybutenolide **B5** to **MP1** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 3 h.



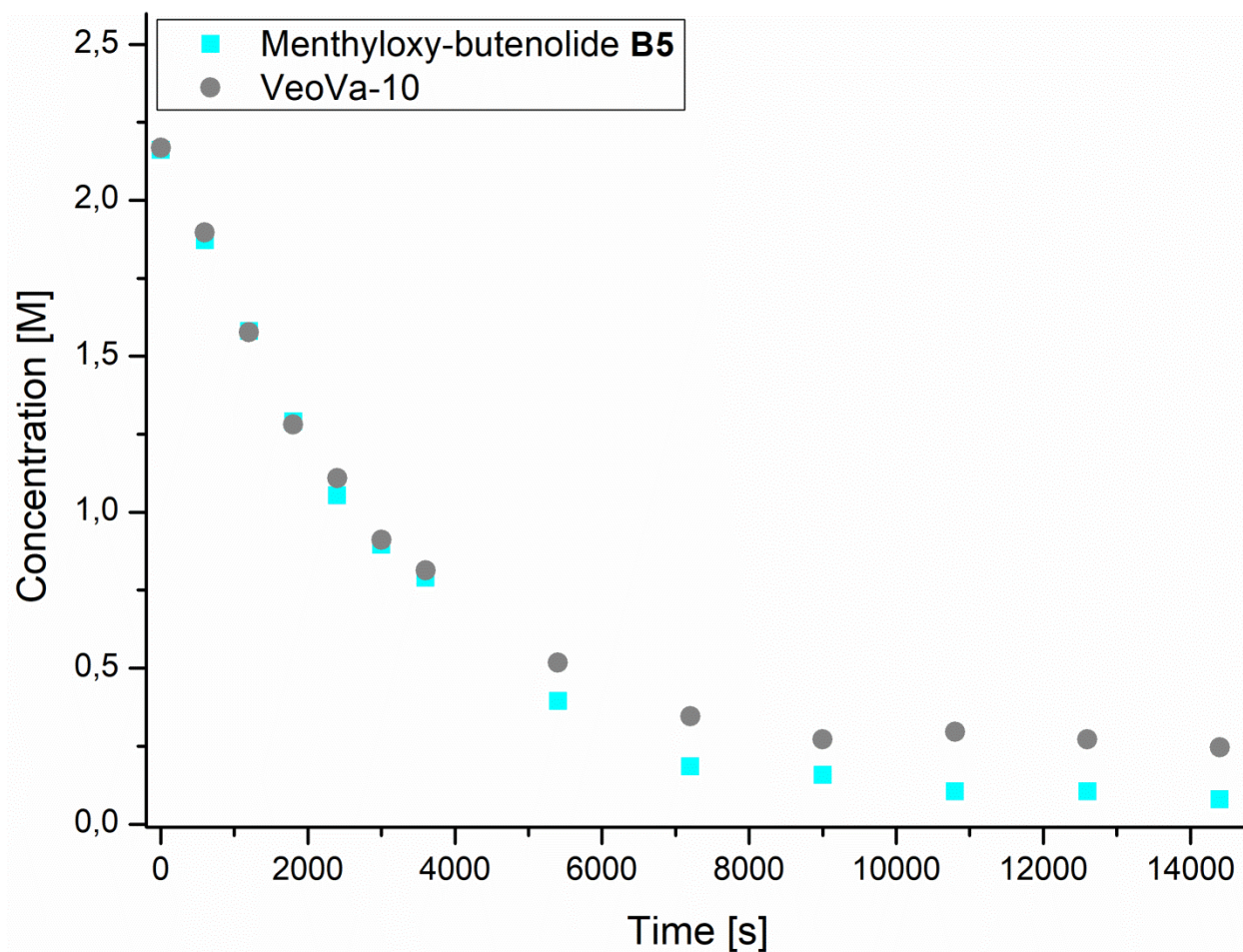
### 5-menthyloxy-2(5H)-furanone-VeoVa-10-copolymer MP2



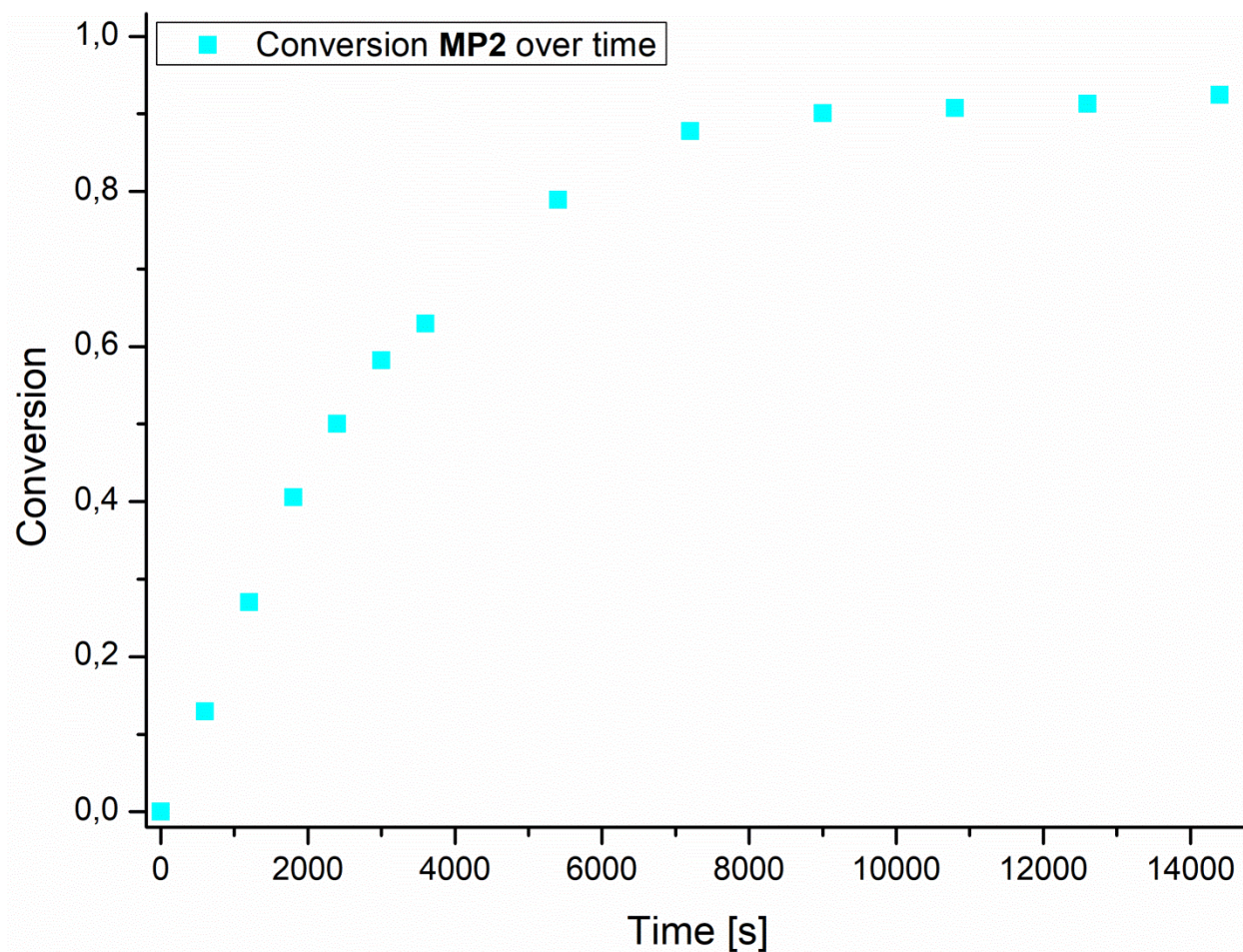
**Fig. S68.** Reaction scheme copolymerization menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S19.** Kinetic studies of the copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.

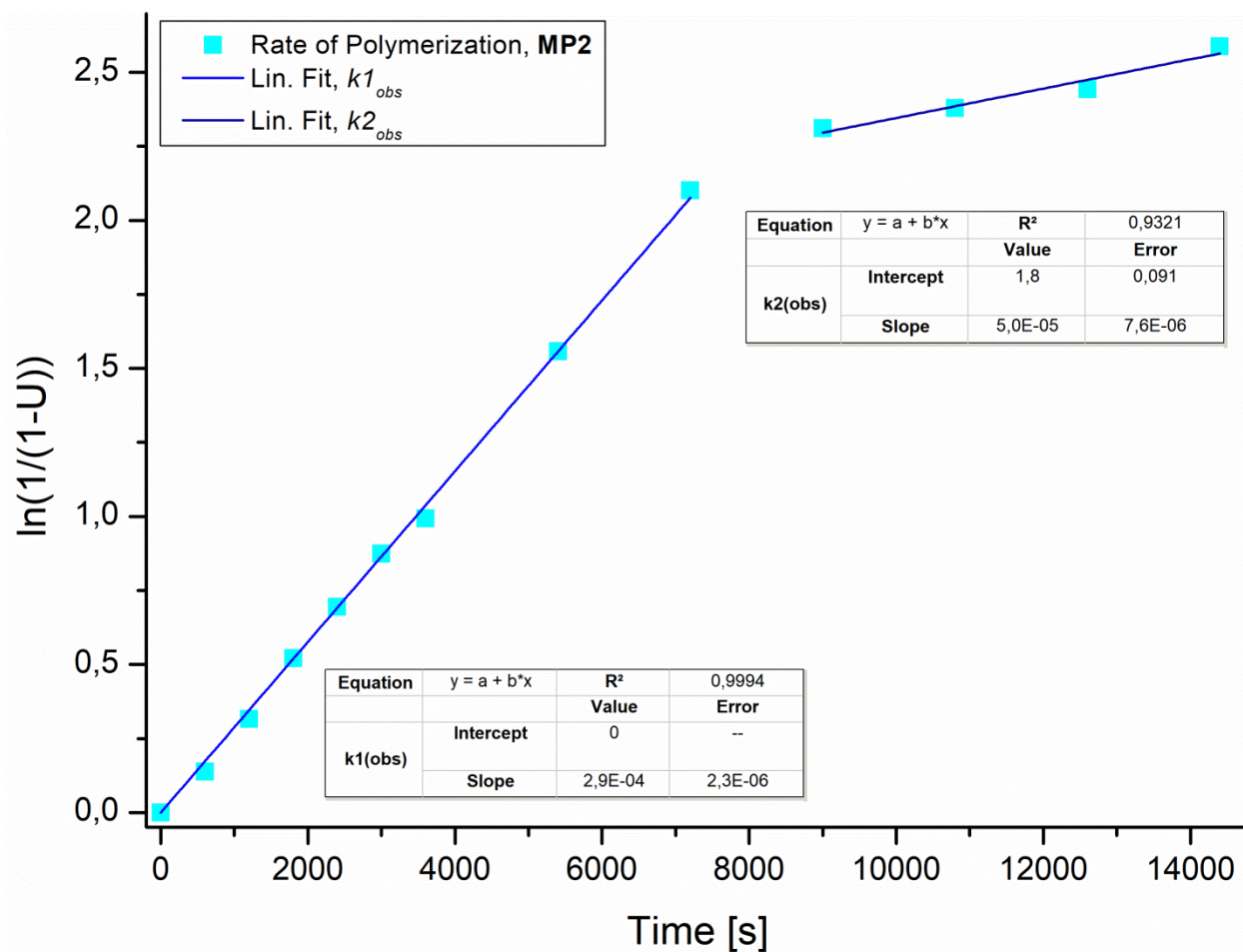
Menthyloxybutenolide-VeoVa-10-copolymer MP2					k1(obs)	(2.9±0.1)·10 <sup>-4</sup> [s <sup>-1</sup> ]
Menthyloxybutenolide B5		VeoVa-10			k2(obs)	(5.0±0.8)·10 <sup>-5</sup> [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,81	2,16	0,87	2,17	0,00	0,00
600	0,70	1,87	0,76	1,90	0,13	0,14
1200	0,59	1,58	0,63	1,58	0,27	0,32
1800	0,49	1,29	0,51	1,28	0,41	0,52
2400	0,40	1,05	0,44	1,11	0,50	0,69
3000	0,34	0,90	0,36	0,91	0,58	0,87
3600	0,30	0,79	0,33	0,81	0,63	0,99
5400	0,15	0,40	0,21	0,52	0,79	1,56
7200	0,07	0,18	0,14	0,34	0,88	2,10
9000	0,06	0,16	0,11	0,27	0,90	2,31
10800	0,04	0,11	0,12	0,30	0,91	2,38
12600	0,04	0,11	0,11	0,27	0,91	2,44
14400	0,03	0,08	0,10	0,25	0,92	2,59



**Fig. S69.** Concentration of monomers over time of the copolymerization of menthylxybutenolide **B5** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.

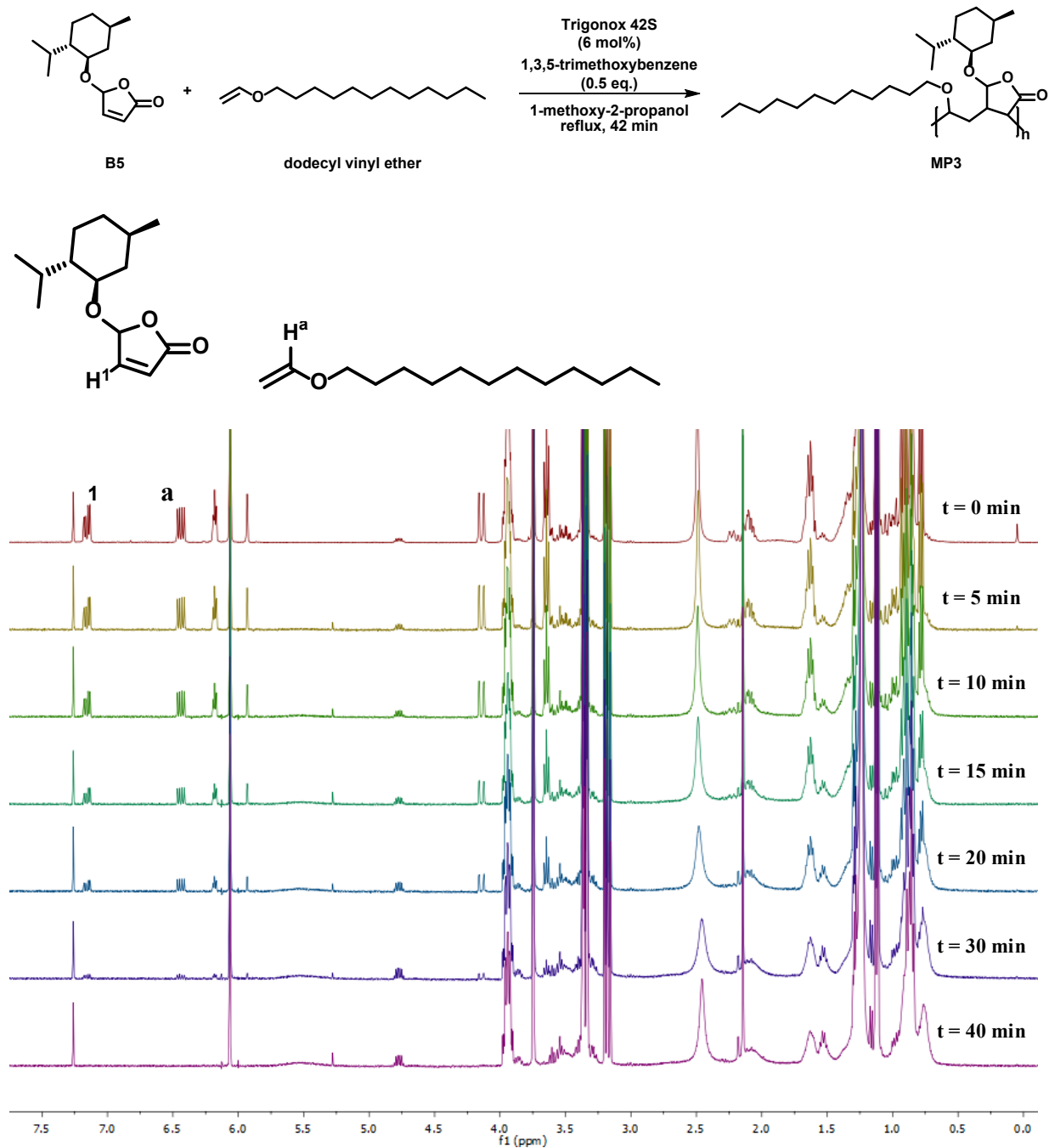


**Fig. S70.** Conversion of polymer **MP2** over time; copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.



**Fig. S71.** Rate of copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) to **MP2** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.

### 5-menthyloxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer MP3

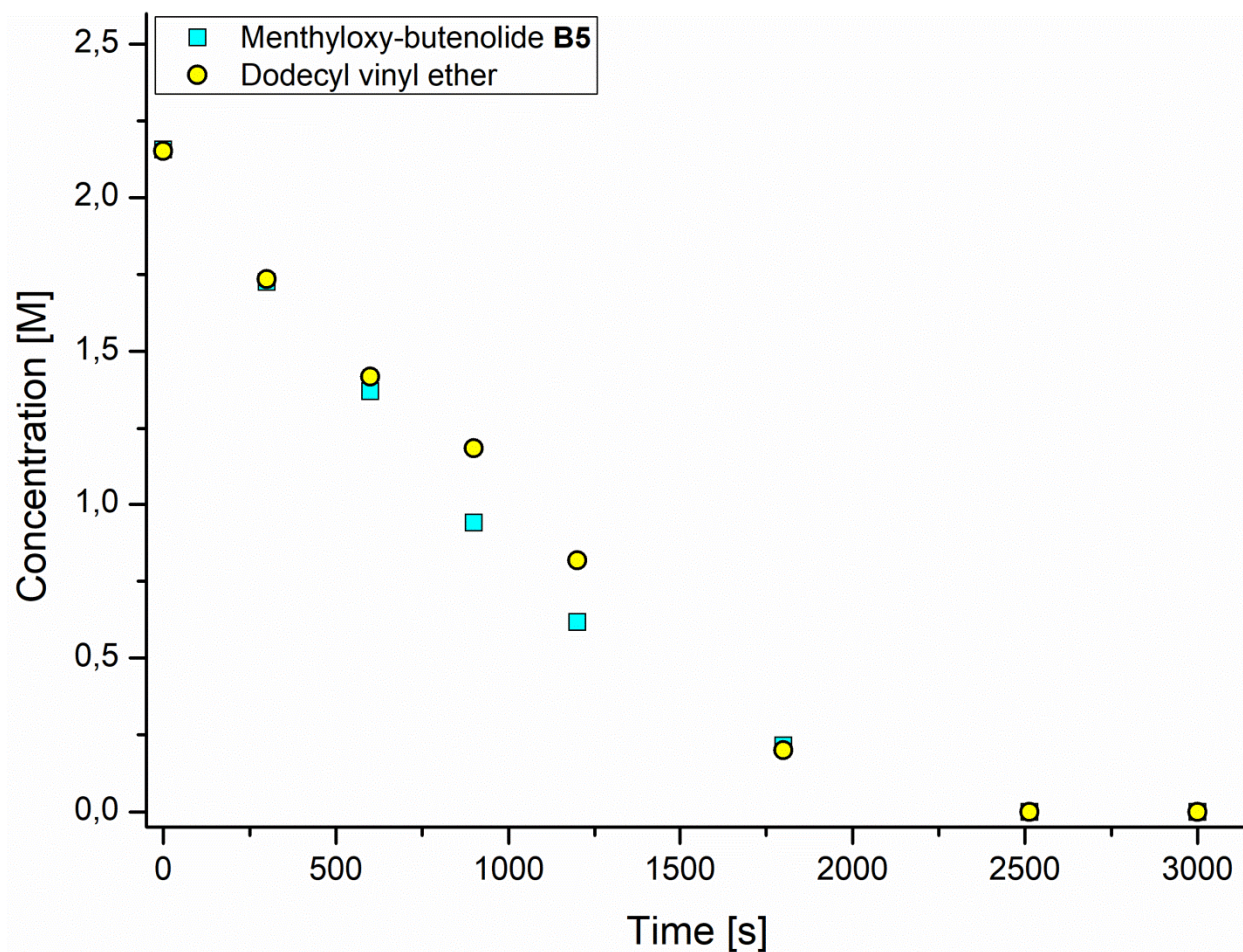


**Fig. S72.** Reaction scheme copolymerization menthyloxybutenolide **B5** with dodecyl vinyl ether (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 42 min (top).  $^1H$  NMR signals over time by taking samples and flash freezing ( $-18^\circ C$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).



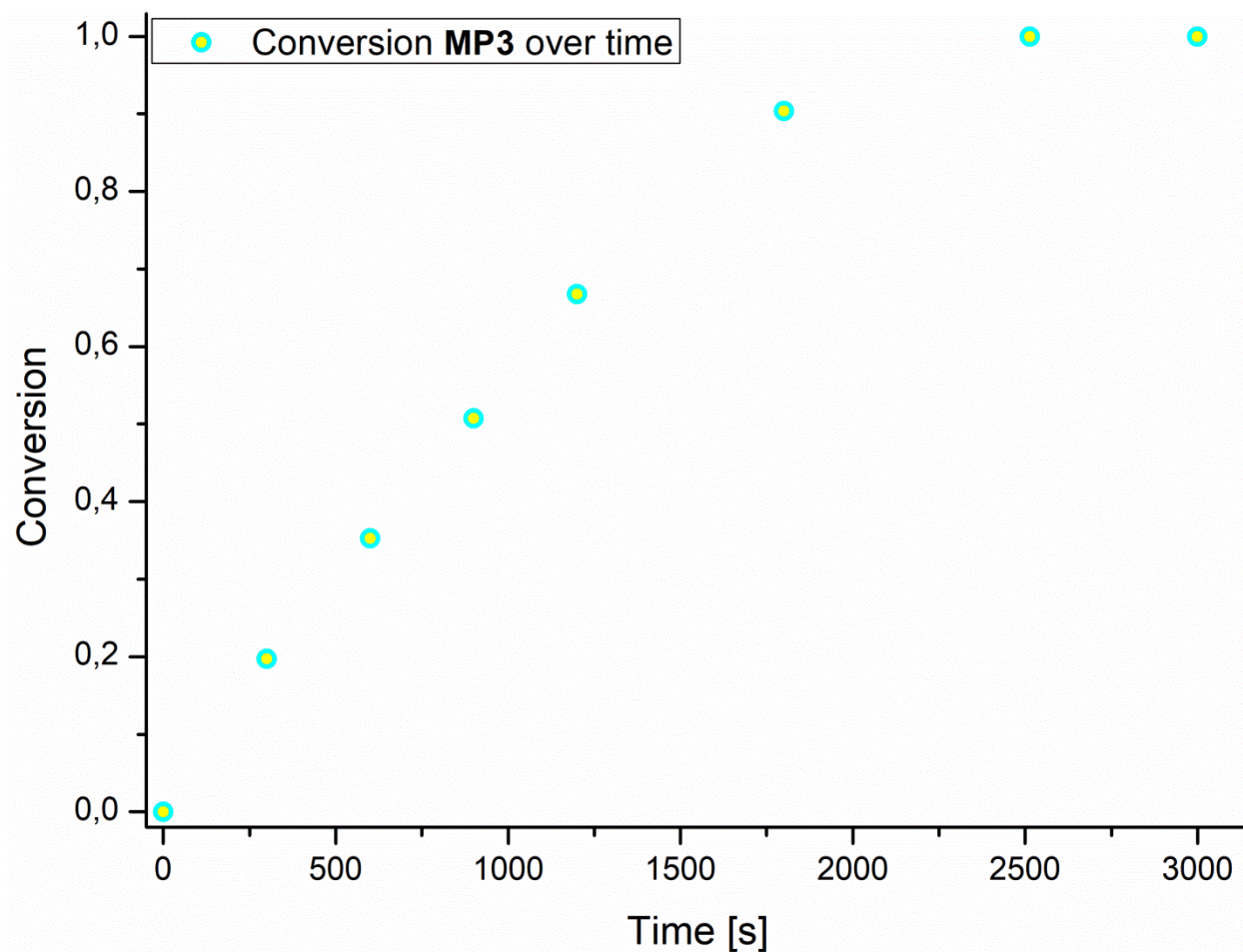
**Table S20.** Kinetic studies of the copolymerization of menthyloxybutenolide **B5** with dodecyl vinyl ether (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 42 min.

<b>Menthyloxybutenolide-dodecyl-vinyl-ether-copolymer MP3</b>						
	<b>Menthyloxybutenolide B5</b>		Dodecyl vinyl ether		<b>k(obs)</b>	<b>(1.1±0.1)·10<sup>-3</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,68	2,16	0,63	2,15	0,00	0,00
300	0,55	1,73	0,51	1,73	0,20	0,22
600	0,44	1,37	0,42	1,42	0,35	0,43
900	0,30	0,94	0,35	1,18	0,51	0,71
1200	0,20	0,62	0,24	0,82	0,67	1,10
1800	0,07	0,22	0,06	0,20	0,90	2,34
2514	0,00	0,00	0,00	0,00	1,00	-

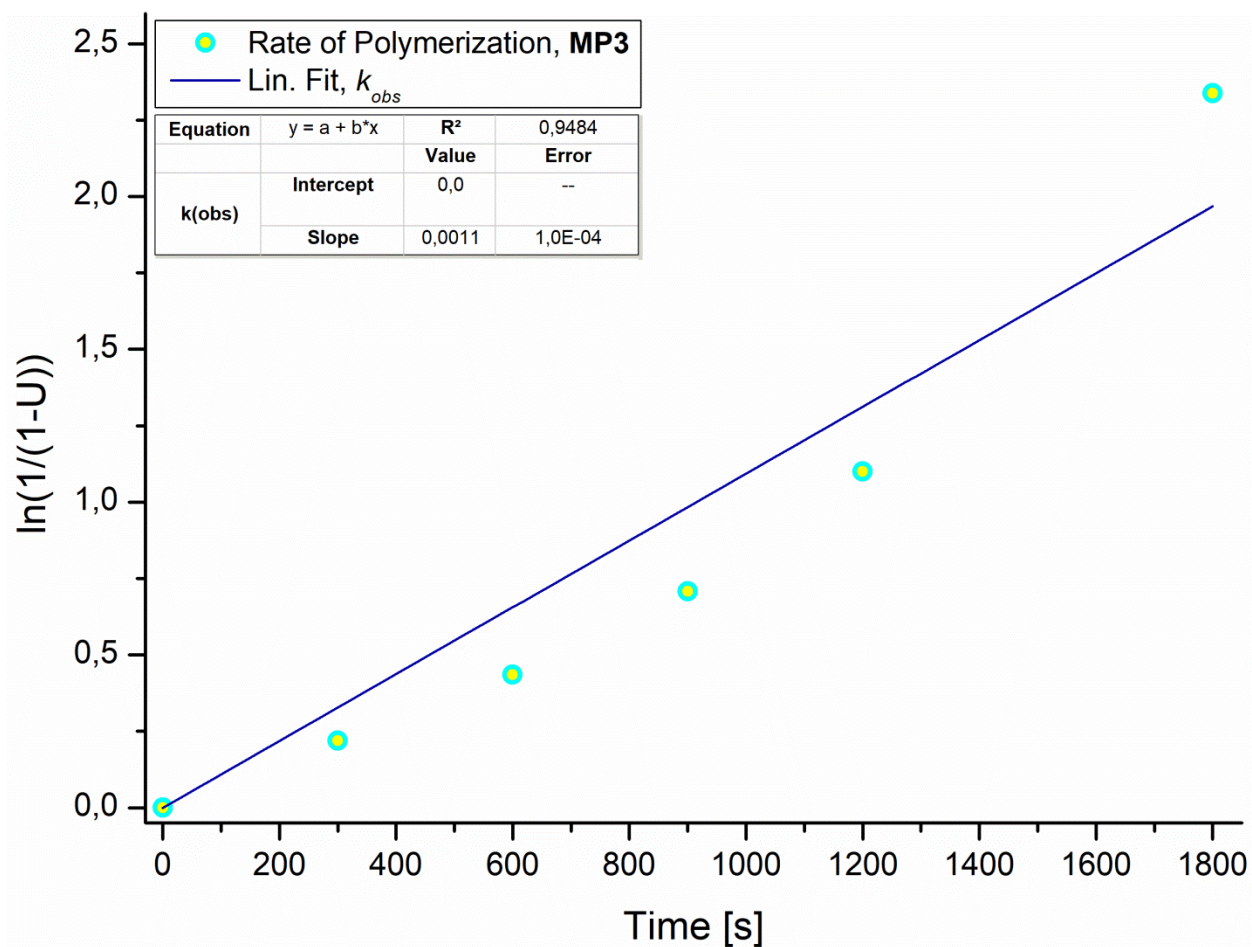


**Fig. S73.** Concentration of monomers over time of the copolymerization of menthyloxybutenolide **B5** with dodecyl vinyl ether (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 42 min.



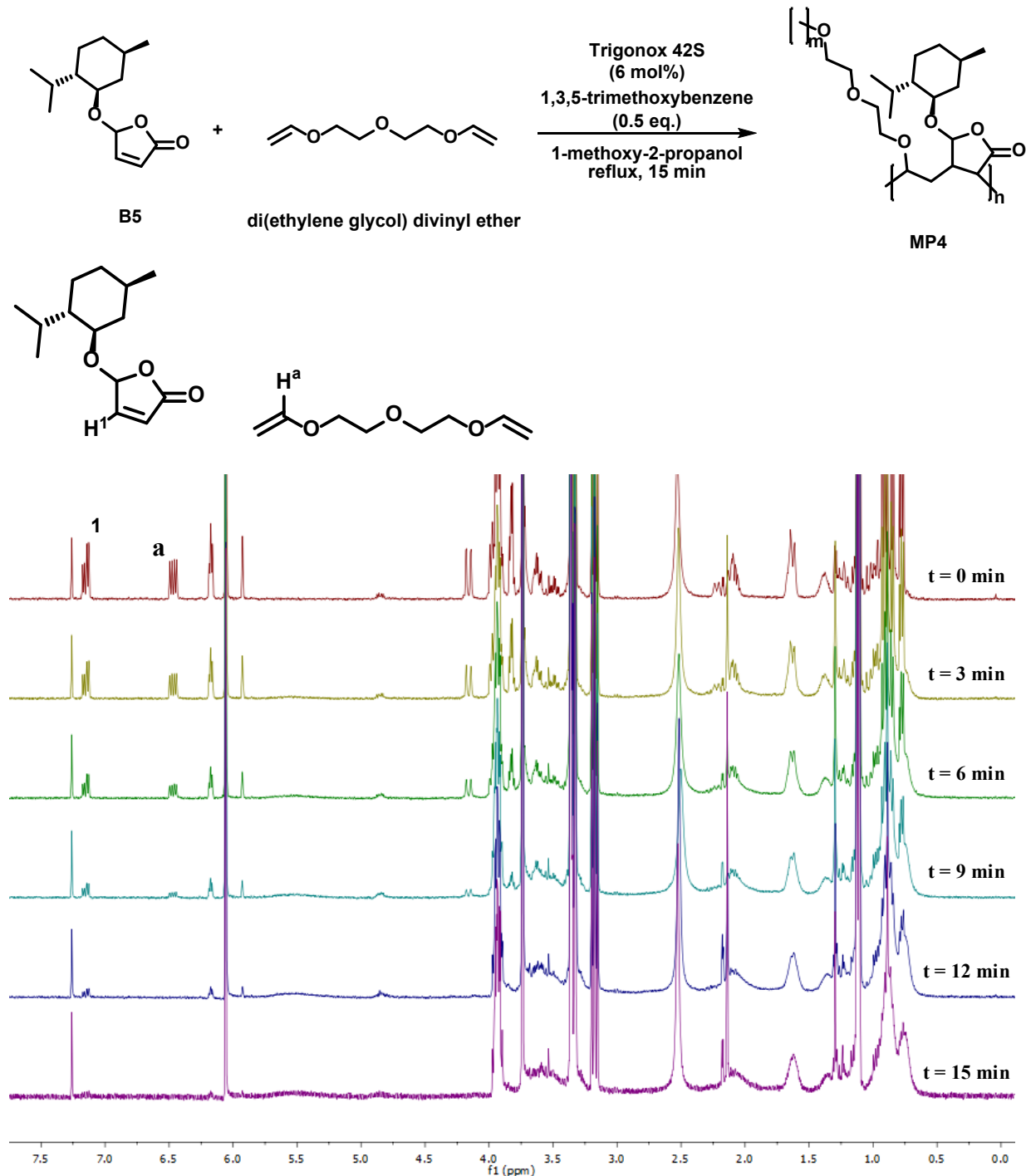


**Fig. S74.** Conversion of polymer **MP3** over time; copolymerization of menthyloxybutenolide **B5** with dodecyl vinyl ether (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 42 min.



**Fig. S75.** Rate of copolymerization of menthyloxybutenolide **B5** with dodecyl vinyl ether (1:1 ratio) to **MP3** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 42 min.

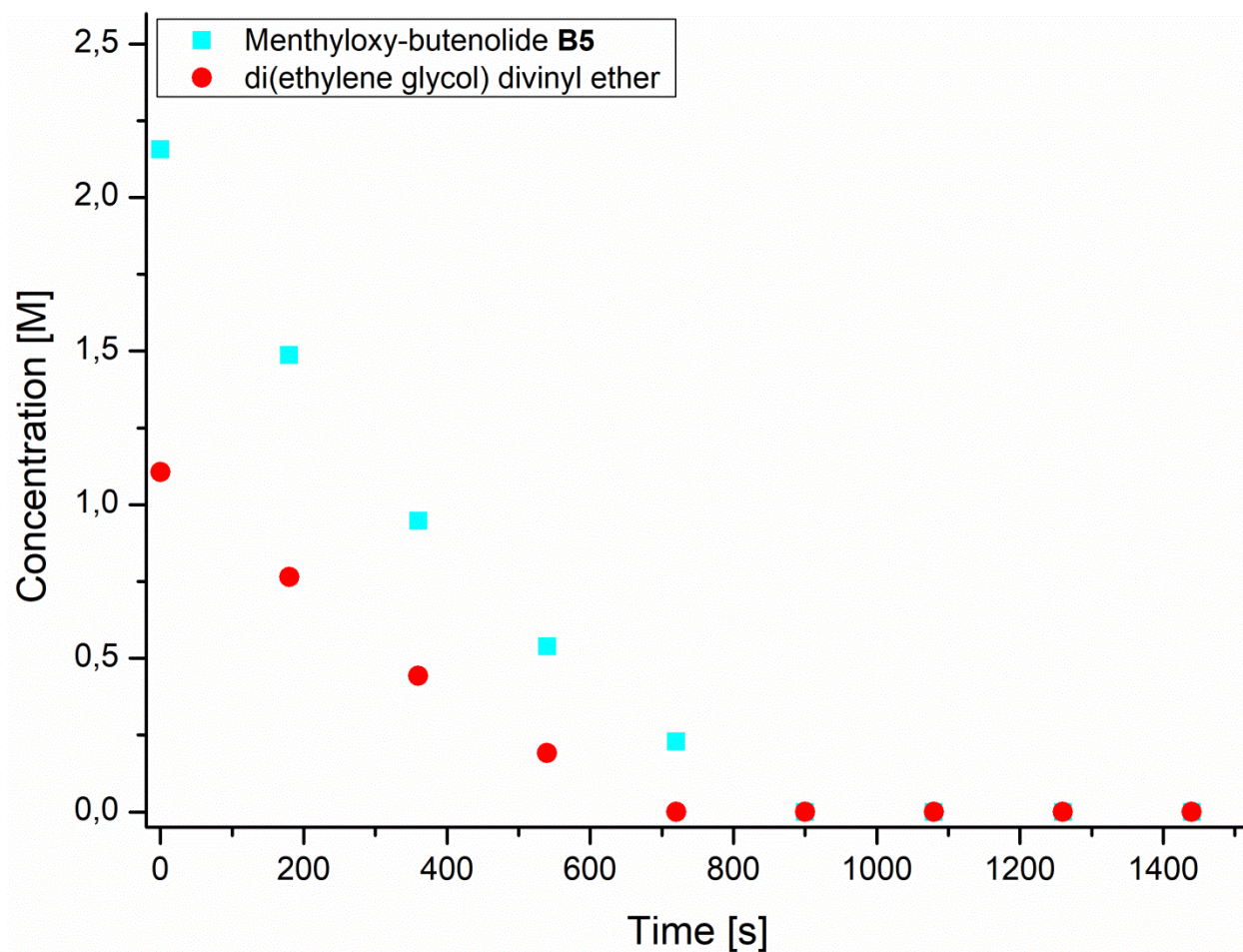
5-menthyloxy-2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer MP4



**Fig. S76.** Reaction scheme copolymerization menthyloxybutenolide **B5** with di(ethylene glycol) divinyl ether (1:0.5 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for di(ethylene glycol) divinyl ether), reflux, 15 min (top).  $^1\text{H NMR}$  signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

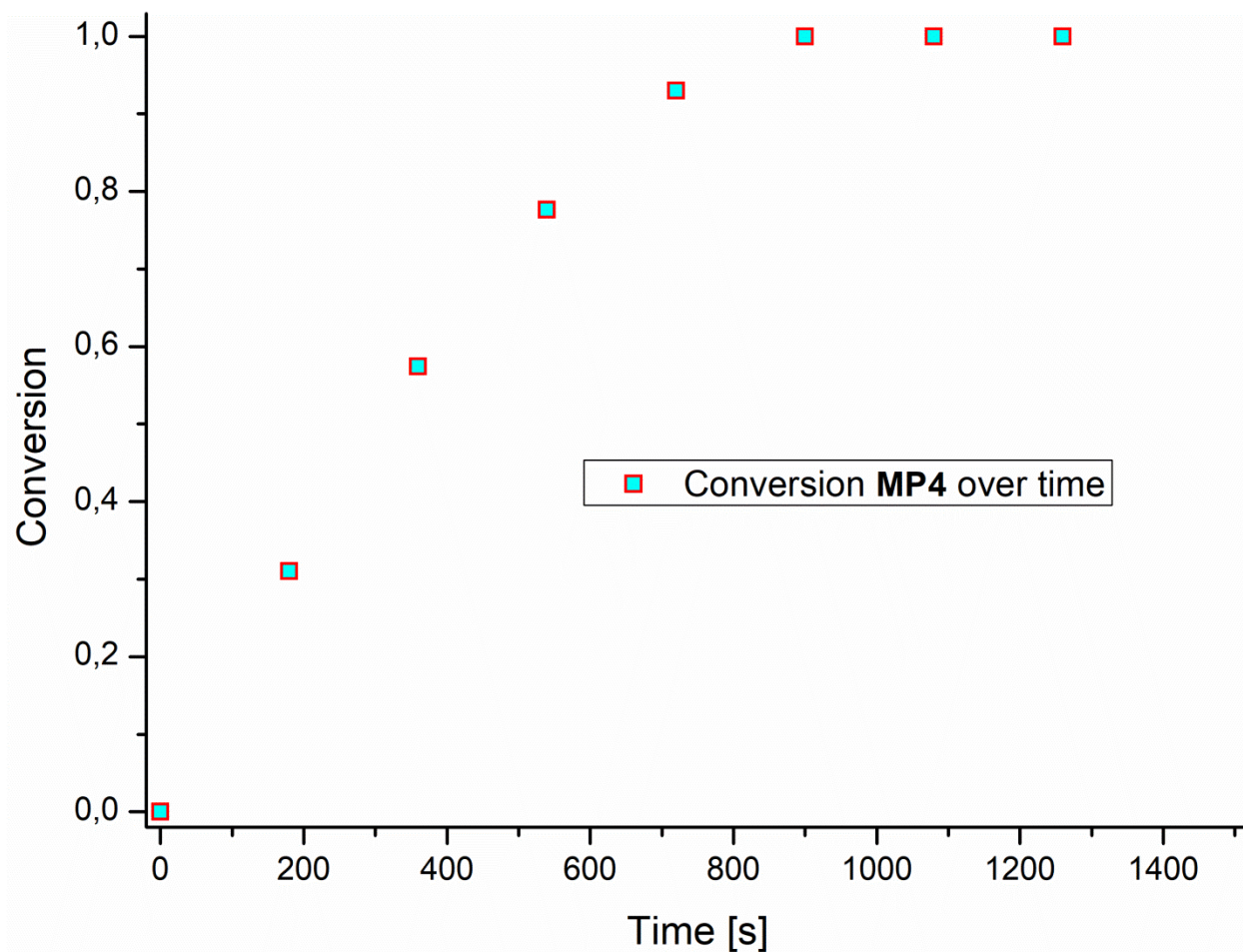
**Table S21.** Kinetic studies of the copolymerization of menthyloxybutenolide **B5** with di(ethylene glycol) divinyl ether (1:0.5 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for di(ethylene glycol) divinyl ether), reflux, 15 min.

<b>Menthloxybutenolide-DVE-copolymer MP4</b>						
	<b>Menthloxybutenolide B5</b>		<b>Di(ethylene glycol) divinyl ether</b>		<b>k(obs)</b>	<b>(3.2±0.3)·10<sup>-3</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,67	2,16	0,55	1,11	0,00	0,00
180	0,46	1,49	0,38	0,76	0,31	0,37
360	0,29	0,95	0,22	0,44	0,57	0,85
540	0,17	0,54	0,09	0,19	0,78	1,50
720	0,07	0,23	0,00	0,00	0,93	2,66
900	0,00	0,00	0,00	0,00	1,00	-

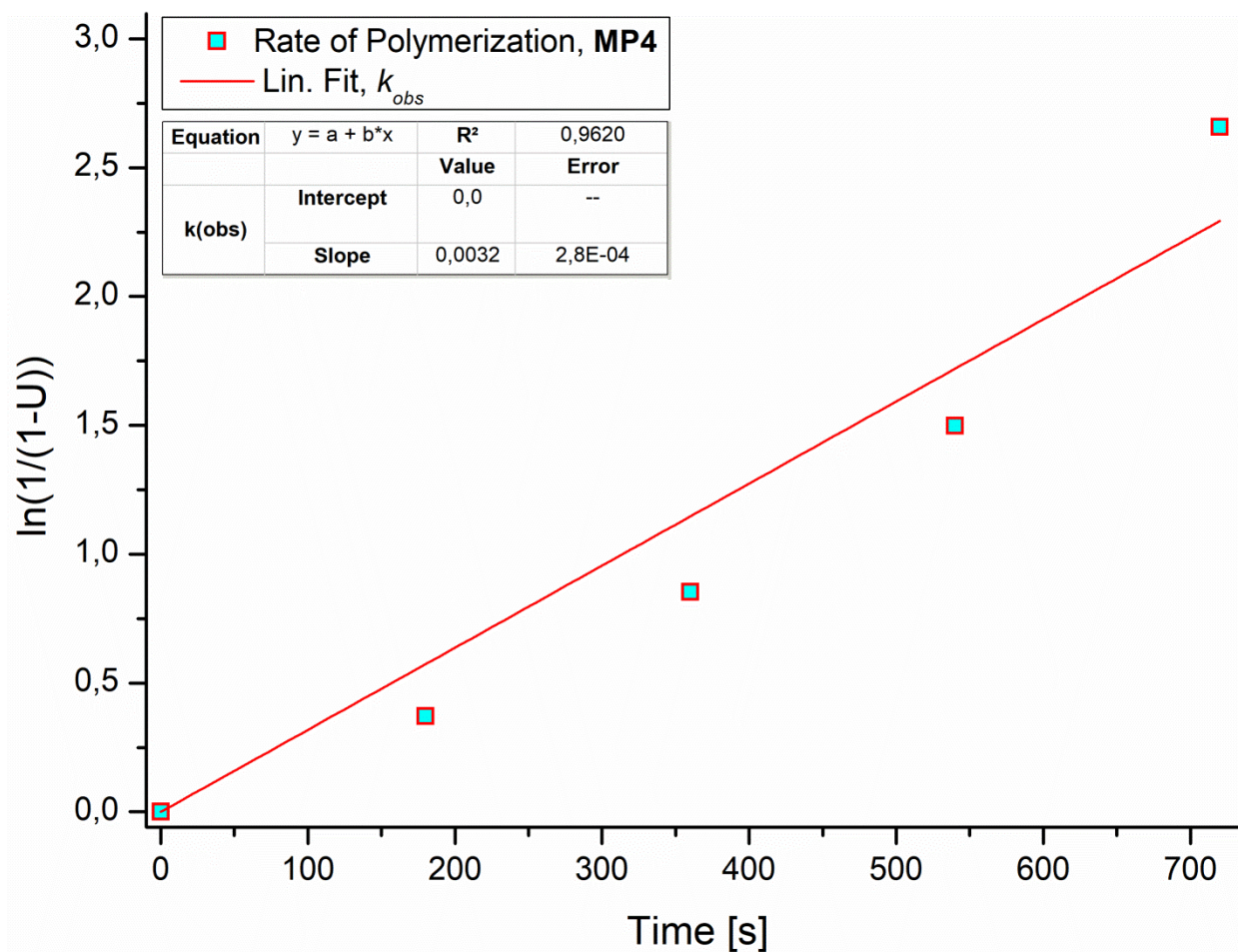


**Fig. S77.** Concentration of monomers over time of the copolymerization of menthyloxybutenolide **B5** with di(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 15 min.





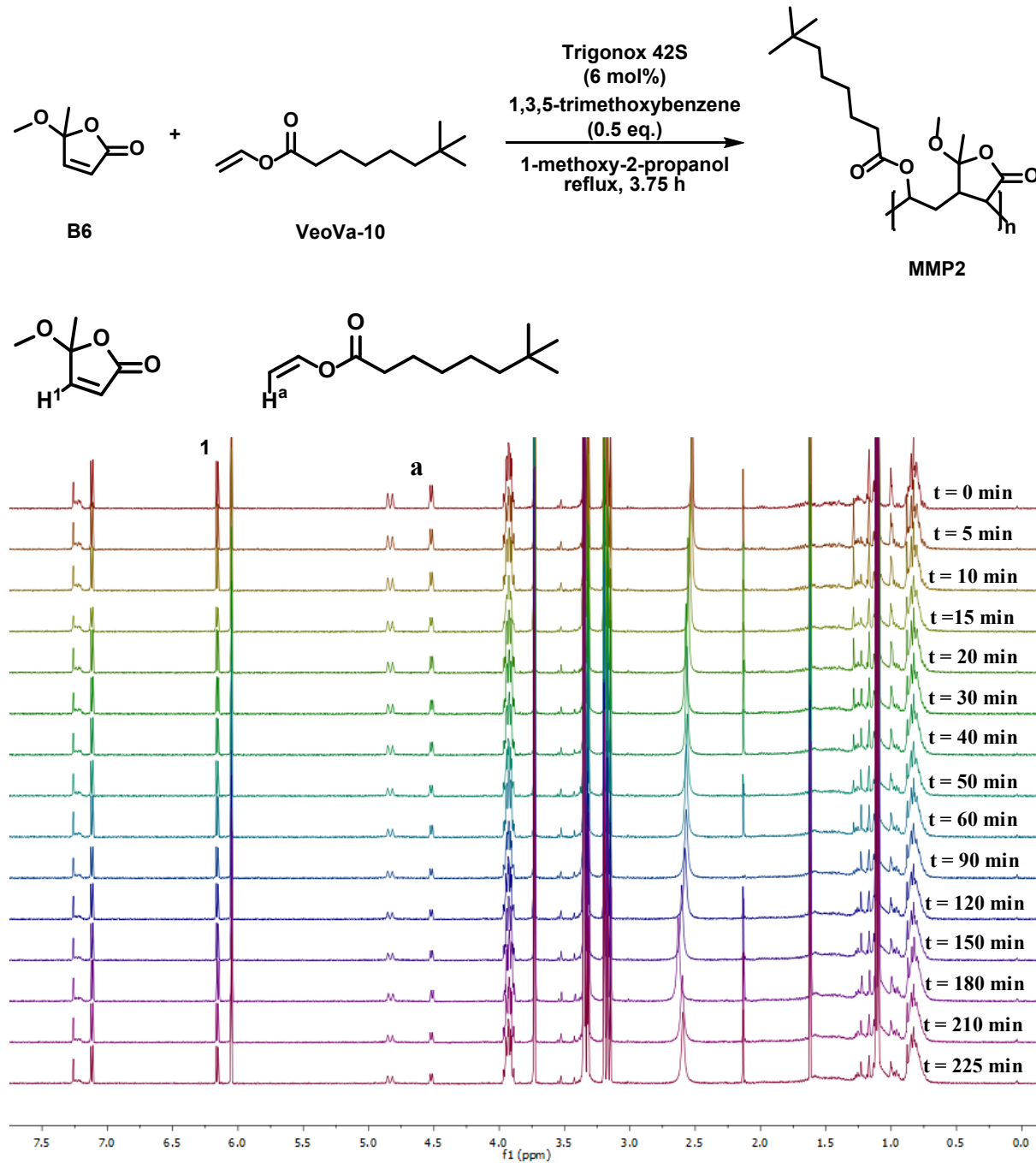
**Fig. S78.** Conversion of polymer **MP4** over time; copolymerization of menthyloxybutenolide **B5** with di(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 15 min.



**Fig. S79.** Rate of copolymerization of menthyloxybutenolide **B5** with di(ethylene glycol) divinyl ether (1:0.5 ratio) to **MP4** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 15 min.



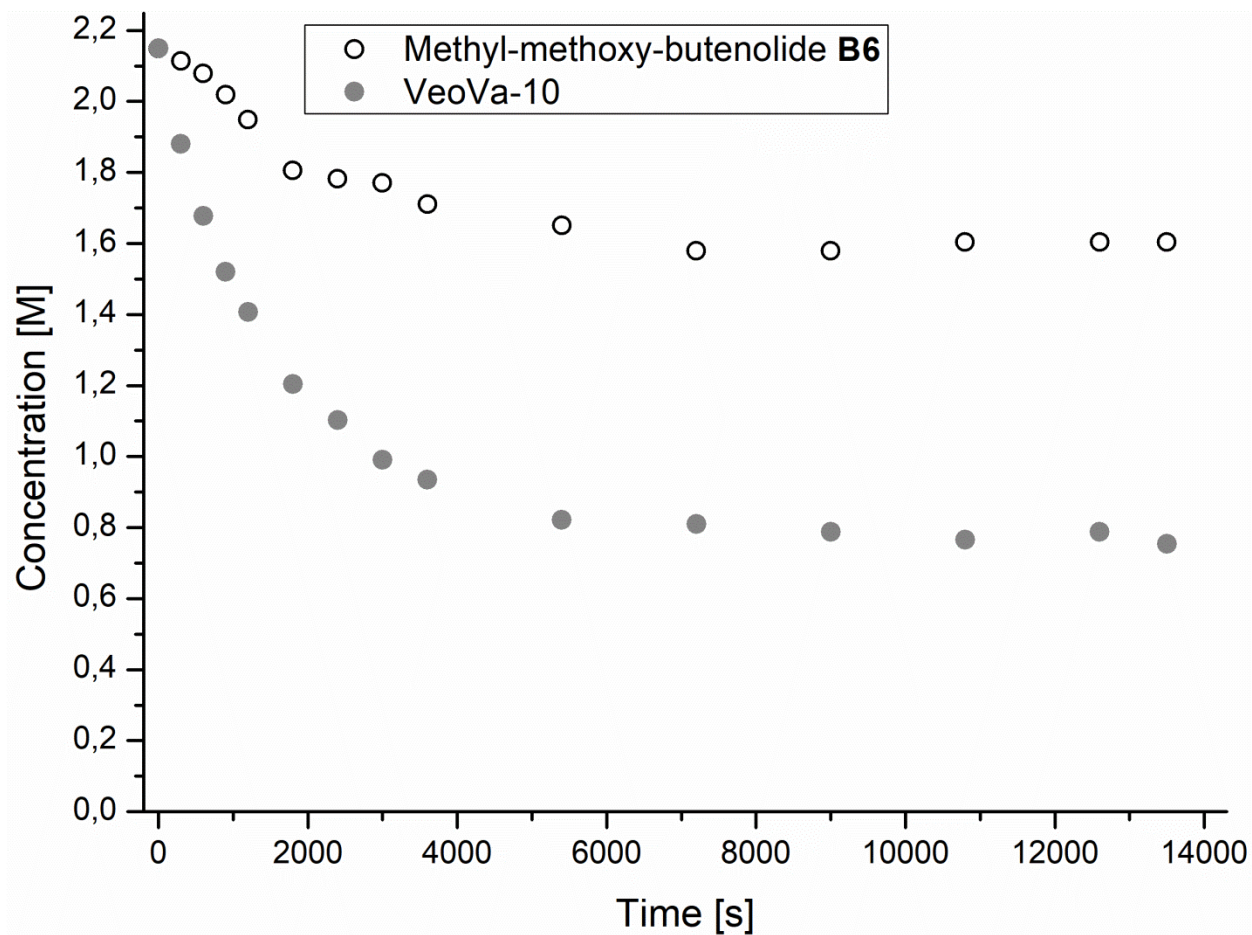
5-methoxy-5-methyl-2(5H)-furanone-VeoVa-10-copolymer MMP2



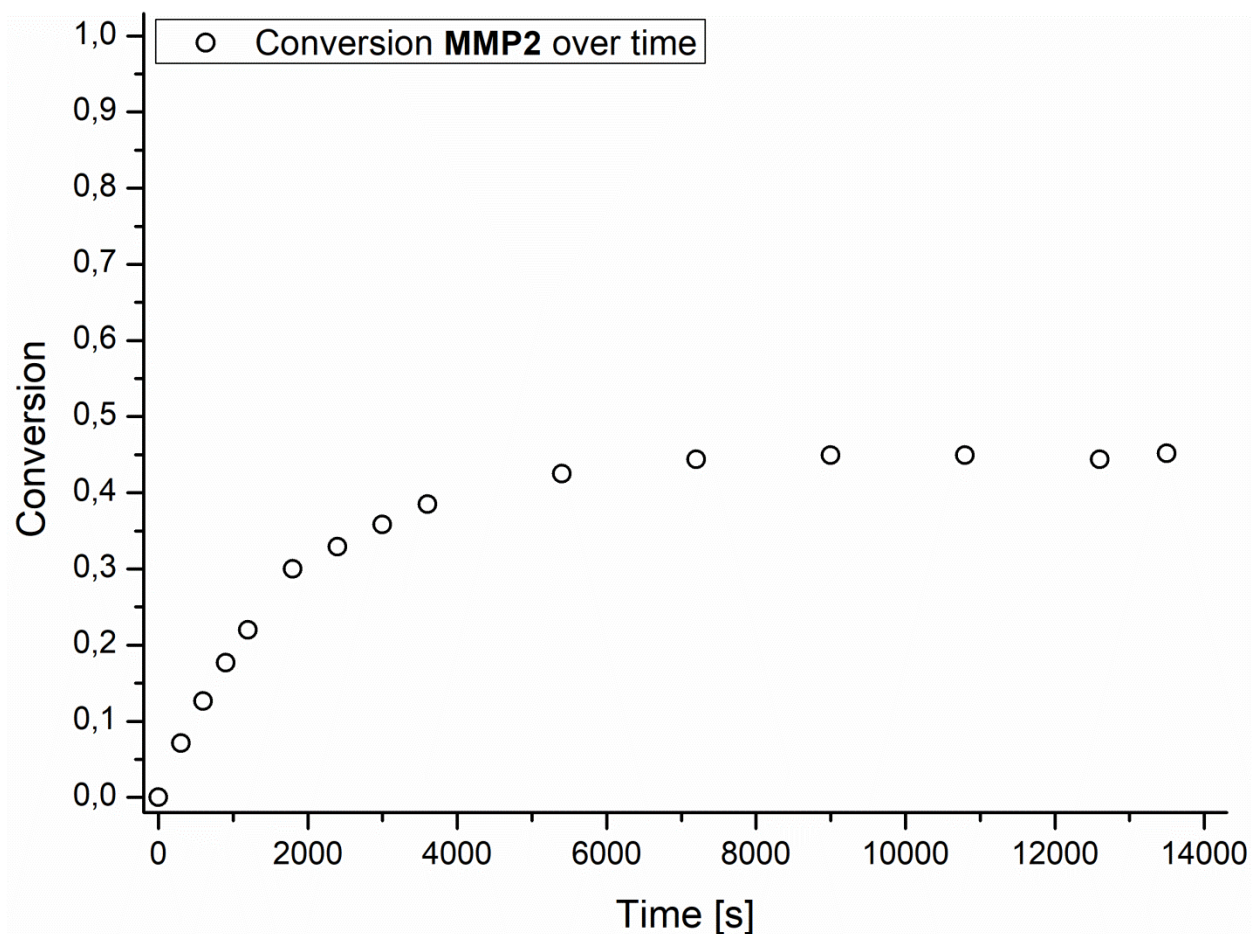
**Fig. S80.** Reaction scheme copolymerization methylmethoxybutenolide **B6** with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 3.75 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S22.** Kinetic studies of the copolymerization of methylmethoxybutenolide **B6** with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 3.75 h.

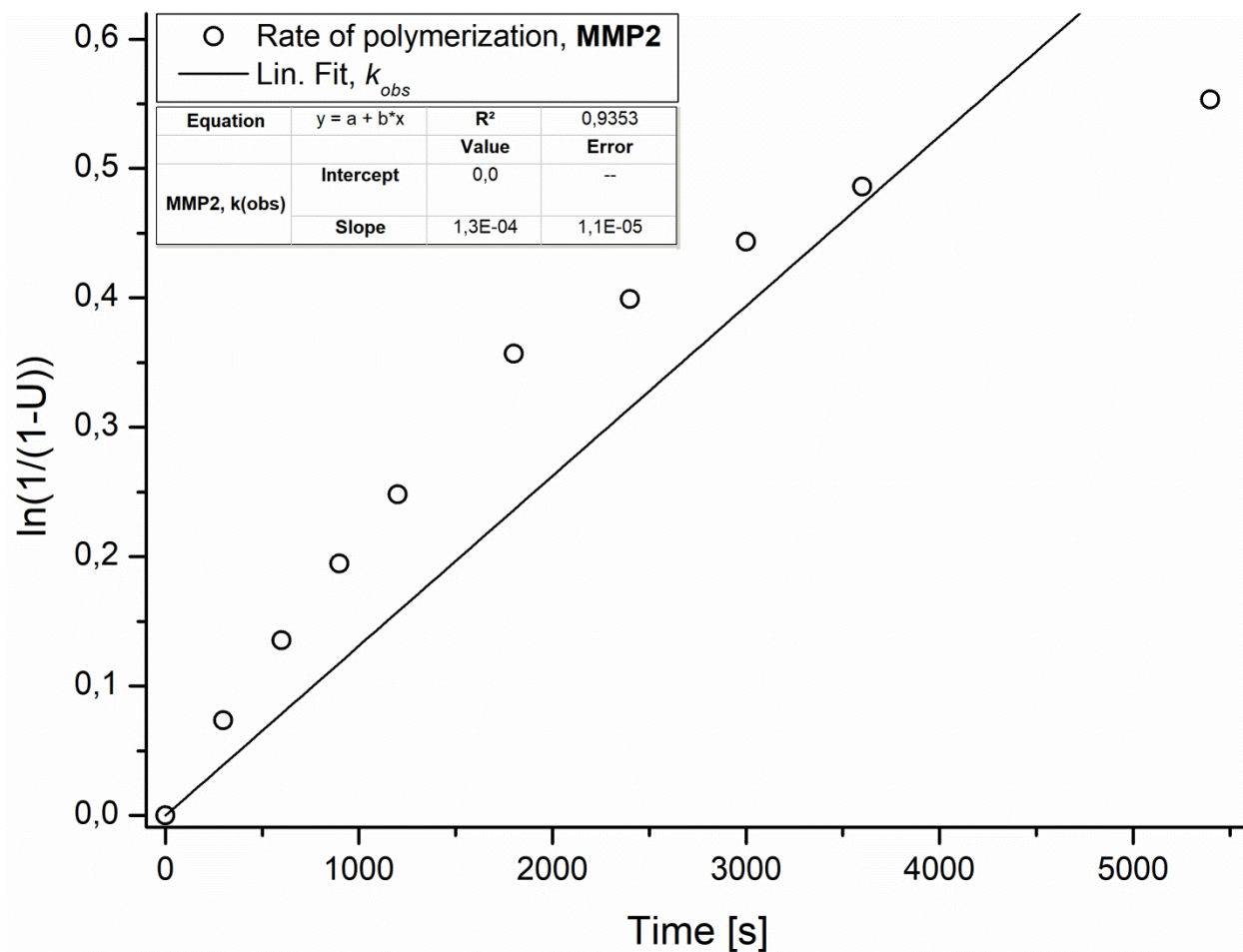
<b>Methylmethoxybutenolide-VeoVa-10-copolymer MMP2</b>						
Methylmethoxybutenolide <b>B6</b>		VeoVa-10			<b>k1(obs)</b>	<b>(1.3±0.1)·10<sup>-4</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,91	2,15	0,96	2,15	0,00	0,00
300	0,89	2,11	0,84	1,88	0,07	0,07
600	0,88	2,08	0,75	1,68	0,13	0,14
900	0,85	2,02	0,68	1,52	0,18	0,19
1200	0,82	1,95	0,63	1,41	0,22	0,25
1800	0,76	1,81	0,54	1,20	0,30	0,36
2400	0,75	1,78	0,49	1,10	0,33	0,40
3000	0,75	1,77	0,44	0,99	0,36	0,44
3600	0,72	1,71	0,42	0,93	0,38	0,49
5400	0,70	1,65	0,37	0,82	0,42	0,55
7200	0,67	1,58	0,36	0,81	0,44	0,59
9000	0,67	1,58	0,35	0,79	0,45	0,60
10800	0,68	1,60	0,34	0,77	0,45	0,60
12600	0,68	1,60	0,35	0,79	0,44	0,59
13500	0,68	1,60	0,34	0,75	0,45	0,60



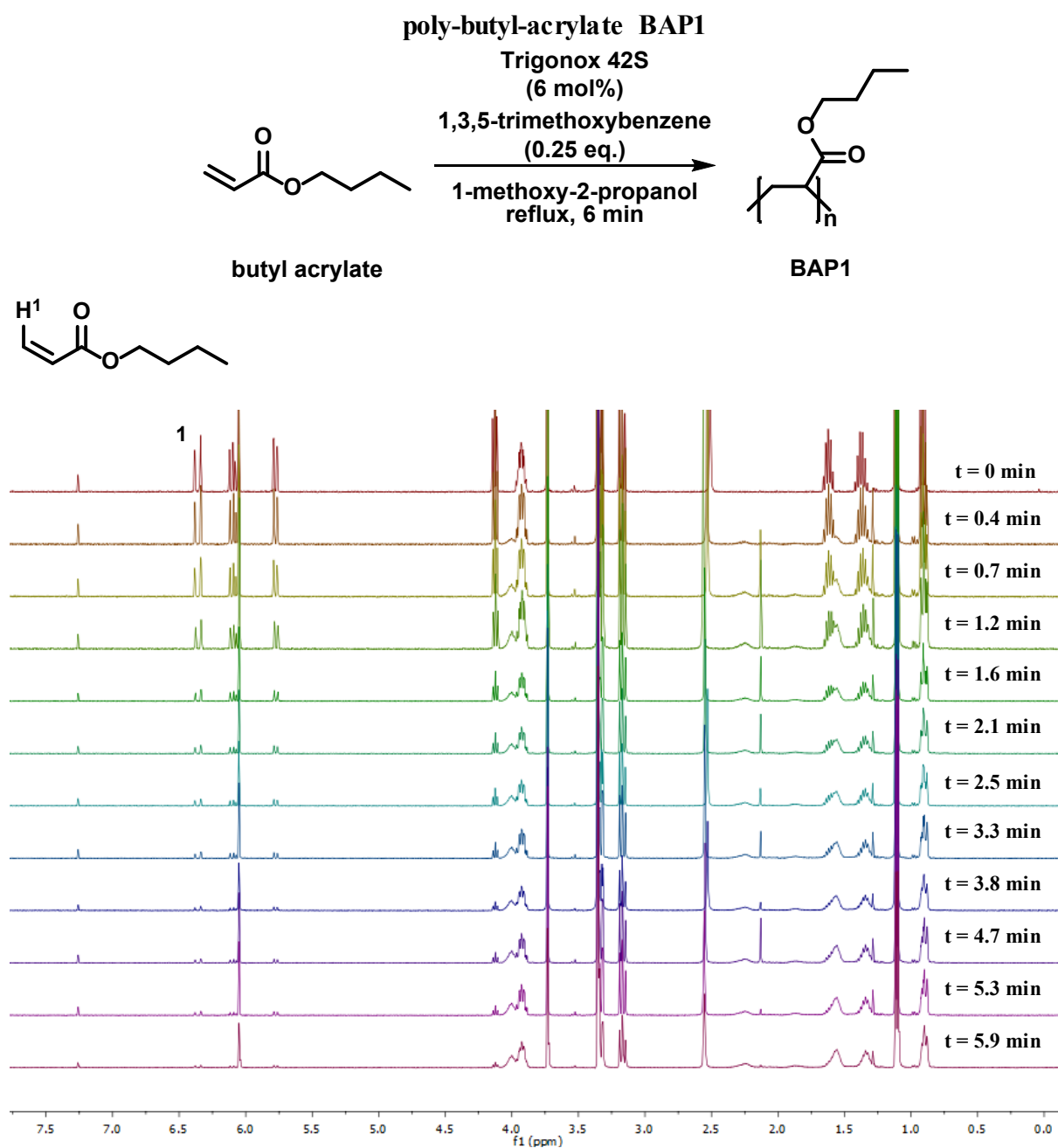
**Fig. S81.** Concentration of monomers over time of the copolymerization of methylmethoxybutenolide **B6** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 3.75 h.



**Fig. S82.** Conversion of polymer **MMP2** over time; copolymerization of methylmethoxybutenolide **B6** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 3.75 h.



**Fig. S83.** Rate of copolymerization of methylmethoxybutenolide **B6** with VeoVa-10 (1:1 ratio) to **MMP2** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 3.75 h.

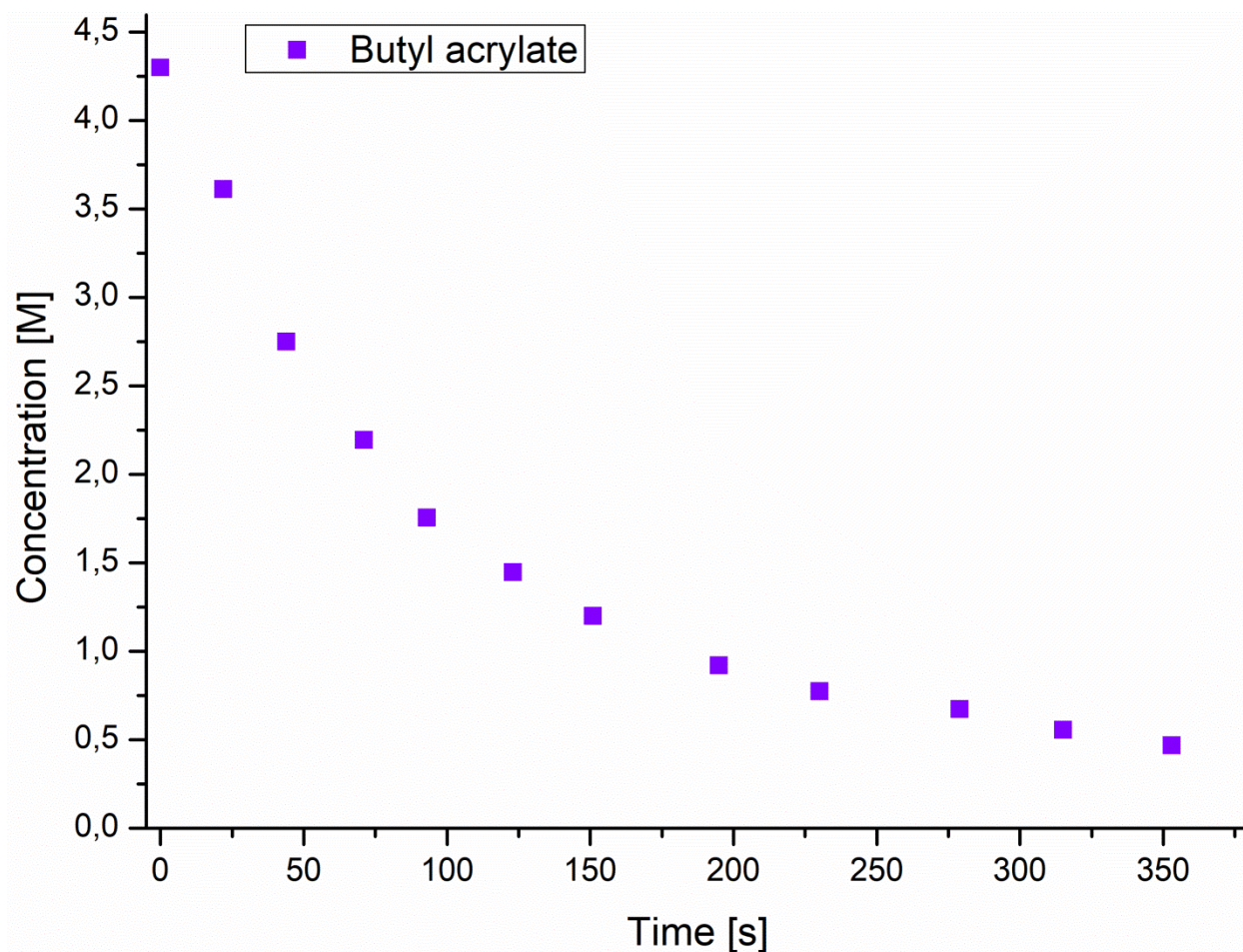


**Fig. S84.** Reaction scheme homopolymerization butyl acrylate (2 eq.), reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 5.9 min (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard (bottom).

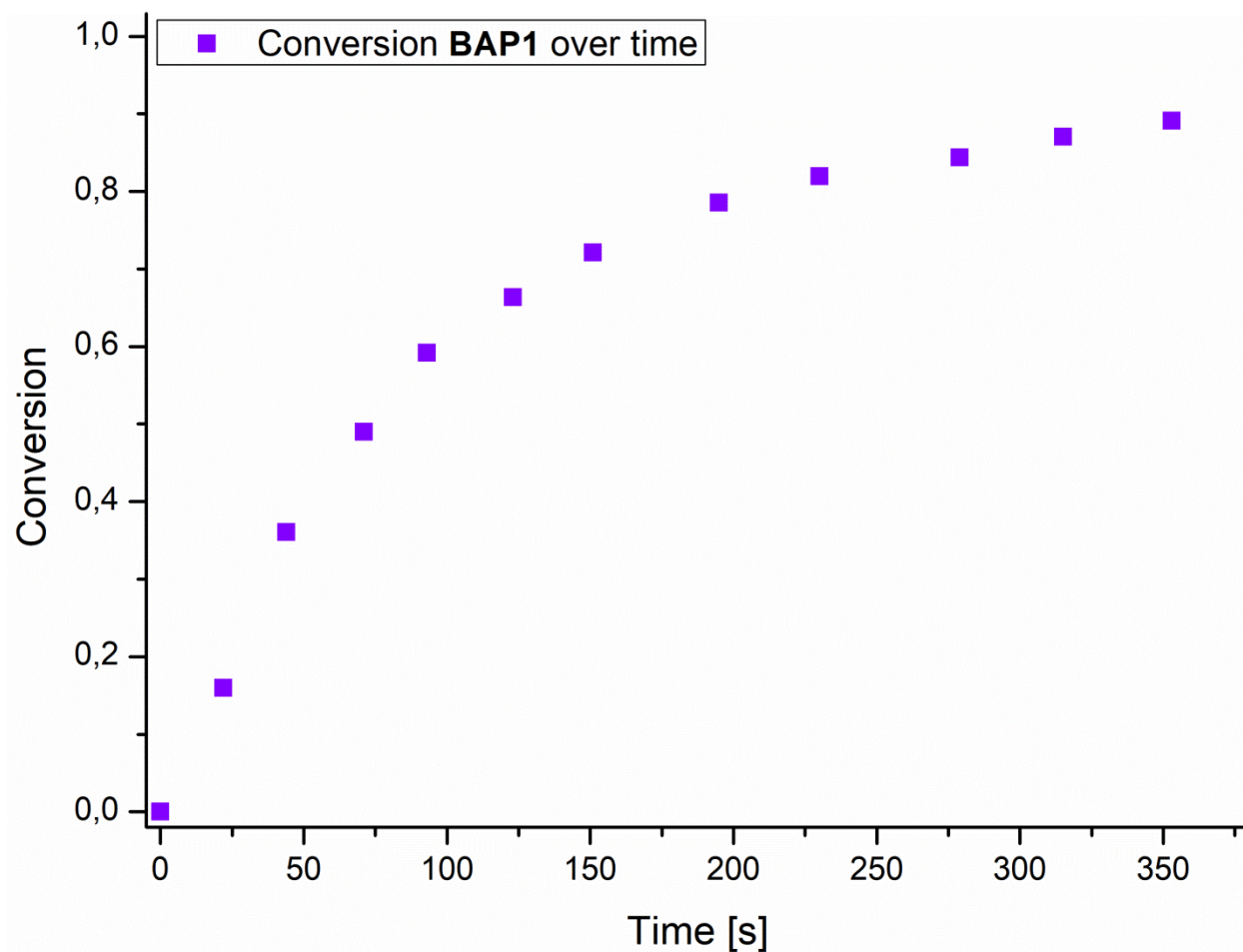
**Table S23.** Kinetic studies of the homopolymerization of butyl acrylate (2 eq.), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.25 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 5.9 min.

Butyl-acrylate-homo-polymer BAP1				
	Butyl acrylate		<b>k(obs)</b>	<b>(7.0±0.3)·10<sup>-3</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,74	4,30	0,00	0,00
22	0,62	3,61	0,16	0,17
44	0,47	2,75	0,36	0,45
71	0,38	2,19	0,49	0,67
93	0,30	1,76	0,59	0,90
123	0,25	1,45	0,66	1,09
151	0,21	1,20	0,72	1,28
195	0,16	0,92	0,79	1,54
230	0,13	0,78	0,82	1,71
279	0,12	0,67	0,84	1,85
315	0,10	0,56	0,87	2,05
353	0,08	0,47	0,89	2,22

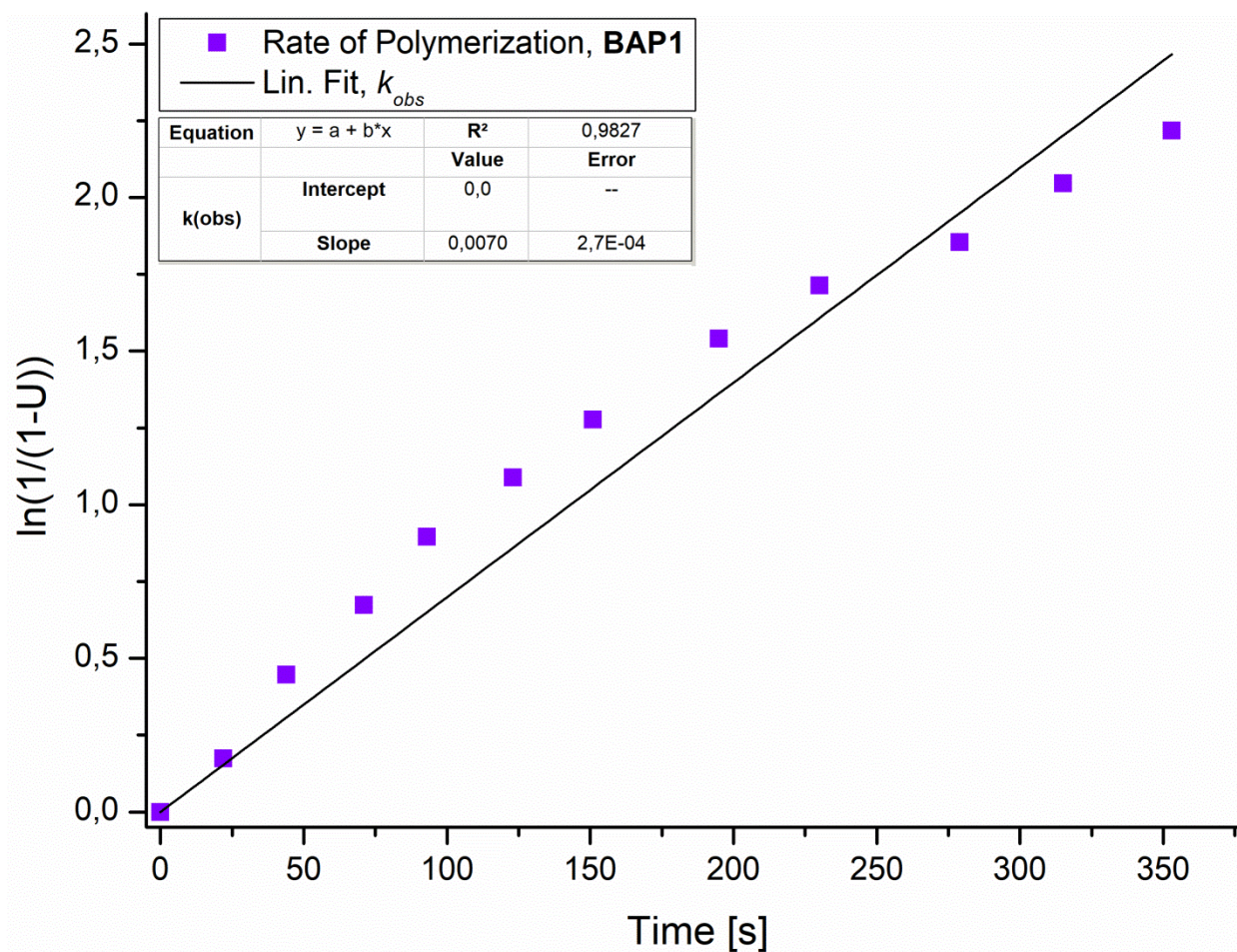




**Fig. S85.** Concentration of the monomer butyl acrylate over time followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 5.9 min.



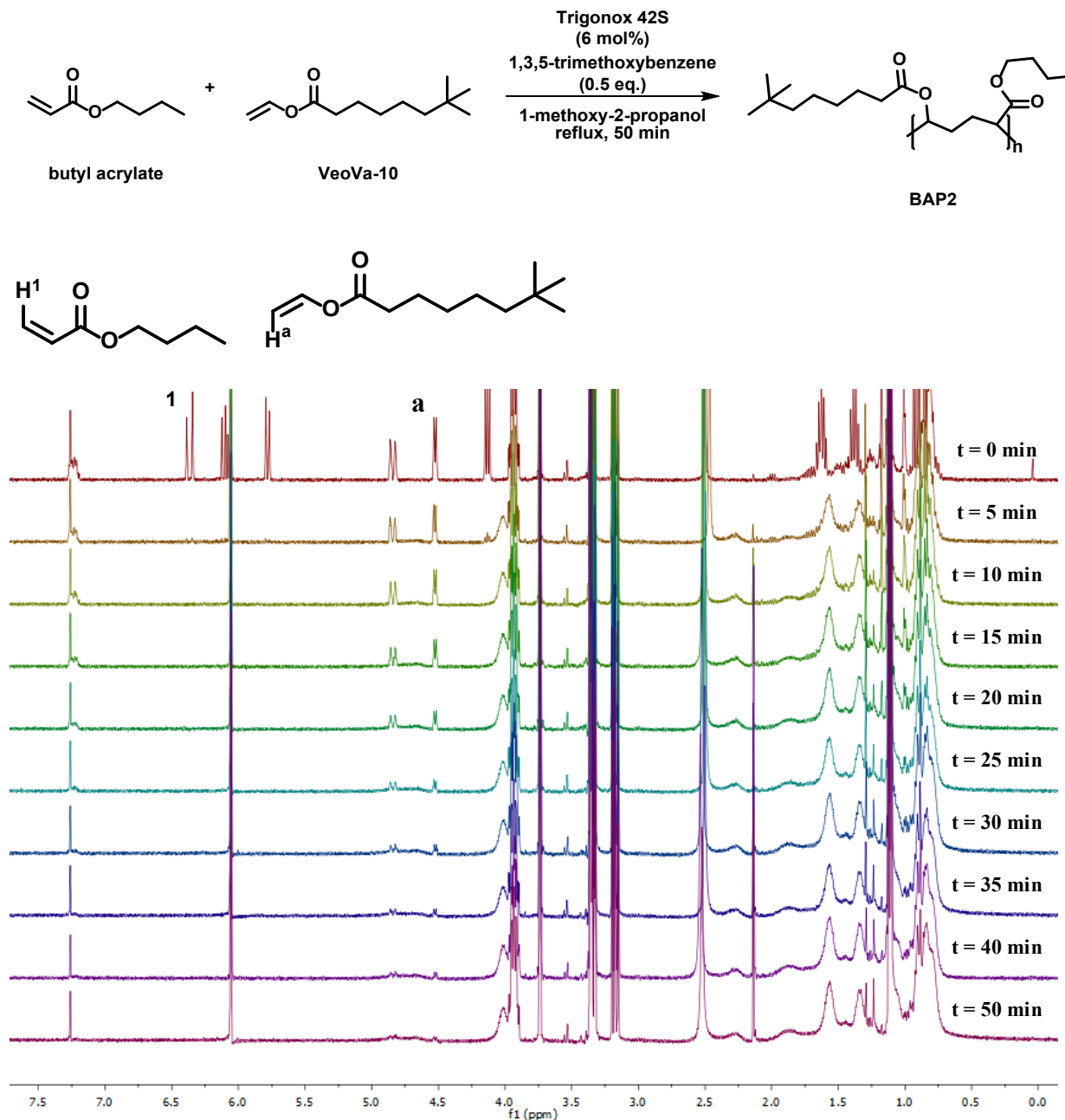
**Fig. S86.** Conversion of polymer **BAP1** over time; homo-polymerization of butyl acrylate followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 5.9 min.



**Fig. S87.** Rate of homo-polymerization of butyl acrylate to **BAP1** over time; followed by <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 5.9 min.



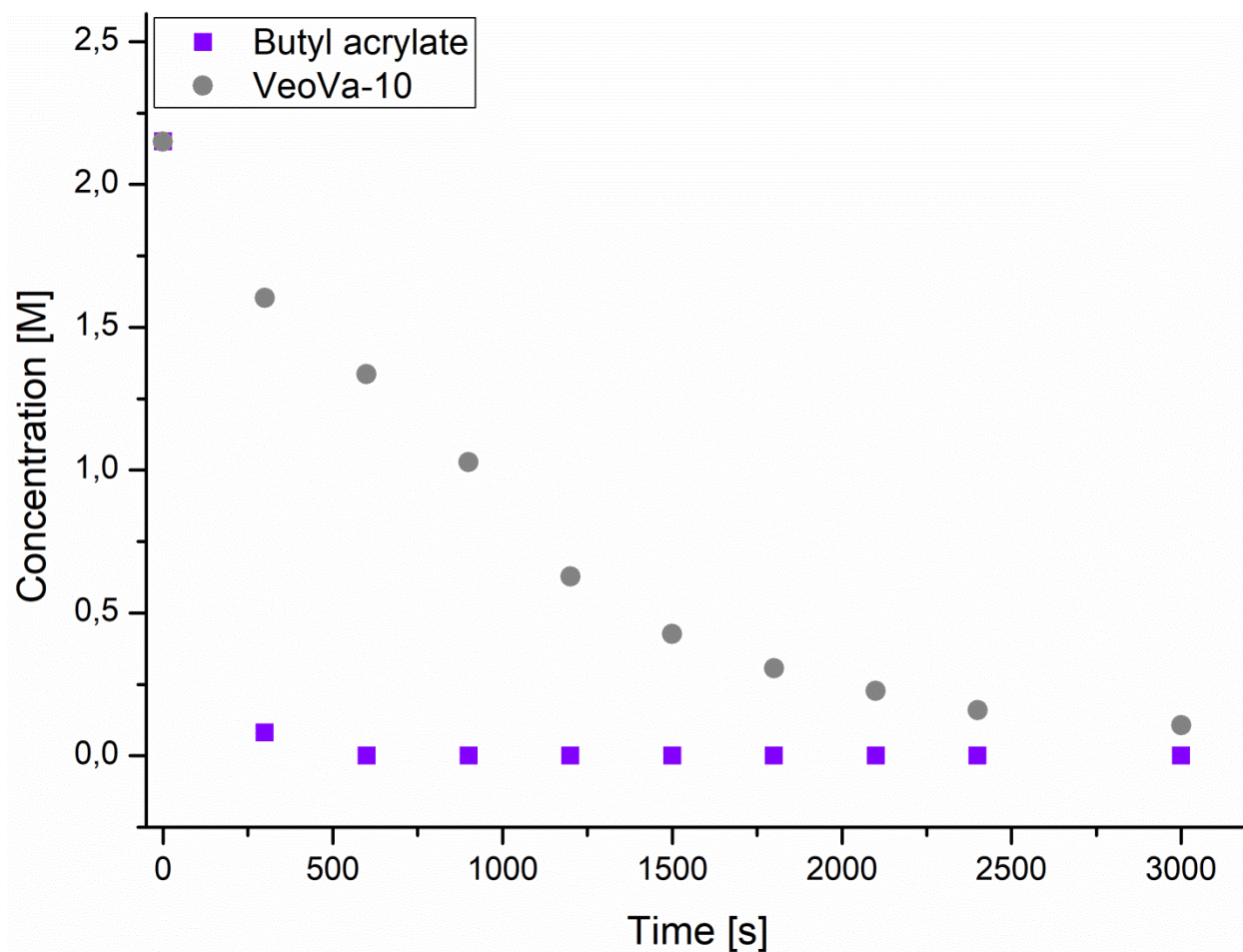
### butyl-acrylate-VeoVa-10-copolymer BAP2



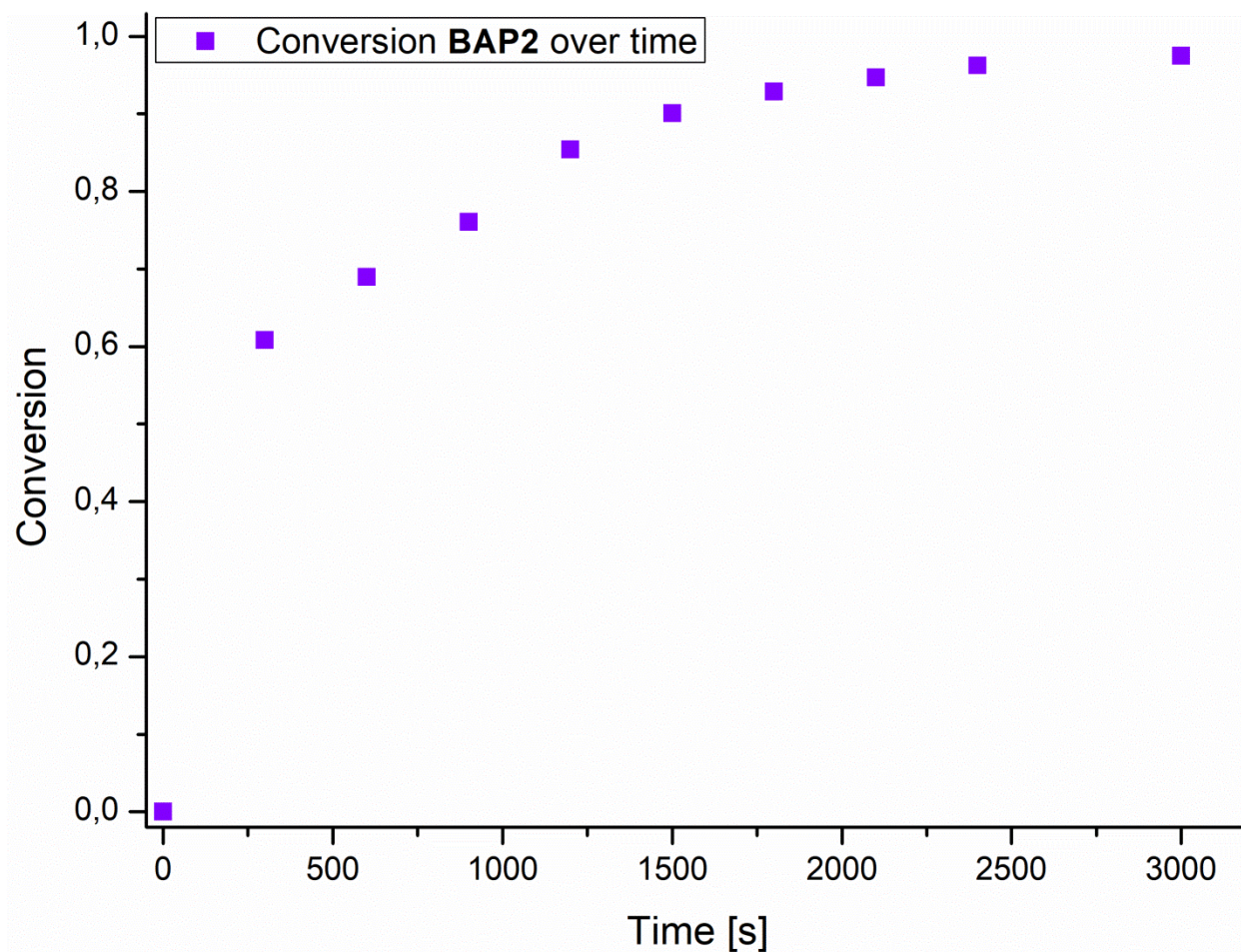
**Fig. S88.** Reaction scheme copolymerization butyl acrylate with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min (top).  $^1H$  NMR signals over time by taking samples and flash freezing ( $-18^\circ C$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S24.** Kinetic studies of the copolymerization of butyl acrylate with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.

Butyl-acrylate-VeoVa-10-copolymer BAP2						
	Butyl acrylate		VeoVa-10		k(obs)	(1.4±0.1)·10 <sup>-3</sup> [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,79	2,15	0,81	2,15	0,00	0,00
300	0,03	0,08	0,60	1,60	0,61	0,94
600	0,00	0,00	0,50	1,34	0,69	1,17
900	0,00	0,00	0,39	1,03	0,76	1,43
1200	0,00	0,00	0,24	0,63	0,85	1,92
1500	0,00	0,00	0,16	0,43	0,90	2,31
1800	0,00	0,00	0,12	0,31	0,93	2,64
2100	0,00	0,00	0,09	0,23	0,95	2,94
2400	0,00	0,00	0,06	0,16	0,96	3,29
3000	0,00	0,00	0,04	0,11	0,98	3,70

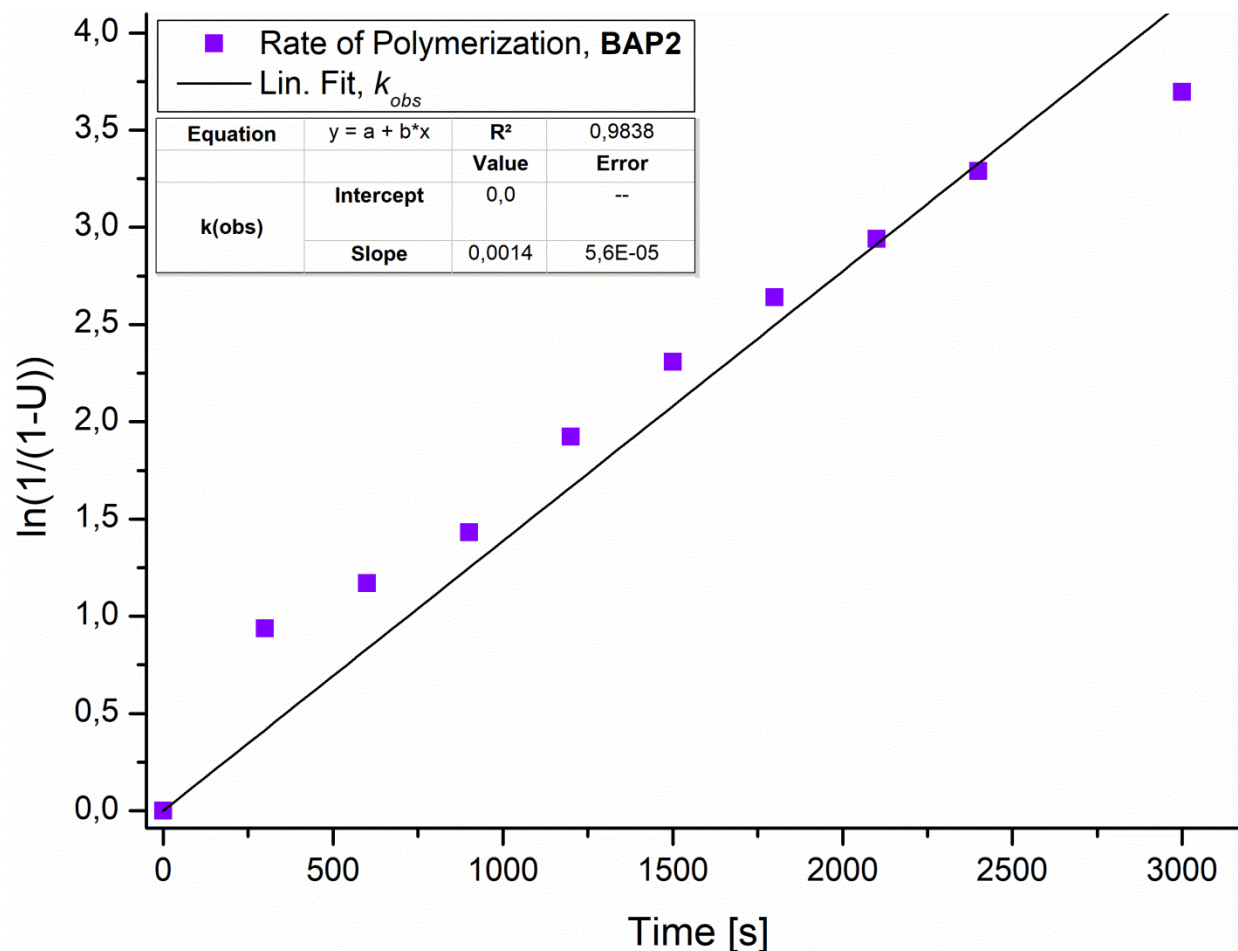


**Fig. S89.** Concentration of monomers over time of the copolymerization of butyl acrylate with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.



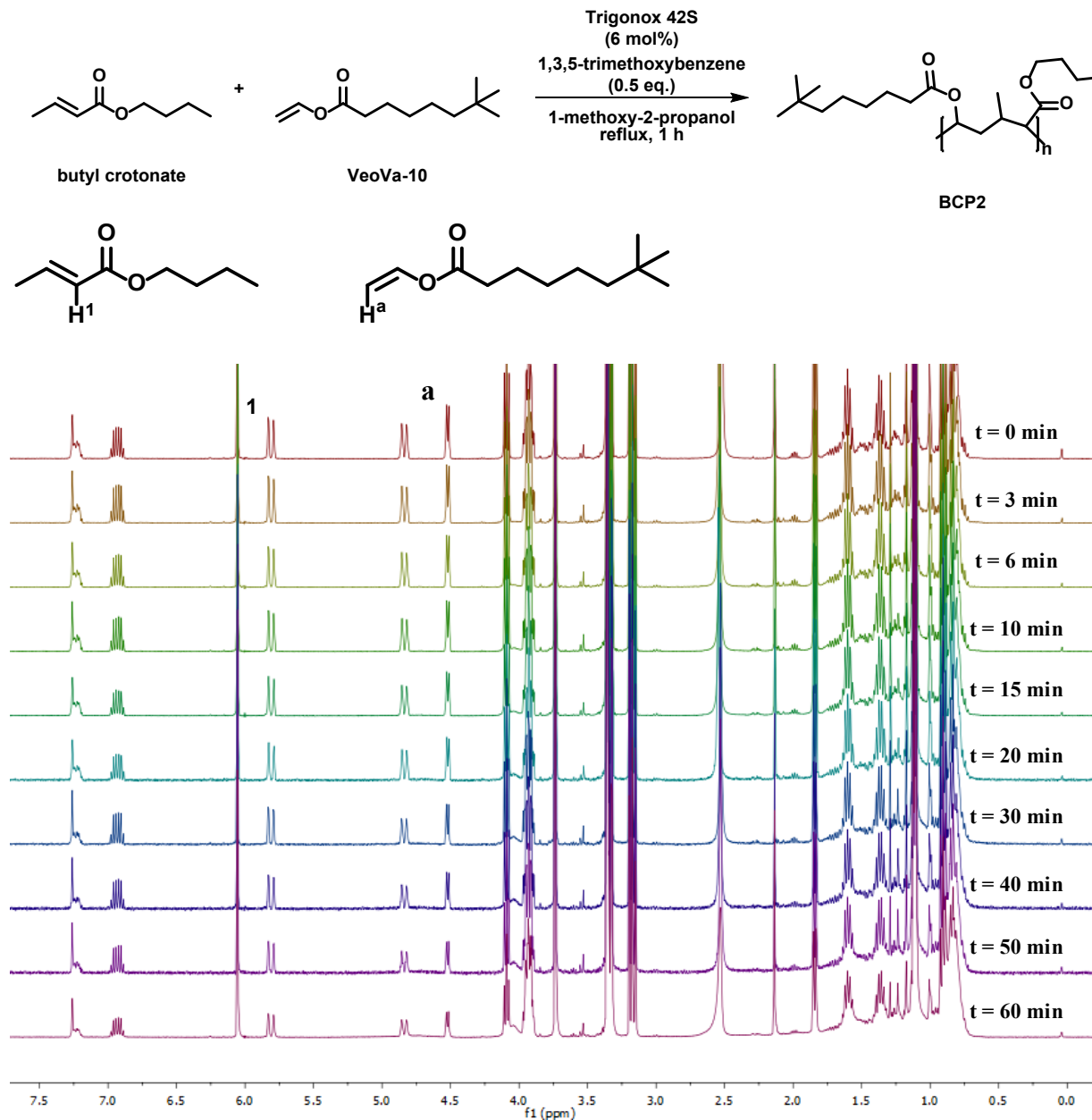
**Fig. S90.** Conversion of polymer **BAP2** over time; copolymerization of butyl acrylate with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.





**Fig. S91.** Rate of copolymerization of butyl acrylate with VeoVa-10 (1:1 ratio) to **BAP2** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 50 min.

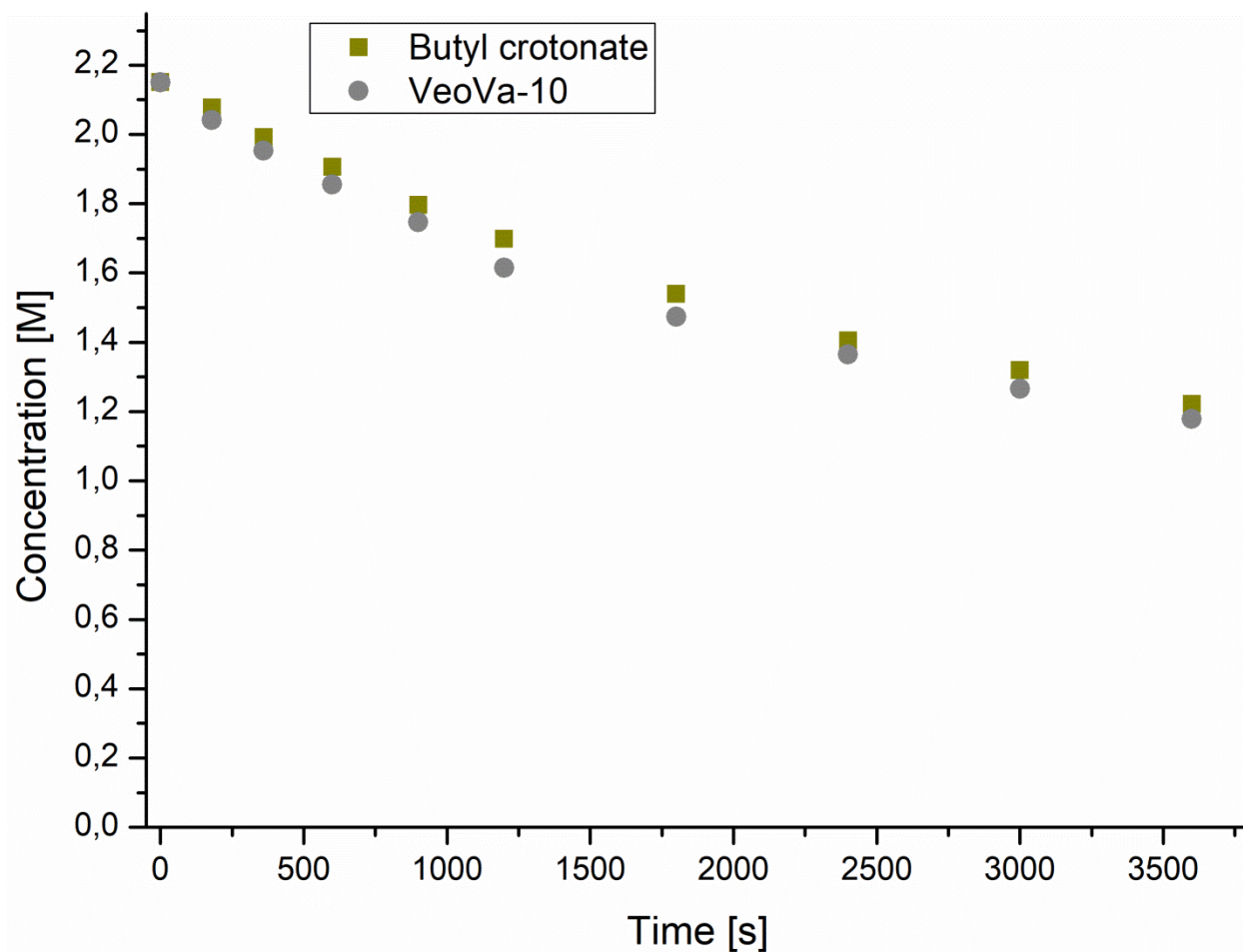
### butyl-crotonate-VeoVa-10-copolymer BCP2



**Fig. S92.** Reaction scheme copolymerization butyl crotonate with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h (top).  $^1\text{H NMR}$  signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

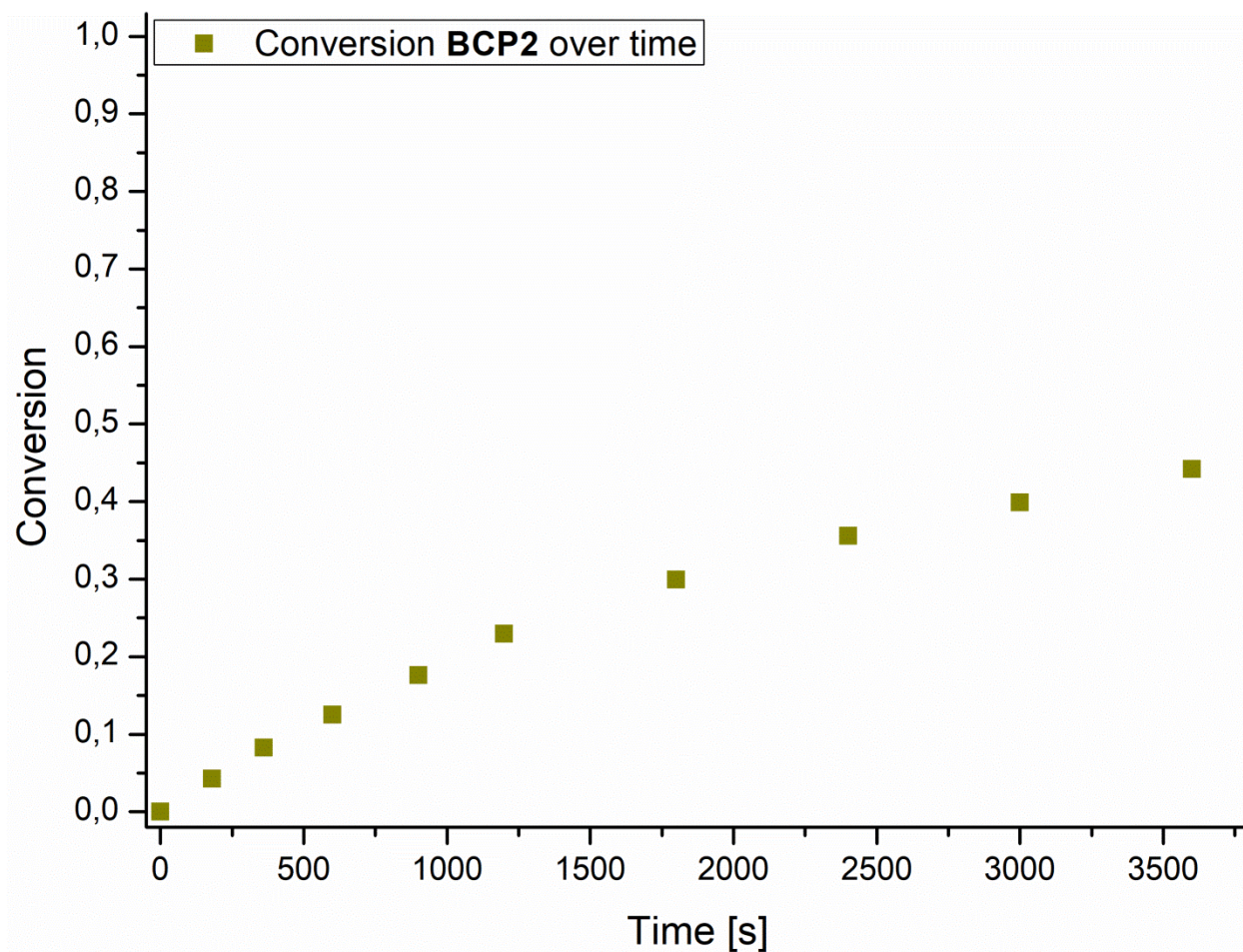
**Table S25.** Kinetic studies of the copolymerization of butyl crotonate with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.

Butyl-crotonate-VeoVa-10-copolymer BCP2						
	Butyl crotonate		VeoVa-10		k(obs)	(1.8±0.1)·10 <sup>-4</sup> [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,88	2,15	0,99	2,15	0,00	0,00
180	0,85	2,08	0,94	2,04	0,04	0,04
360	0,82	1,99	0,90	1,95	0,08	0,09
600	0,78	1,91	0,85	1,86	0,13	0,13
900	0,74	1,80	0,80	1,75	0,18	0,19
1200	0,70	1,70	0,74	1,62	0,23	0,26
1800	0,63	1,54	0,68	1,47	0,30	0,36
2400	0,58	1,40	0,63	1,36	0,36	0,44
3000	0,54	1,32	0,58	1,27	0,40	0,51
3600	0,50	1,22	0,54	1,18	0,44	0,58

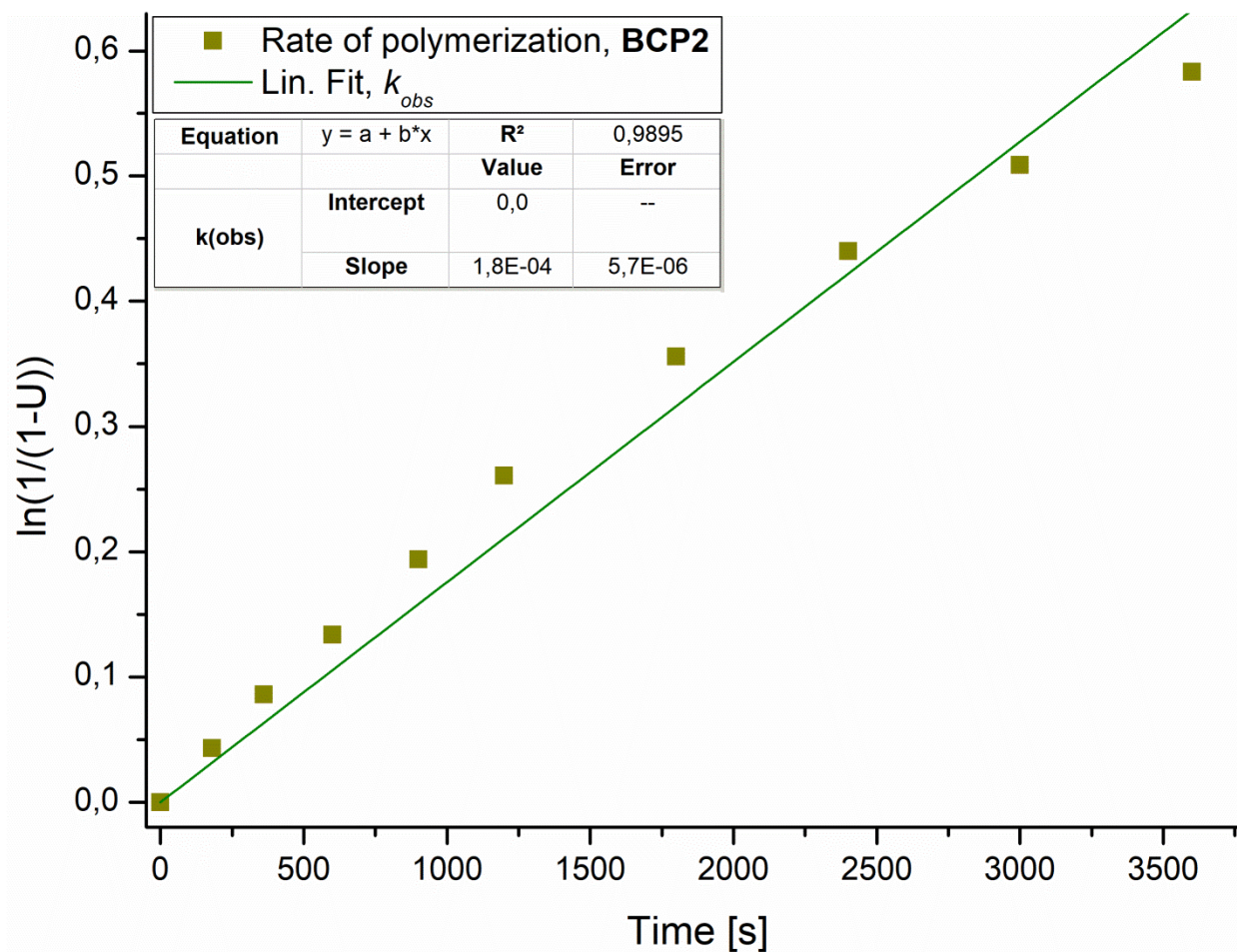


**Fig. S93.** Concentration of monomers over time of the copolymerization of butyl crotonate with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.



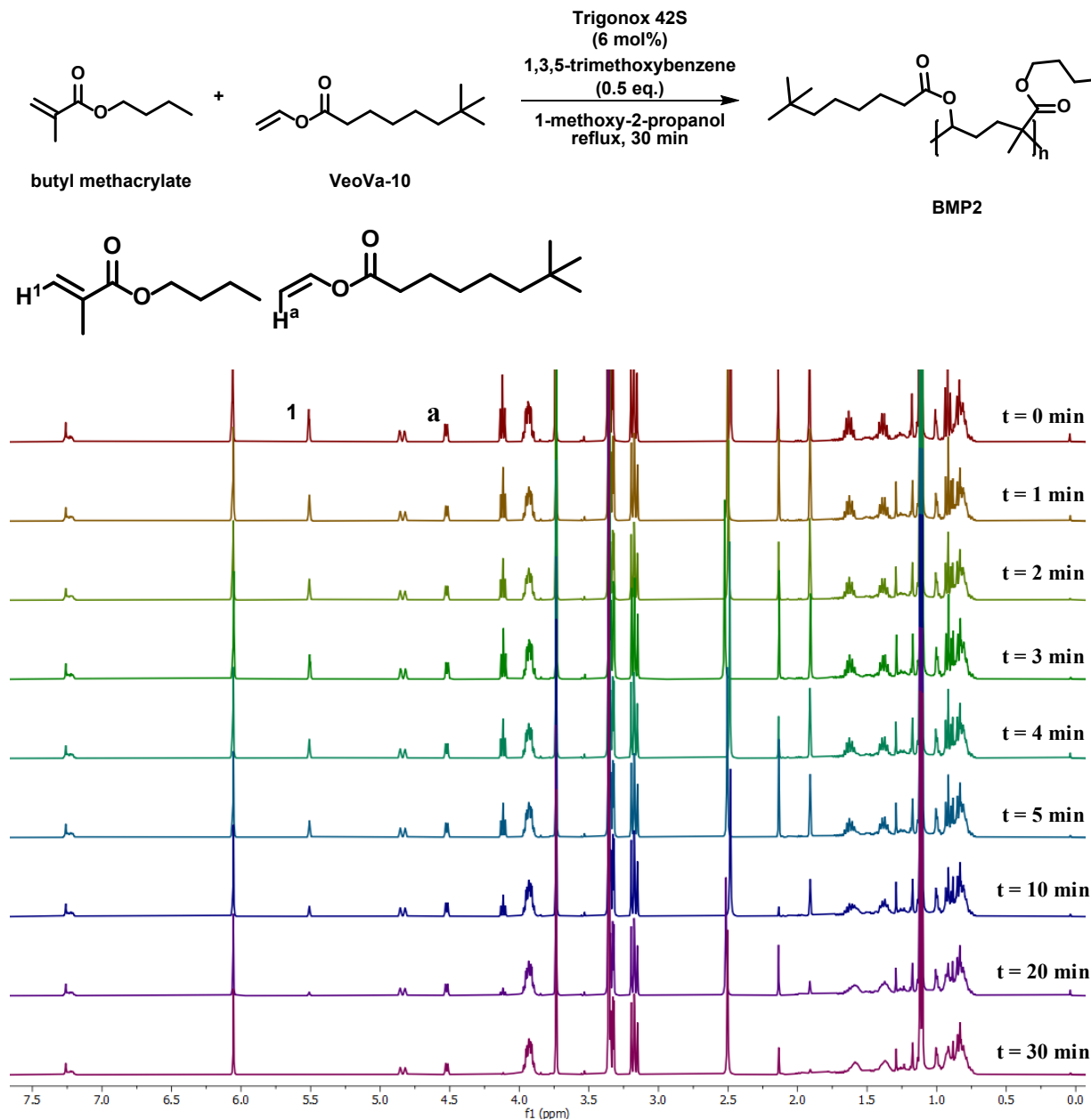


**Fig. S94.** Conversion of polymer **BCP2** over time; copolymerization of butyl crotonate with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.



**Fig. S95.** Rate of copolymerization of butyl crotonate with VeoVa-10 (1:1 ratio) to **BCP2** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.

### butyl-methacrylate-VeoVa-10-copolymer BMP2

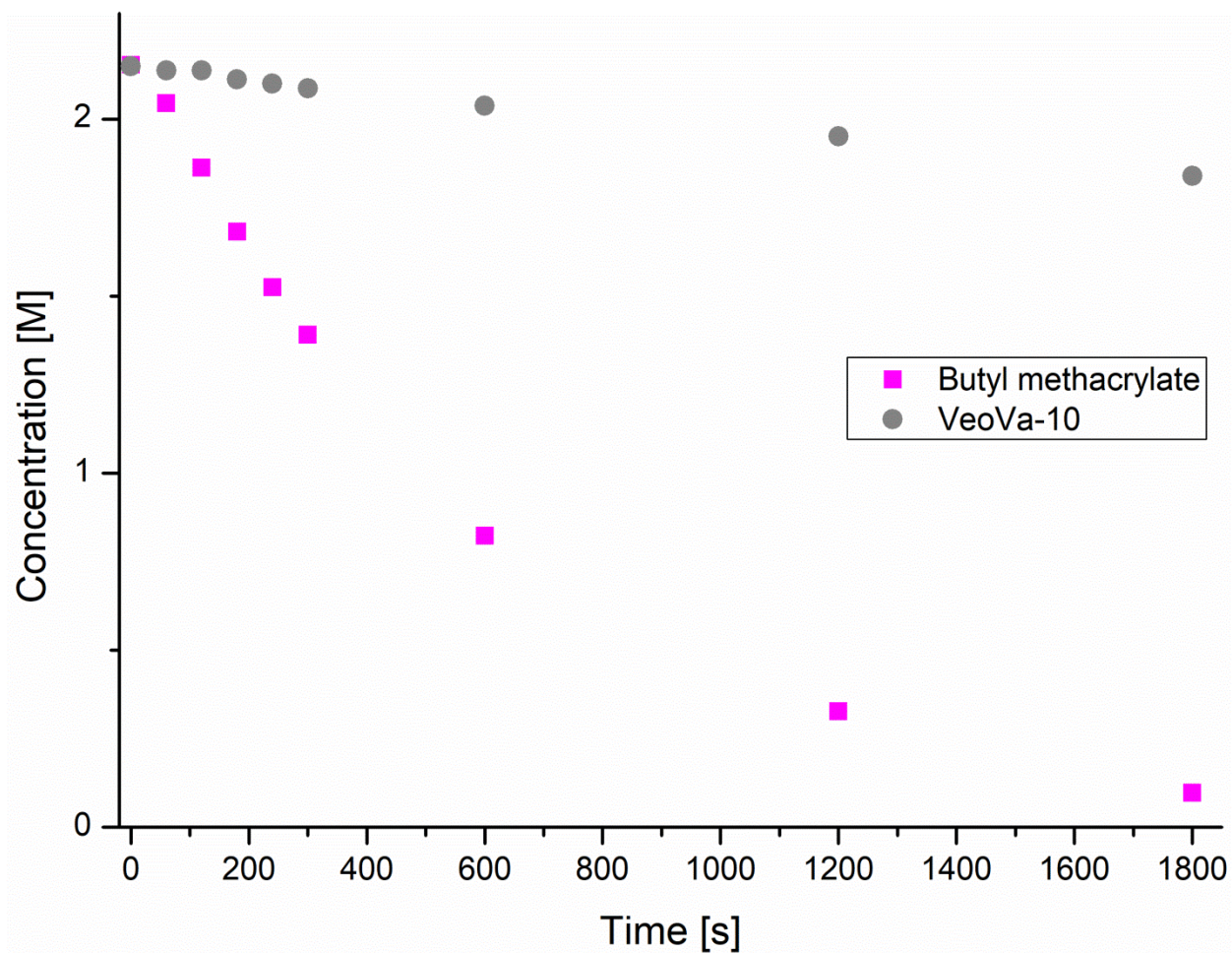


**Fig. S96.** Reaction scheme copolymerization butyl methacrylate with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 30 min (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

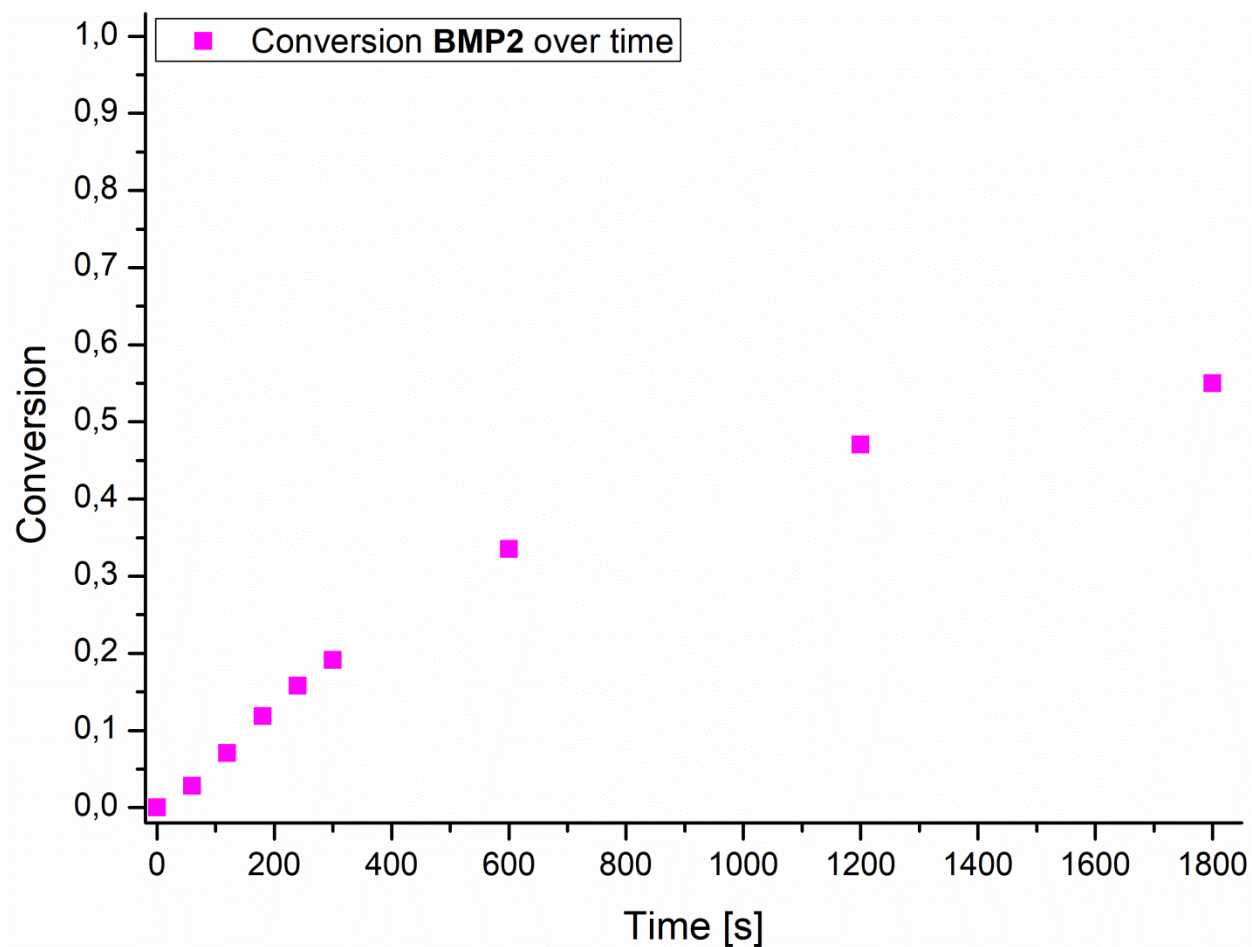


**Table S26.** Kinetic studies of the copolymerization of butyl methacrylate with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 30 min.

Butyl-methacrylate-VeoVa-10-copolymer BMP2						
	Butyl methacrylate		VeoVa-10		k(obs)	$(4.9 \pm 0.3) \cdot 10^{-4} [s^{-1}]$
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	0,89	2,15	0,87	2,15	0,00	0,00
60	0,85	2,05	0,86	2,14	0,03	0,03
120	0,77	1,86	0,86	2,14	0,07	0,07
180	0,70	1,68	0,85	2,11	0,12	0,13
240	0,63	1,52	0,85	2,10	0,16	0,17
300	0,58	1,39	0,84	2,09	0,19	0,21
600	0,34	0,82	0,82	2,04	0,34	0,41
1200	0,14	0,33	0,79	1,95	0,47	0,64
1800	0,04	0,10	0,74	1,84	0,55	0,80

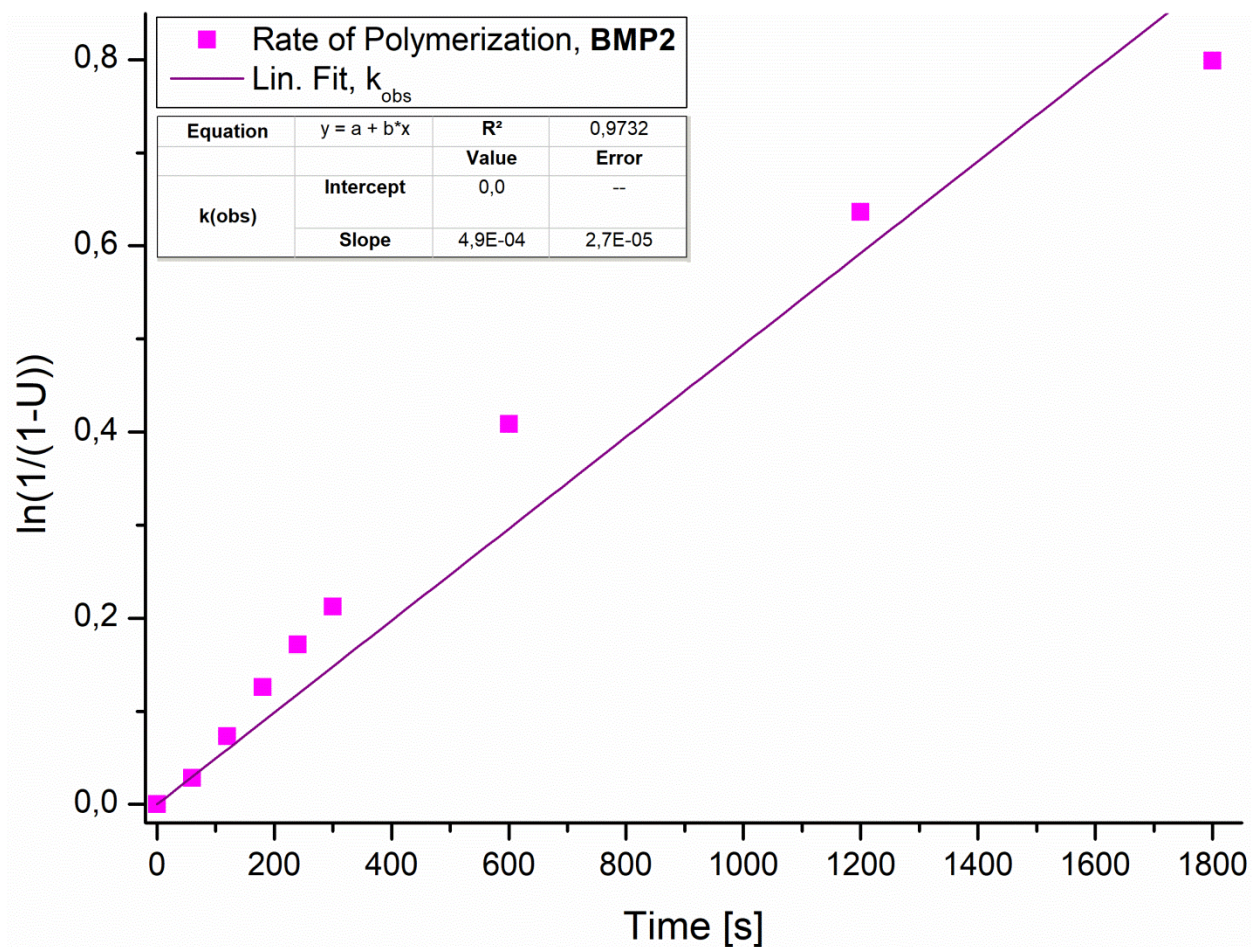


**Fig. S97.** Concentration of monomers over time of the copolymerization of butyl methacrylate with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 30 min.



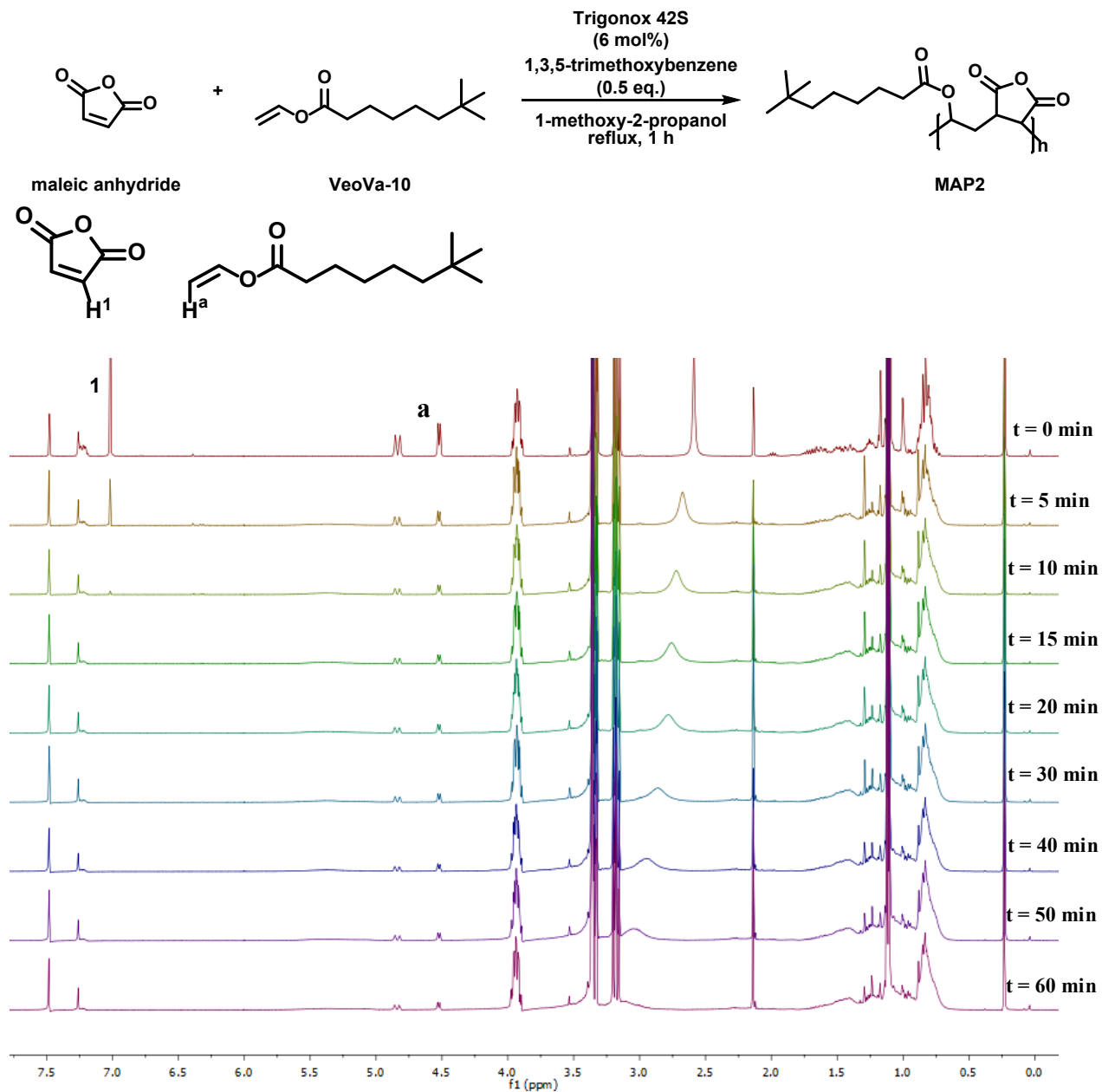
**Fig. S98.** Conversion of polymer **BMP2** over time; copolymerization of butyl methacrylate with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 30 min.





**Fig. S99.** Rate of copolymerization of butyl methacrylate with VeoVa-10 (1:1 ratio) to **BMP2** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 30 min.

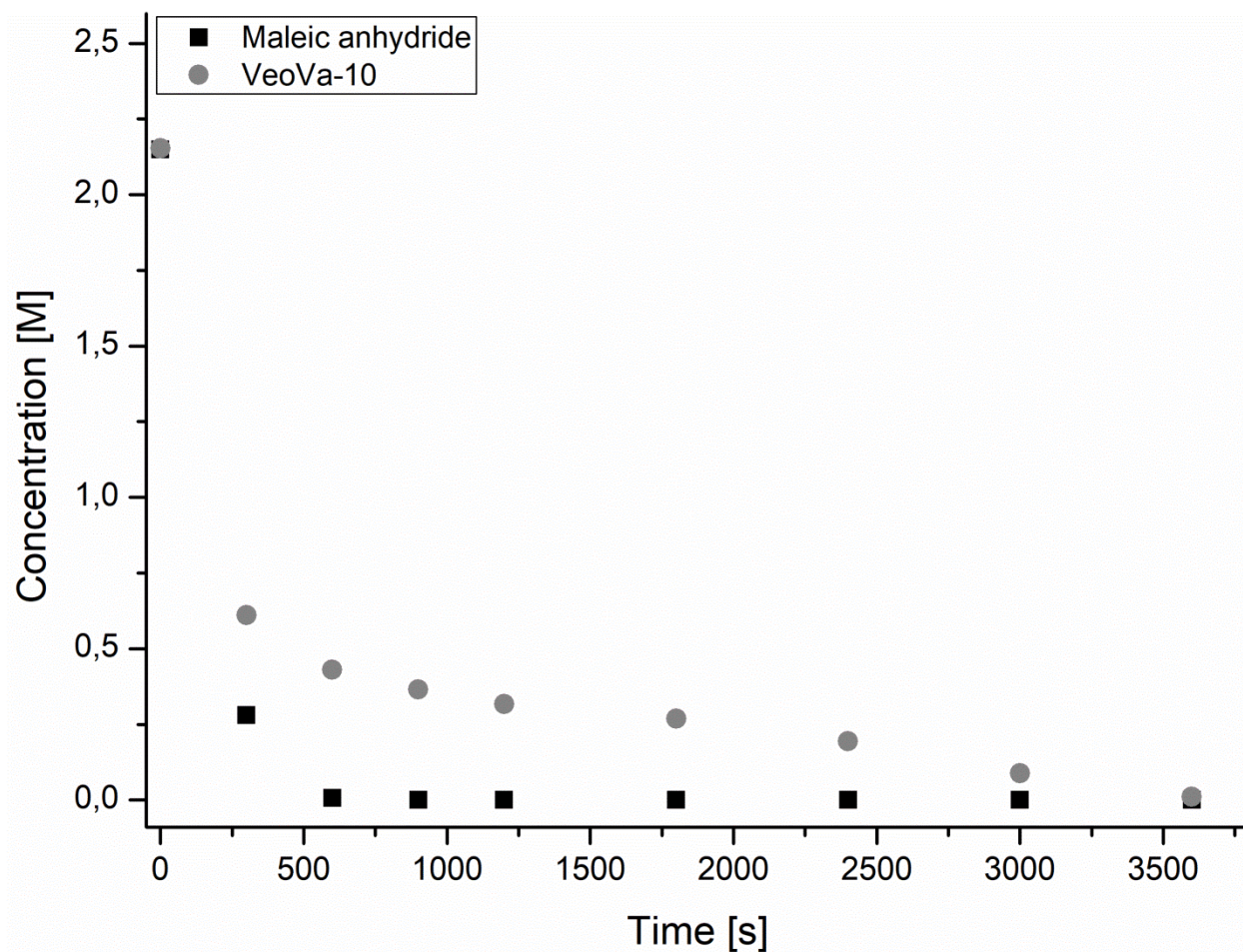
### maleic-anhydride-VeoVa-10-copolymer MAP2



**Fig. S100.** Reaction scheme copolymerization maleic anhydride with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h (top).  $^1H$  NMR signals over time by taking samples and flash freezing ( $-18^\circ C$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

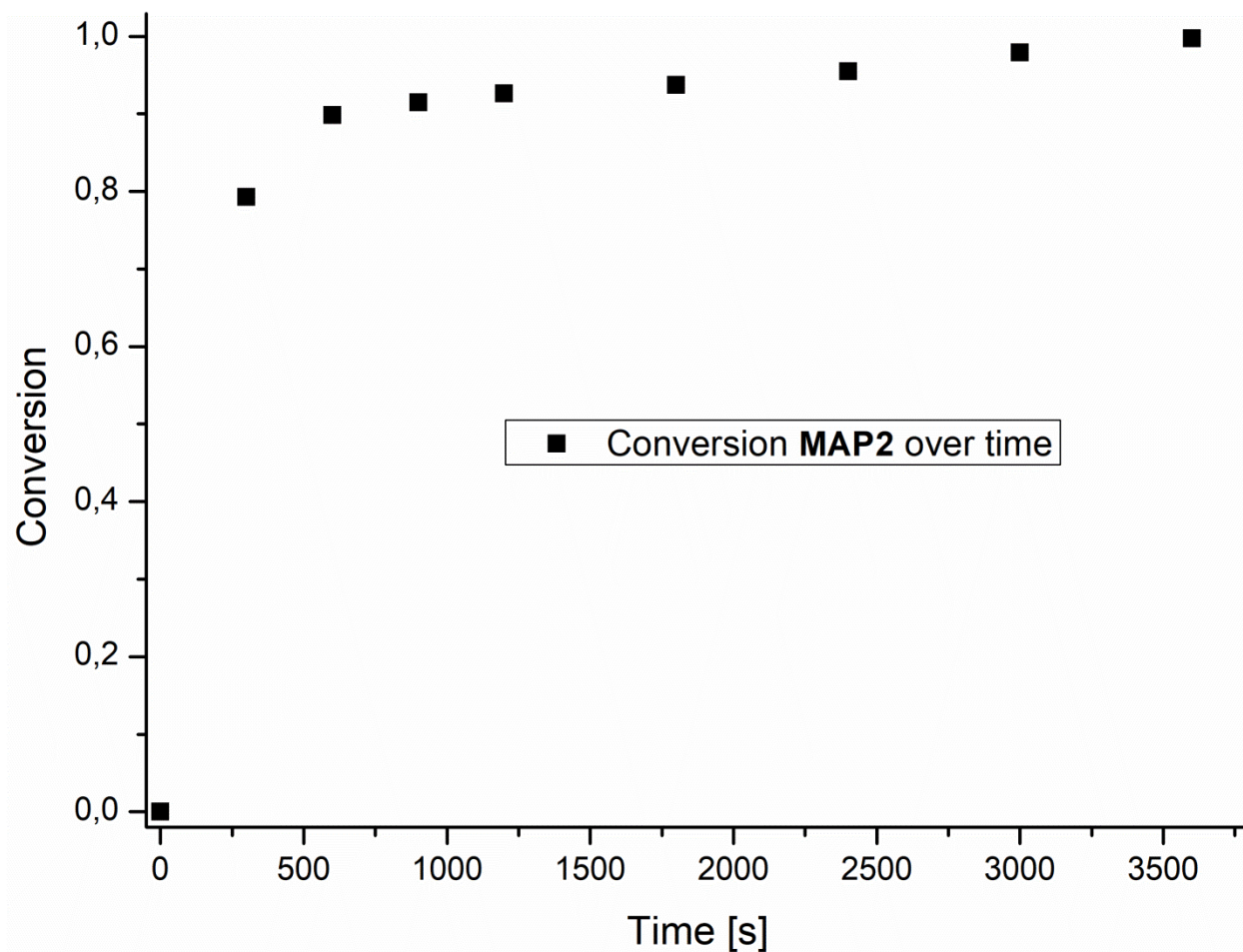
**Table S27.** Kinetic studies of the copolymerization of maleic anhydride with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.

<b>Maleic-anhydride-VeoVa-10-copolymer MAP2</b>						
	Maleic anhydride		VeoVa-10		<b>k(obs)</b>	<b>(1.6±0.2)·10<sup>-3</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,85	2,15	1,07	2,15	0,00	0,00
300	0,11	0,28	0,30	0,61	0,79	1,57
600	0,00	0,01	0,21	0,43	0,90	2,29
900	0,00	0,00	0,18	0,37	0,92	2,47
1200	0,00	0,00	0,16	0,32	0,93	2,61
1800	0,00	0,00	0,13	0,27	0,94	2,77
2400	0,00	0,00	0,10	0,19	0,95	3,09
3000	0,00	0,00	0,04	0,09	0,98	3,89
3600	0,00	0,00	0,01	0,01	1,00	6,06

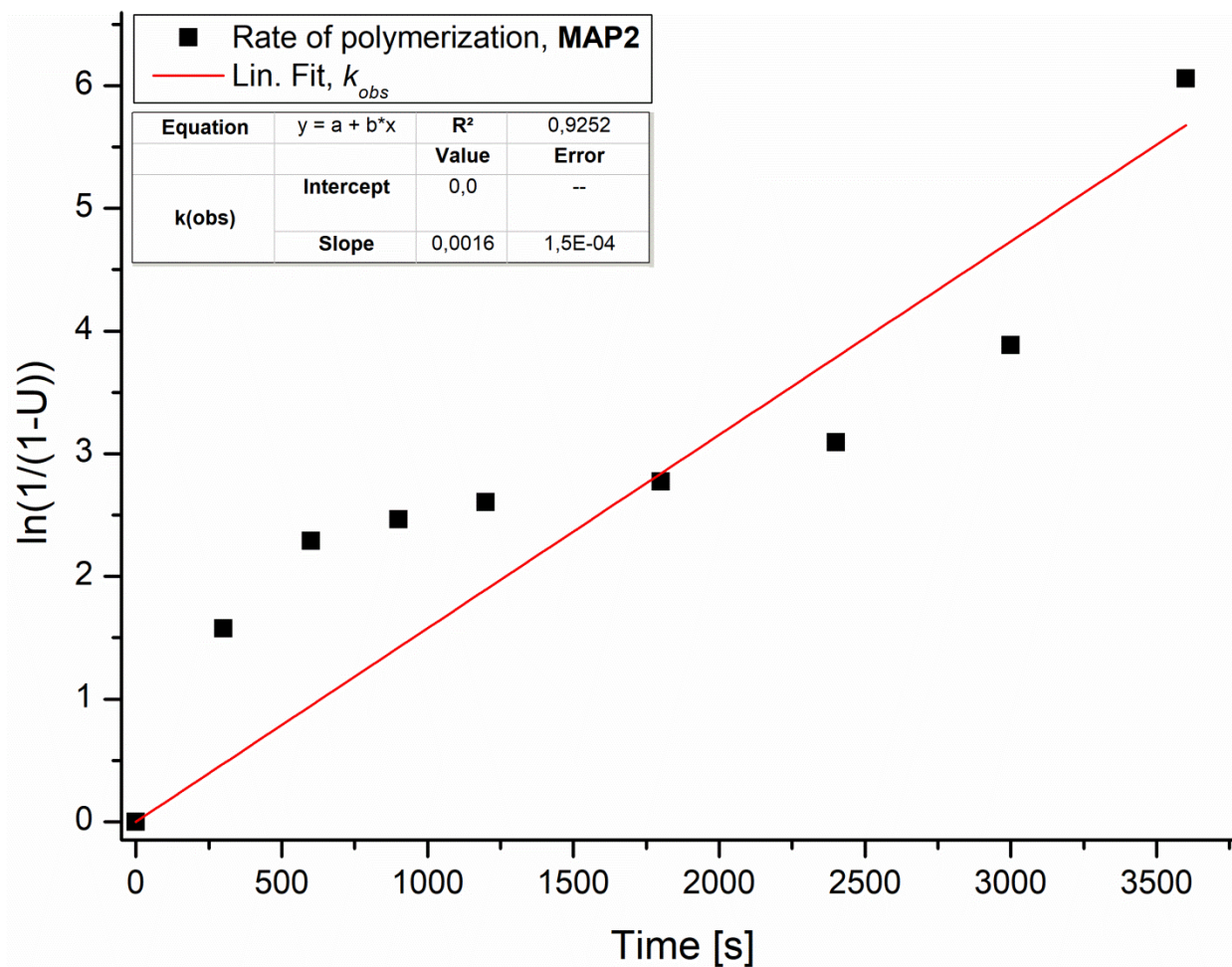


**Fig. S101.** Concentration of monomers over time of the copolymerization of maleic anhydride with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.

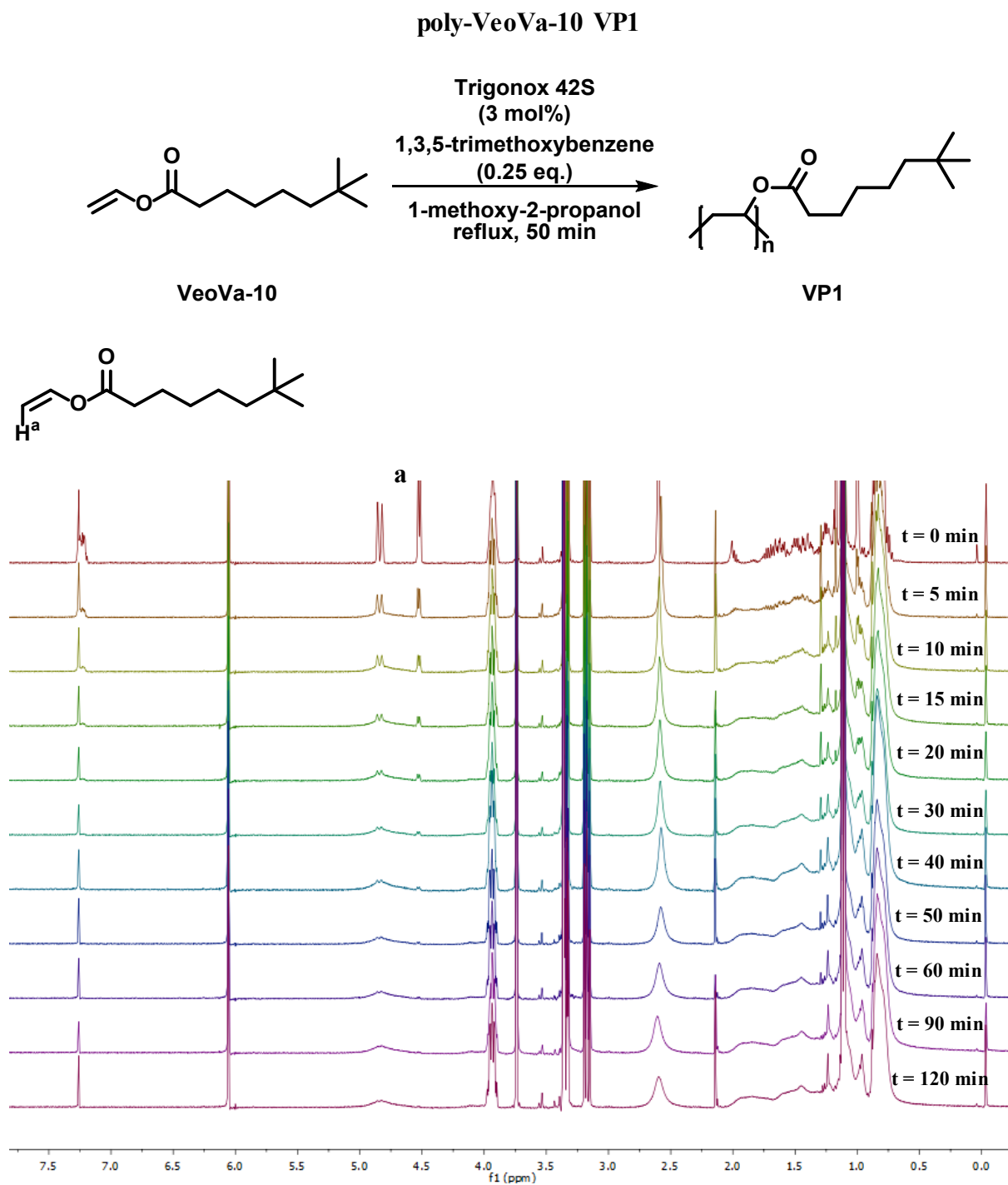




**Fig. S102.** Conversion of polymer **MAP2** over time; copolymerization of maleic anhydride with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.



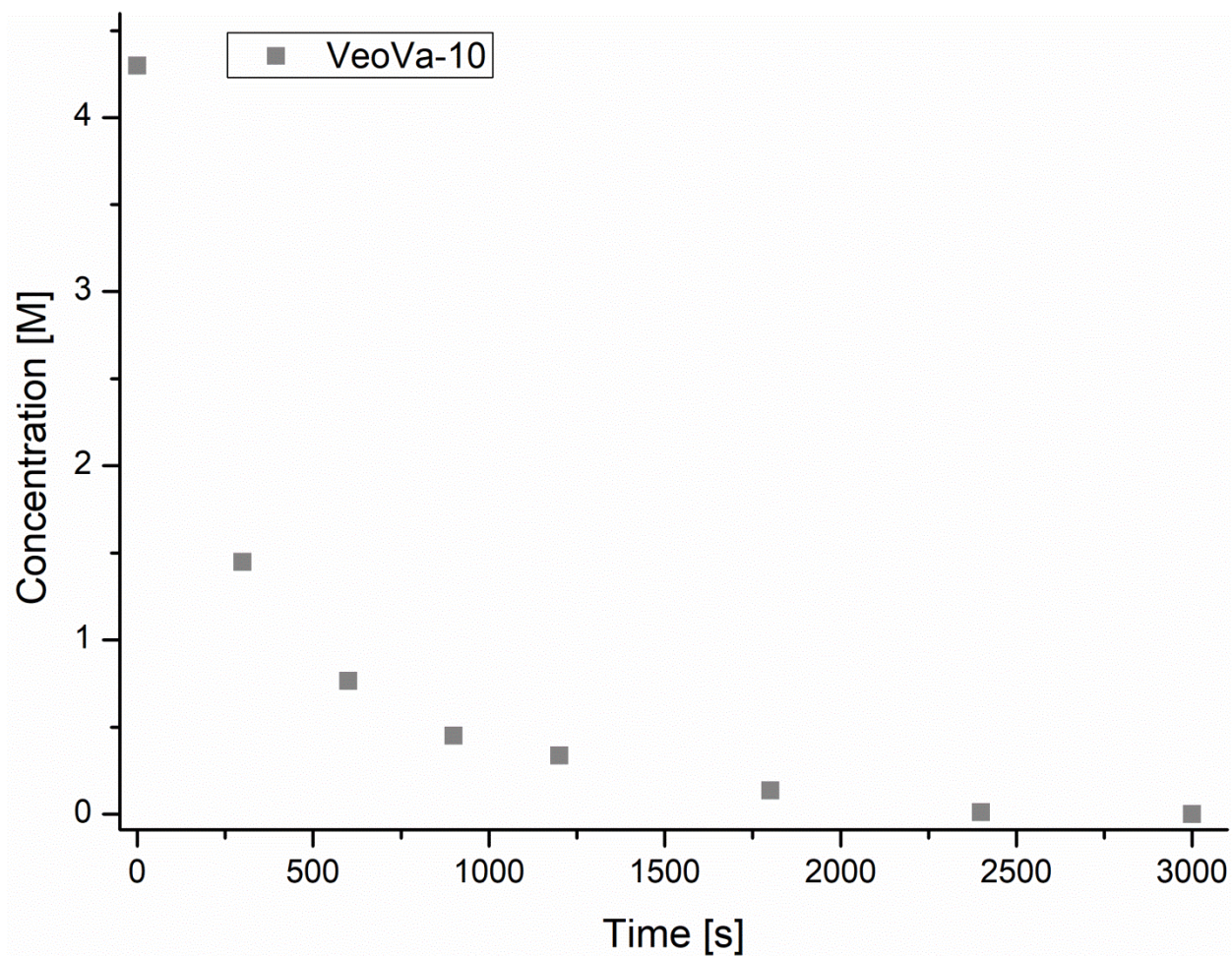
**Fig. S103.** Rate of copolymerization of maleic anhydride with VeoVa-10 (1:1 ratio) to **MAP2** over time; followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.



**Fig. S104.** Reaction scheme homopolymerization VeoVa-10 (2 eq.), reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 50 min (top).  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard (bottom).

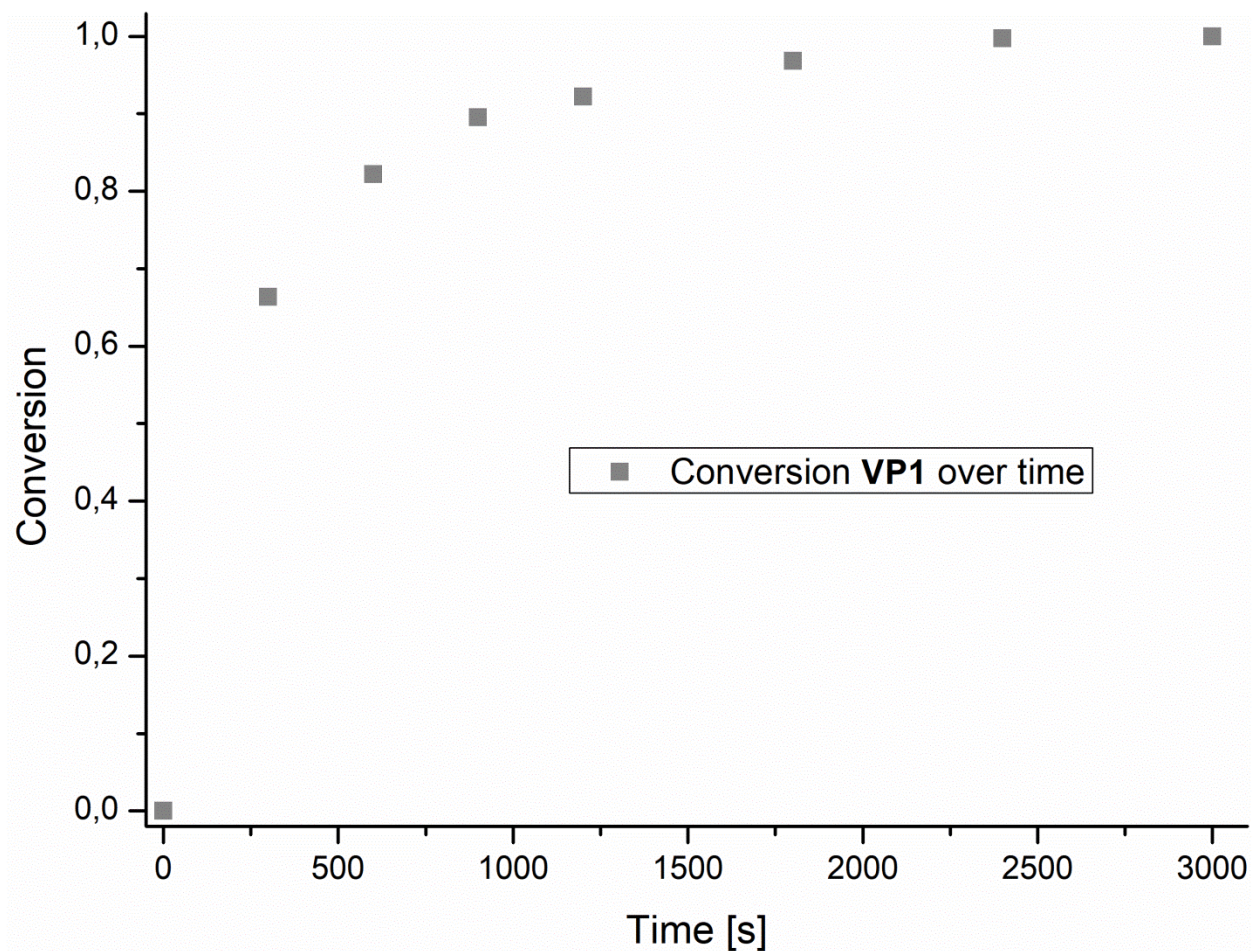
**Table S28.** Kinetic studies of the homopolymerization of VeoVa-10 (2 eq.), followed by  $^1\text{H}$  NMR spectroscopy. Integrated  $^1\text{H}$  NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.25 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (3 mol%), 4.3 M in 1-methoxy-2-propanol, reflux, 50 min.

VeoVa-10-polymer VP1				
	VeoVa-10		<b>k(obs)</b>	<b><math>(2.0 \pm 0.1) \cdot 10^{-3} [\text{s}^{-1}]</math></b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b><math>\ln(1/[1-U])</math></b>
0	1,03	4,30	0,00	0,00
300	0,35	1,45	0,66	1,09
600	0,18	0,77	0,82	1,73
900	0,11	0,45	0,90	2,25
1200	0,08	0,34	0,92	2,55
1800	0,03	0,14	0,97	3,45
2400	0,00	0,01	1,00	6,02
3000	0,00	0,00	1,00	-



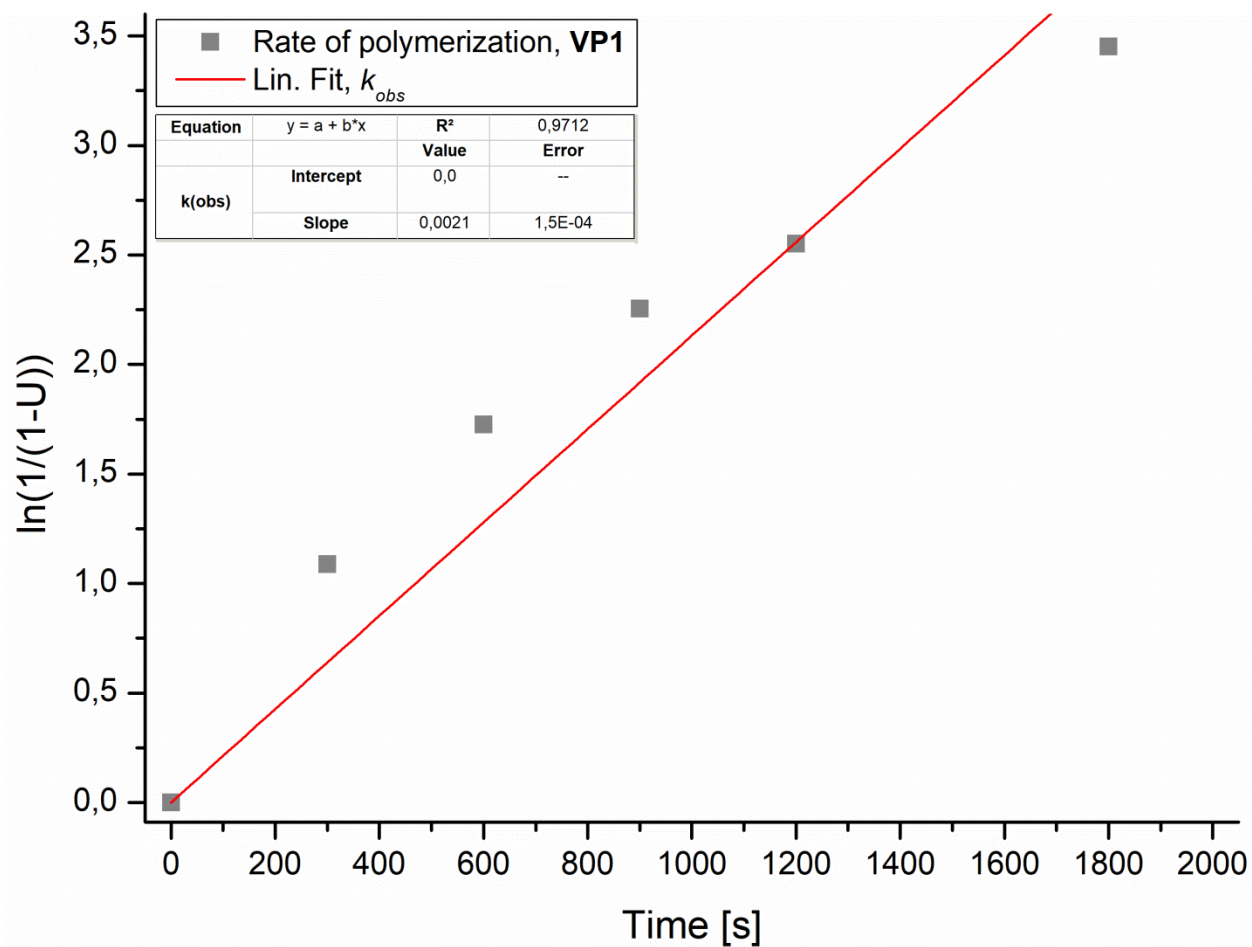
**Fig. S105.** Concentration of the monomer VeoVa-10 over time followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 50 min.





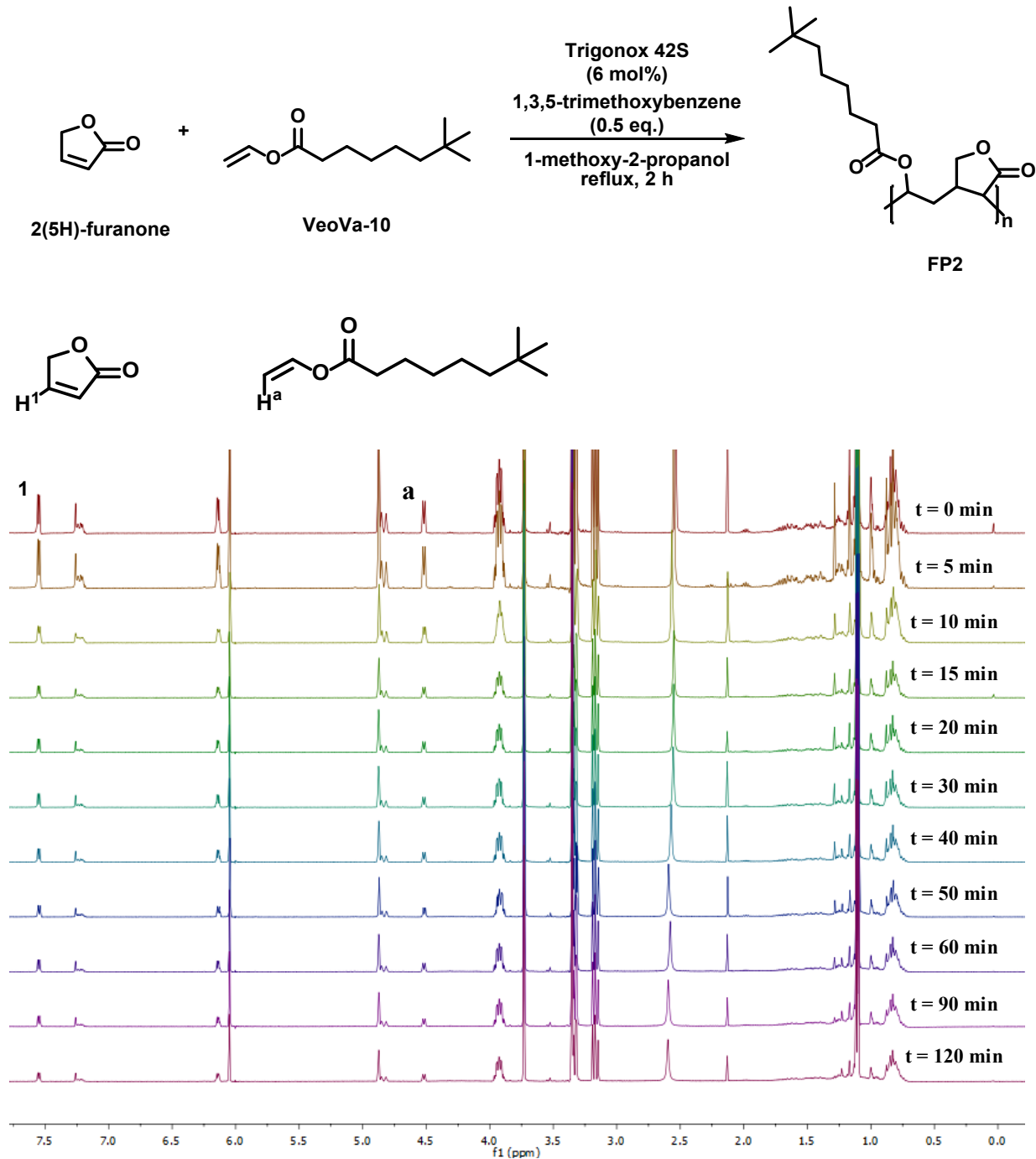
**Fig. S106.** Conversion of polymer **VP1** over time; homo-polymerization of VeoVa-10 followed by  $^1\text{H NMR}$  signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 50 min.





**Fig. S107.** Rate of homo-polymerization of VeoVa-10 to **VP1** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.25 eq.) as internal standard, reaction conditions: Trigonox 42S (3 mol%), 4.30 M in 1-methoxy-2-propanol, reflux, 50 min.

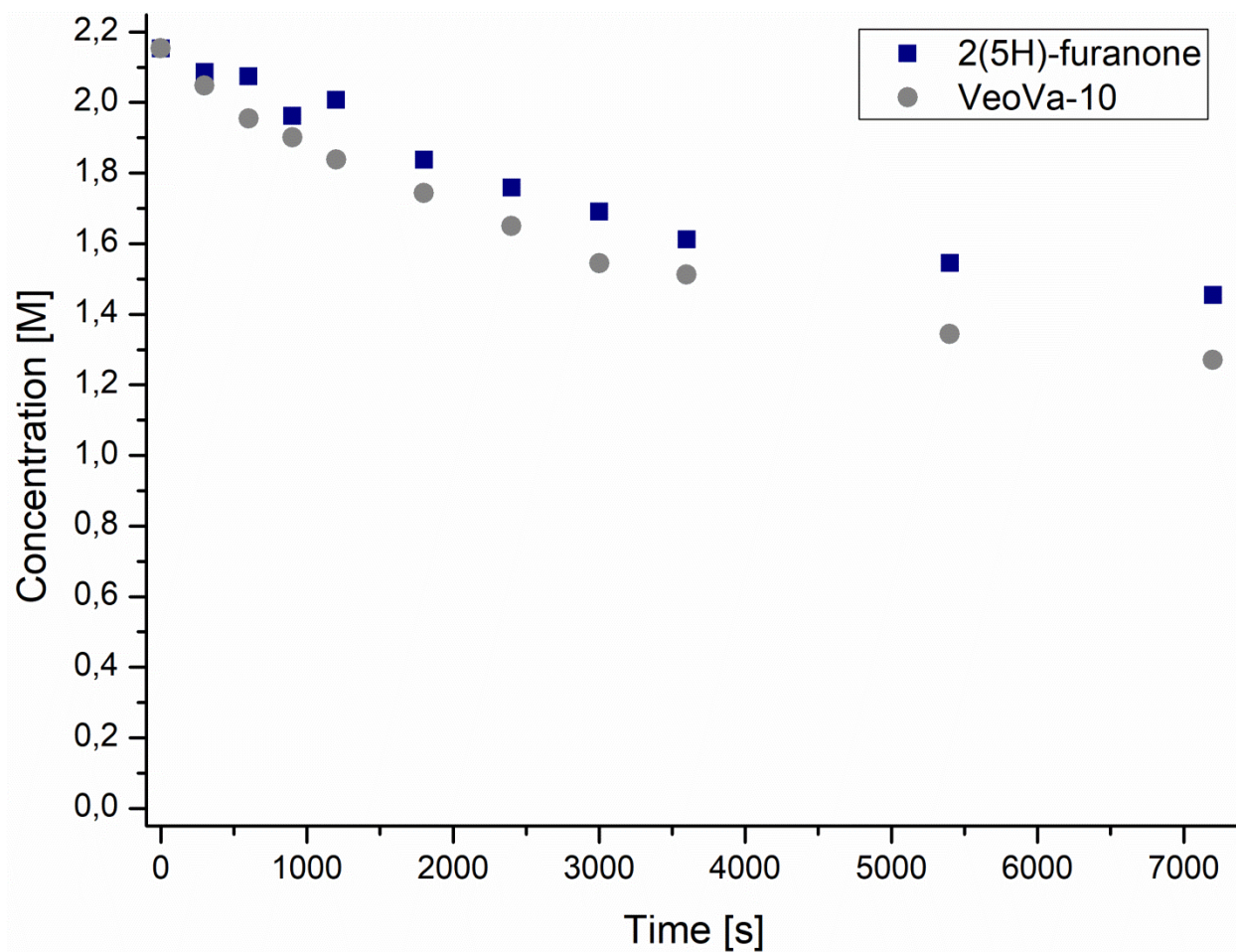
## 2(5H)-furanone-VeoVa-10-copolymer FP2



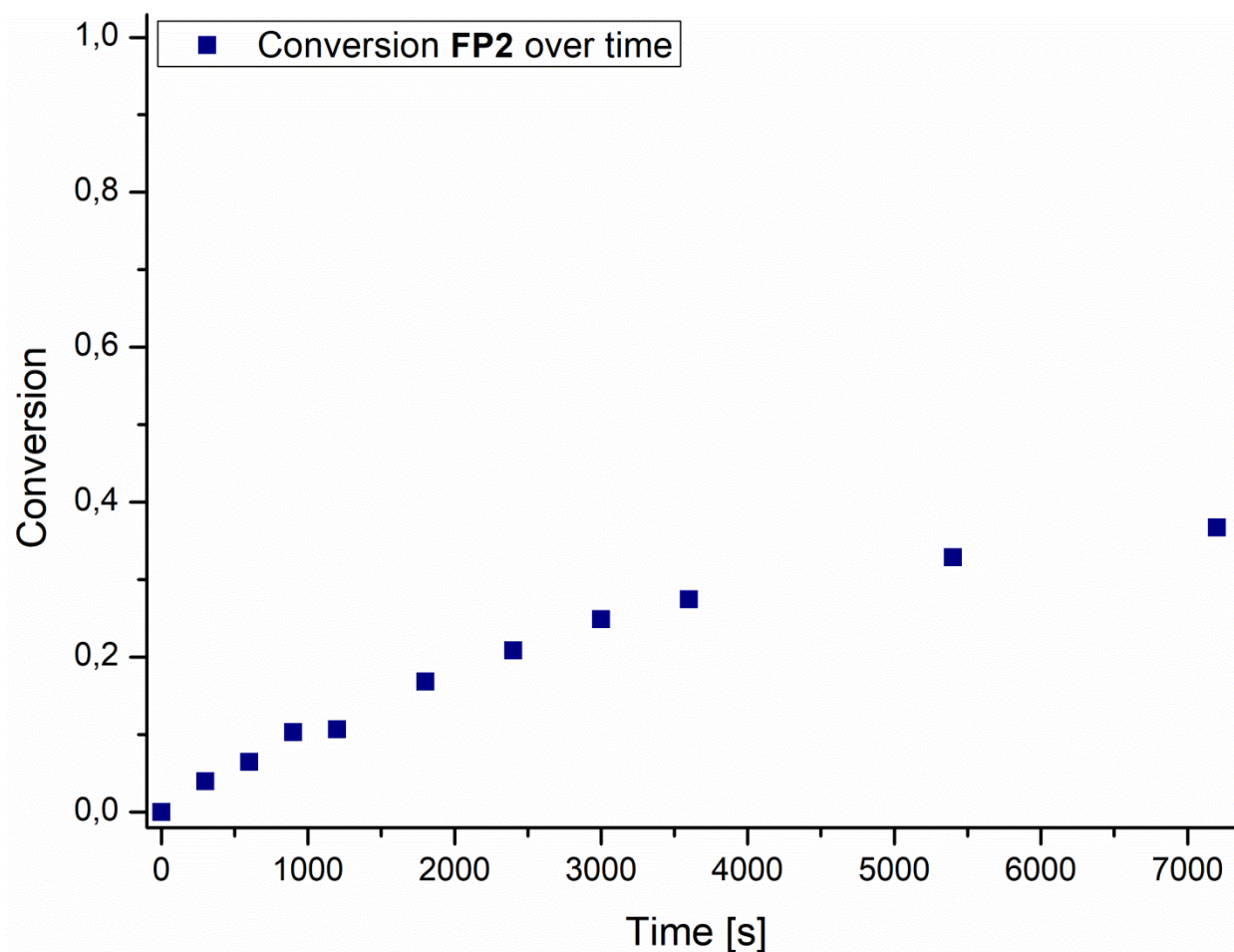
**Fig. S108.** Reaction scheme copolymerization 2(5H)-furanone with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S29.** Kinetic studies of the copolymerization of 2(5H)-furanone with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

Furanone-VeoVa-10-copolymer FP2						
	Furanone		VeoVa-10		<b>k(obs)</b>	<b>(7.5±0.4)·10<sup>-5</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,96	2,15	1,03	2,15	0,00	0,00
300	0,93	2,09	0,98	2,05	0,04	0,04
600	0,92	2,07	0,93	1,95	0,06	0,07
900	0,87	1,96	0,91	1,90	0,10	0,11
1200	0,89	2,01	0,88	1,84	0,11	0,11
1800	0,82	1,84	0,83	1,74	0,17	0,18
2400	0,78	1,76	0,79	1,65	0,21	0,23
3000	0,75	1,69	0,74	1,54	0,25	0,29
3600	0,72	1,61	0,72	1,51	0,27	0,32
5400	0,69	1,54	0,64	1,34	0,33	0,40
7200	0,65	1,45	0,61	1,27	0,37	0,46

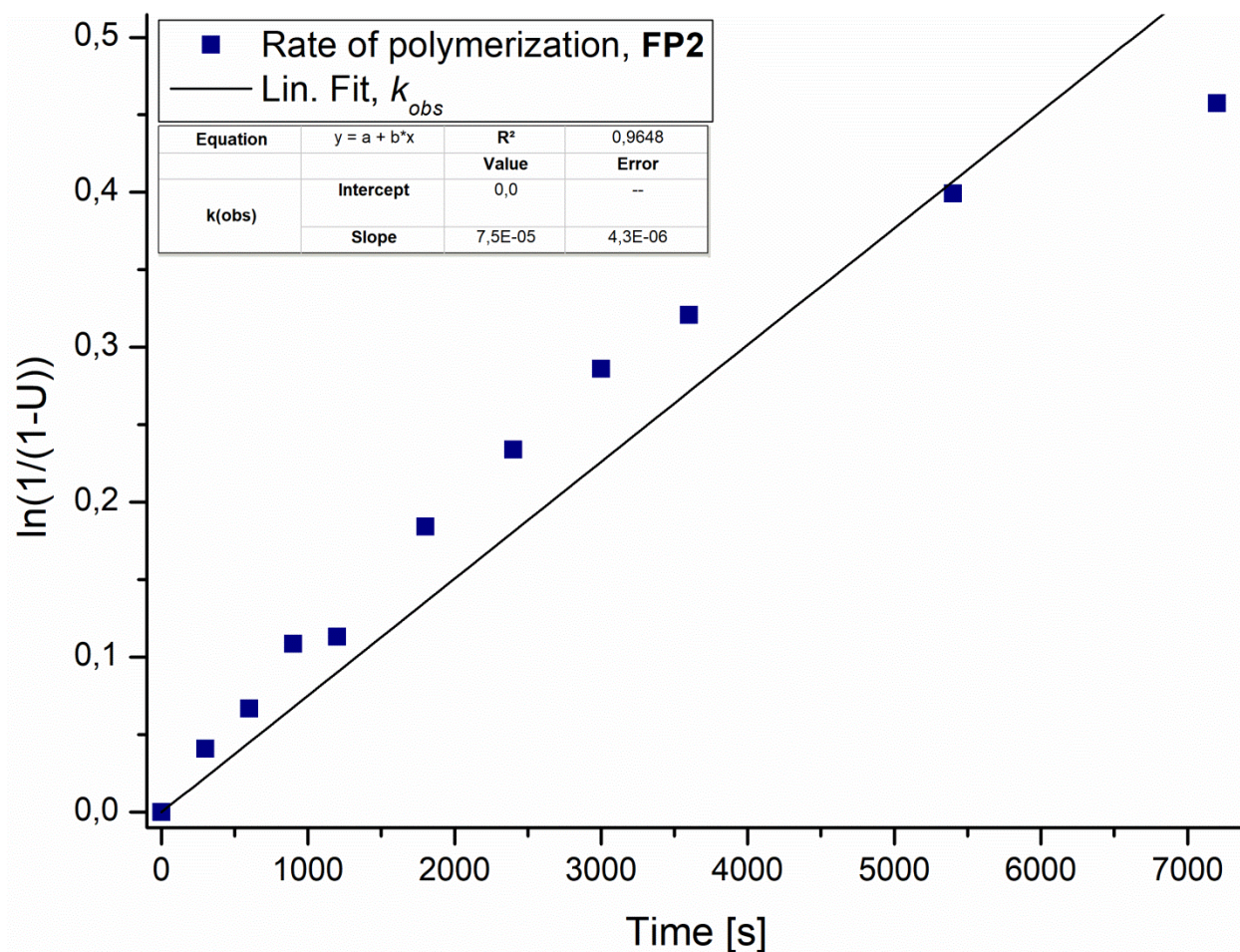


**Fig. S109.** Concentration of monomers over time of the copolymerization of 2(5H)-furanone with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.



**Fig. S110.** Conversion of polymer **FP2** over time; copolymerization of 2(5H)-furanone with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.

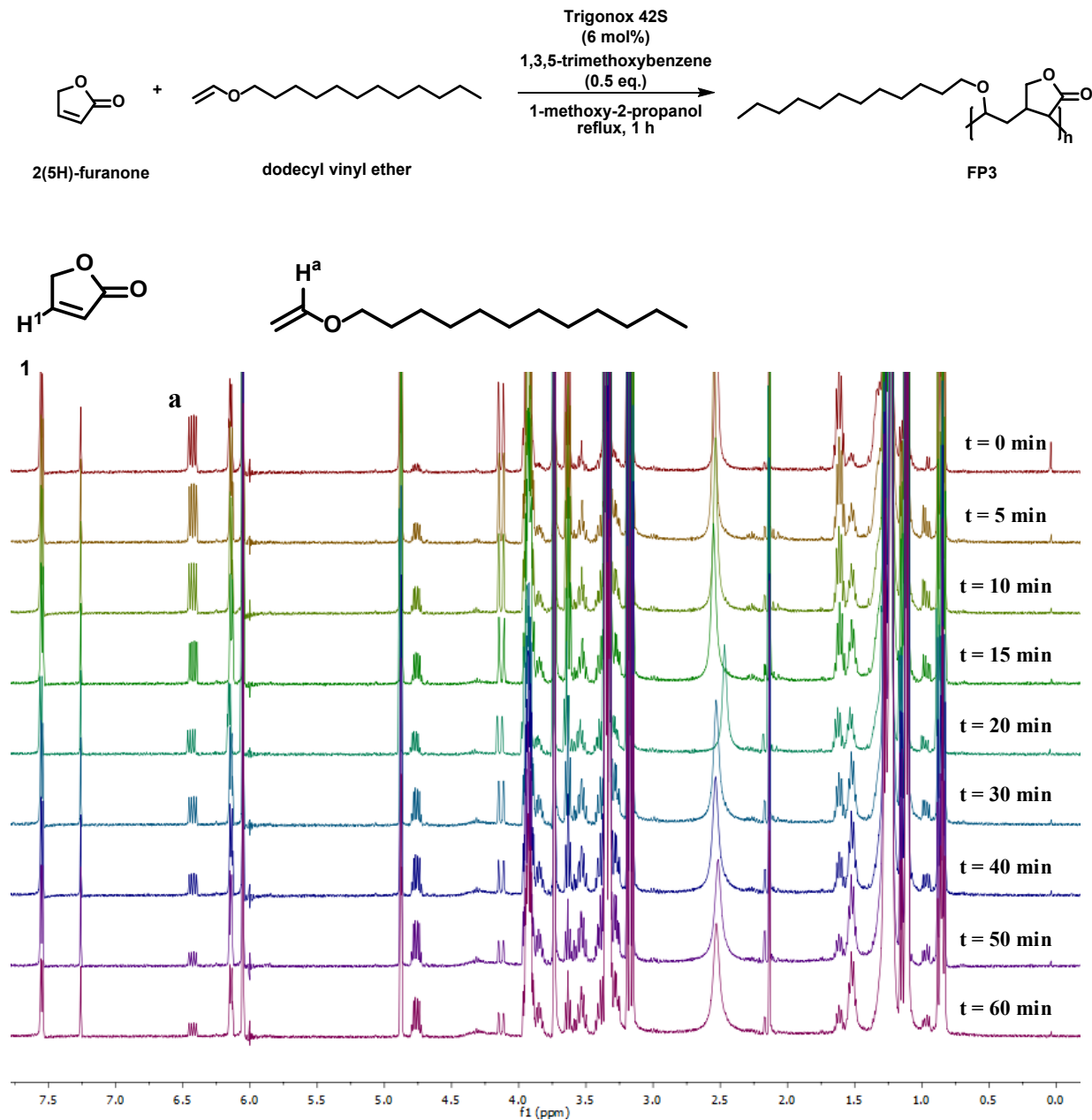




**Fig. S111.** Rate of copolymerization of 2(5H)-furanone with VeoVa-10 (1:1 ratio) to **FP2** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2 h.



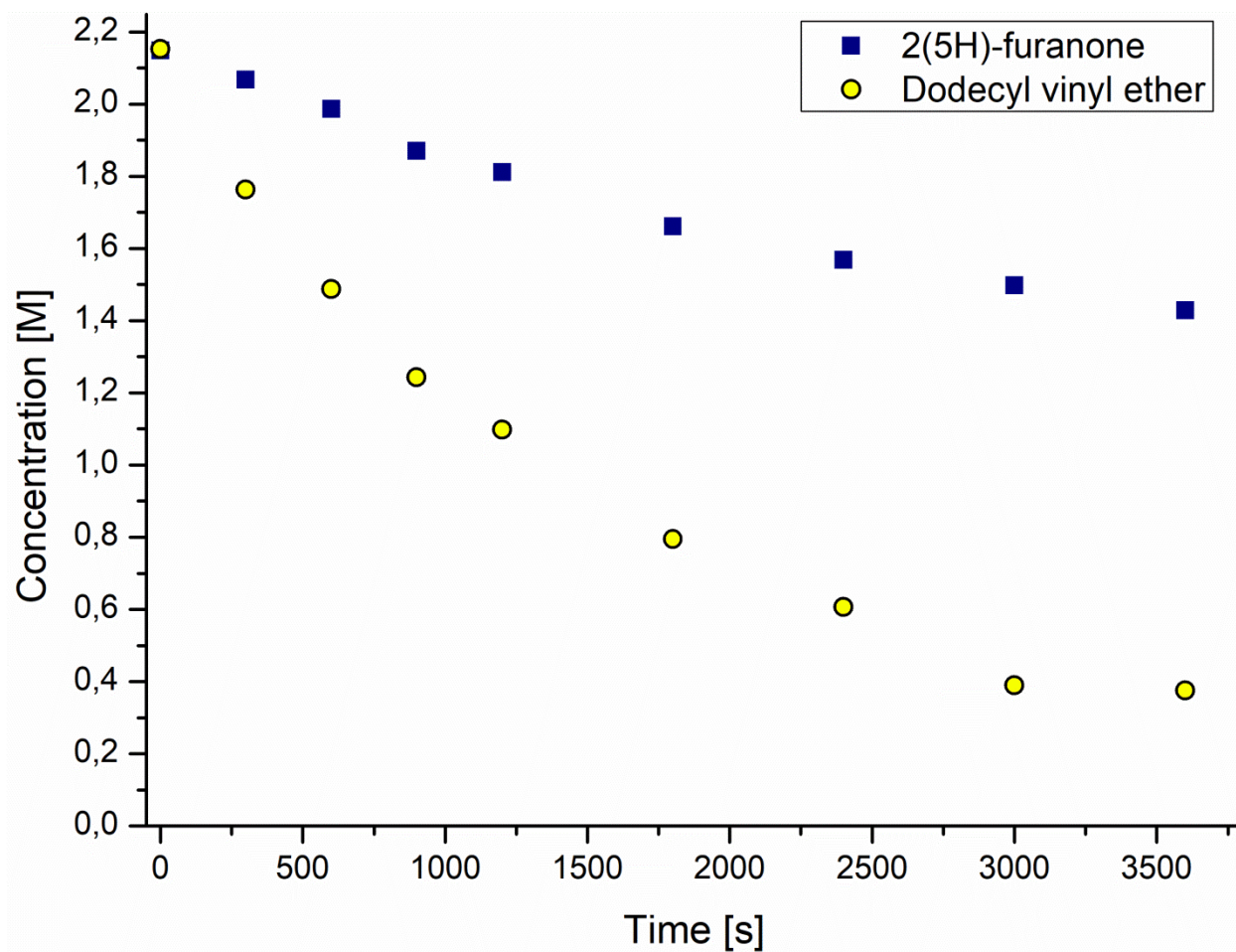
## 2(5H)-furanone-dodecyl-vinyl-ether-copolymer FP3



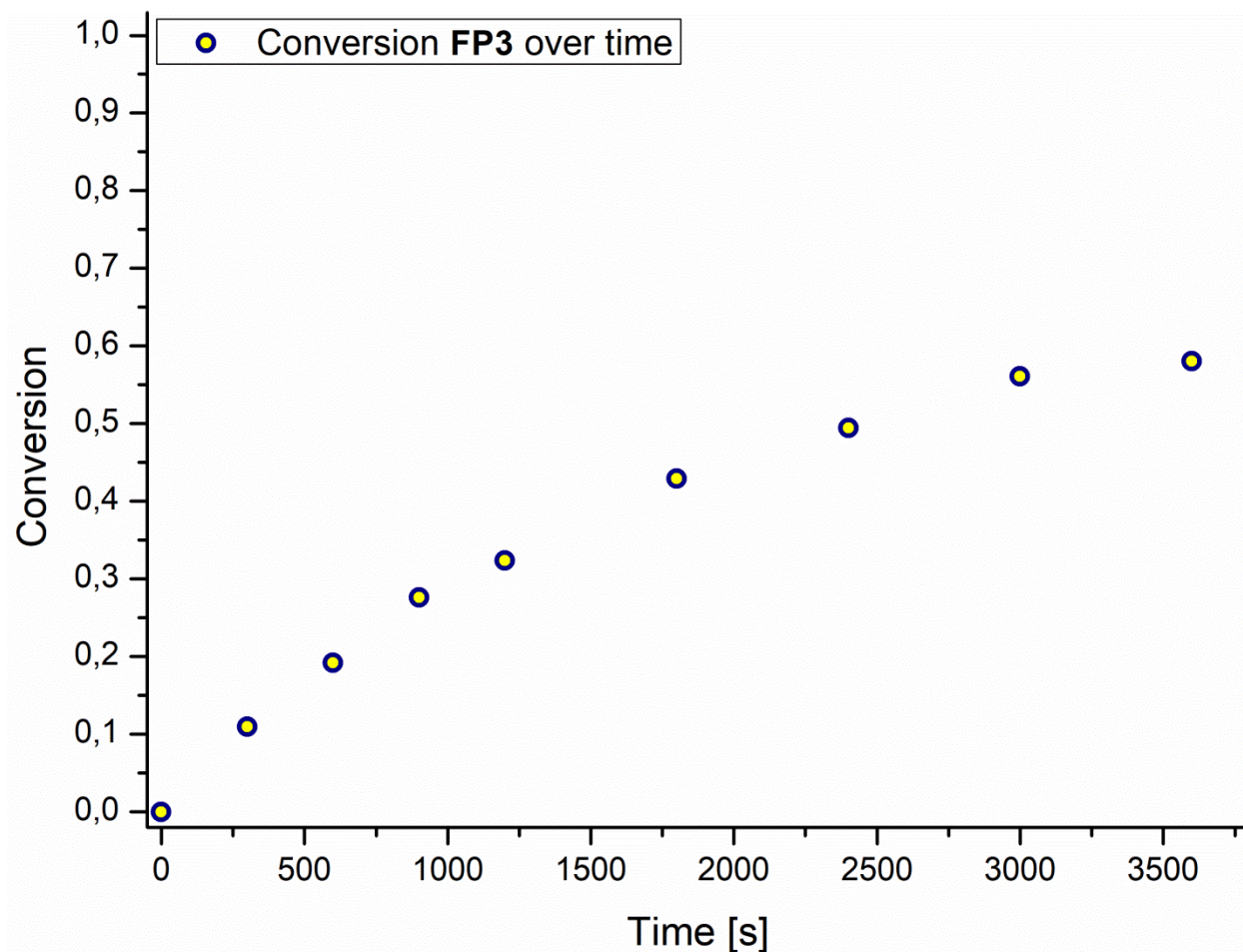
**Fig. S112.** Reaction scheme copolymerization 2(5H)-furanone with dodecyl vinyl ether (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S30.** Kinetic studies of the copolymerization of 2(5H)-furanone with dodecyl vinyl ether (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.

Furanone-vinyl-ether-copolymer FP3						
	Furanone		Dodecyl vinyl ether		k(obs)	(2.7±0.1)·10 <sup>-4</sup> [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,93	2,15	0,75	2,15	0,00	0,00
300	0,89	2,07	0,61	1,76	0,11	0,12
600	0,86	1,99	0,52	1,49	0,19	0,21
900	0,81	1,87	0,43	1,24	0,28	0,32
1200	0,78	1,81	0,38	1,10	0,32	0,39
1800	0,72	1,66	0,28	0,79	0,43	0,56
2400	0,68	1,57	0,21	0,61	0,49	0,68
3000	0,65	1,50	0,14	0,39	0,56	0,82
3600	0,62	1,43	0,13	0,38	0,58	0,87

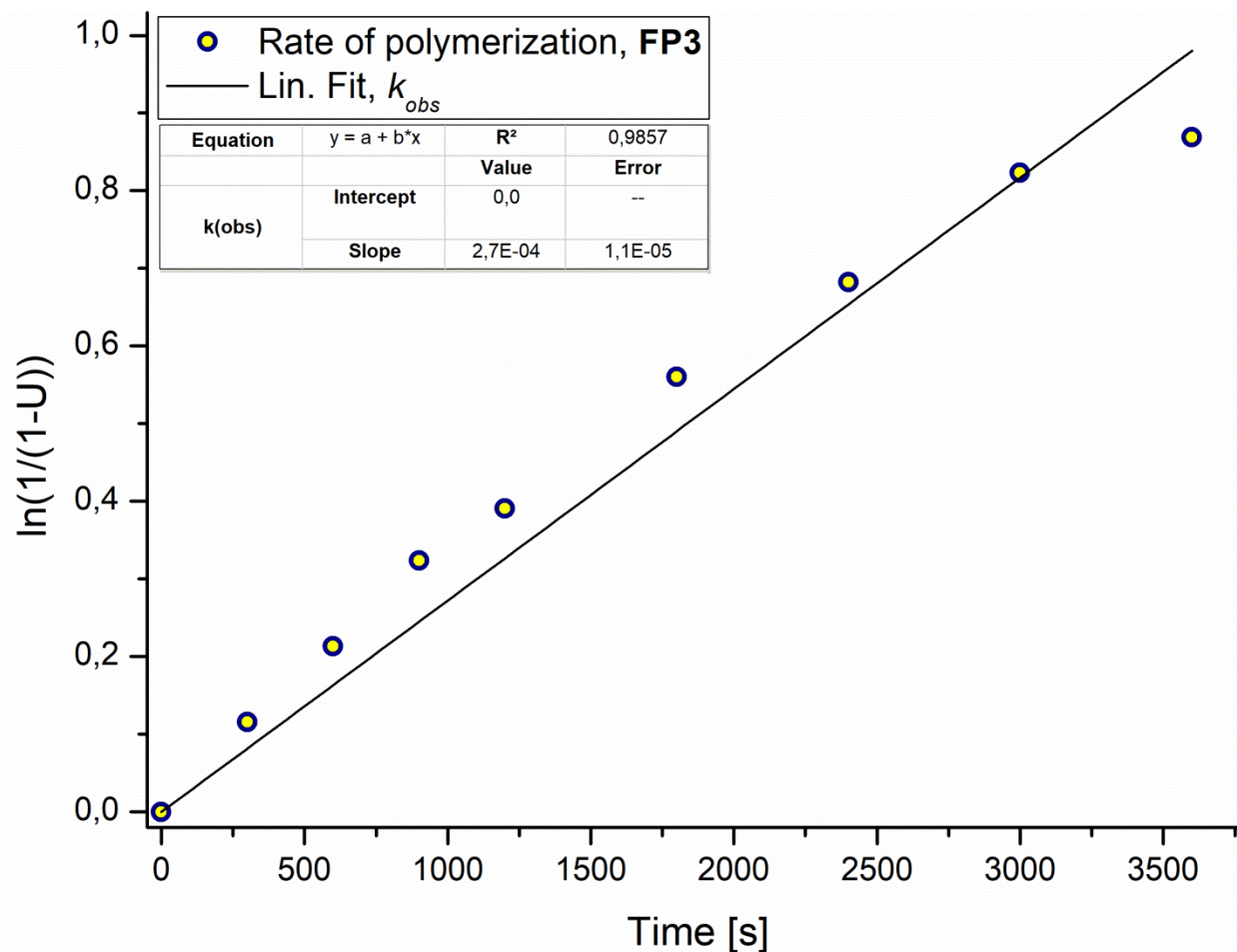


**Fig. S113.** Concentration of monomers over time of the copolymerization of 2(5H)-furanone with dodecyl vinyl ether (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.



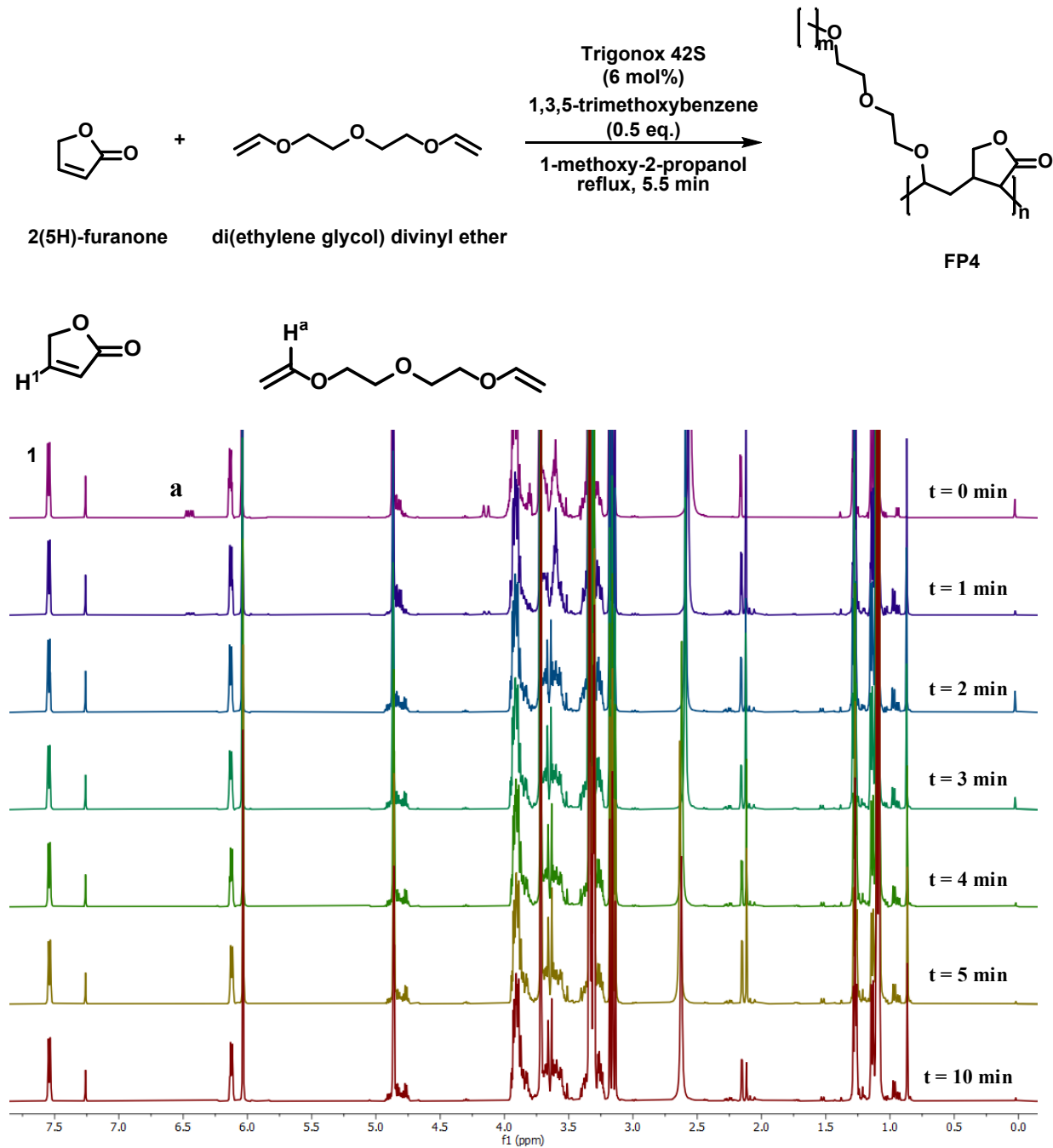
**Fig. S114.** Conversion of polymer **FP3** over time; copolymerization of 2(5H)-furanone with dodecyl vinyl ether (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.





**Fig. S115.** Rate of copolymerization of 2(5H)-furanone with dodecyl vinyl ether (1:1 ratio) to **FP3** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h.

## 2(5H)-furanone-di(ethylene glycol)-di-vinyl-ether-copolymer FP4

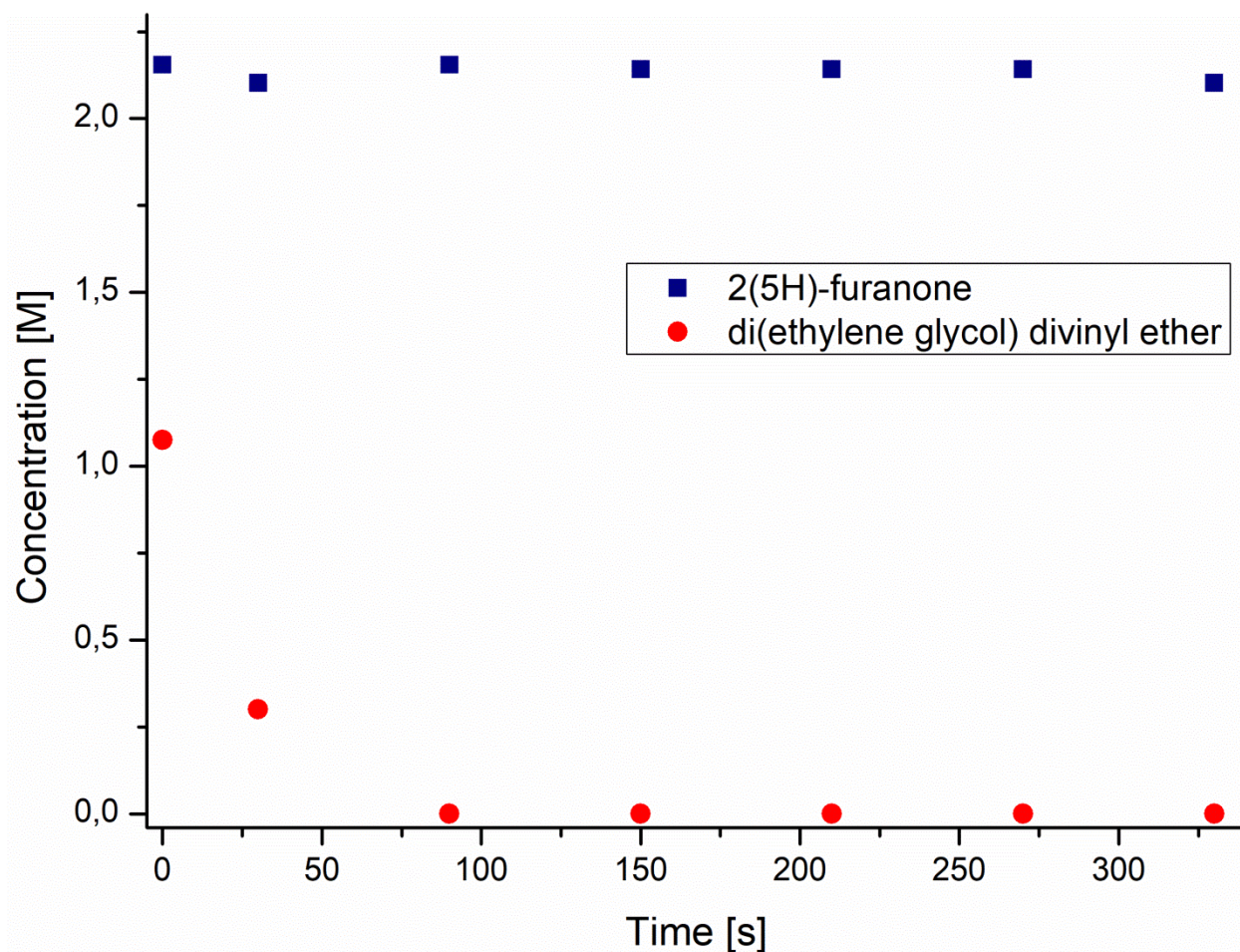


**Fig. S116.** Reaction scheme copolymerization 2(5H)-furanone with di(ethylene glycol) divinyl ether (1:0.5 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for di(ethylene glycol) divinyl ether), reflux, 5.5 min (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

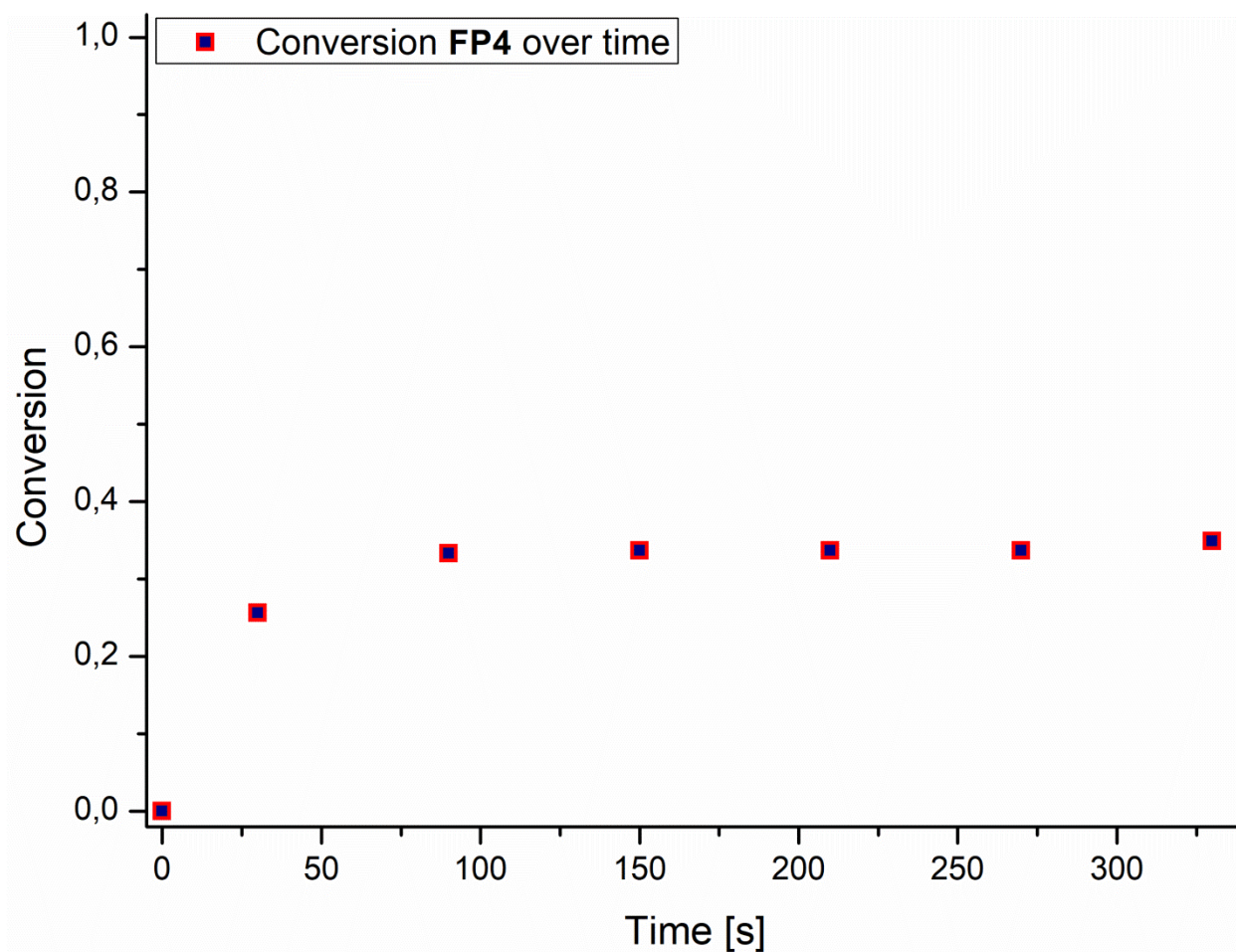


**Table S31.** Kinetic studies of the copolymerization of 2(5H)-furanone with di(ethylene glycol) divinyl ether (1:0.5 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for di(ethylene glycol) divinyl ether), reflux, 5.5 min.

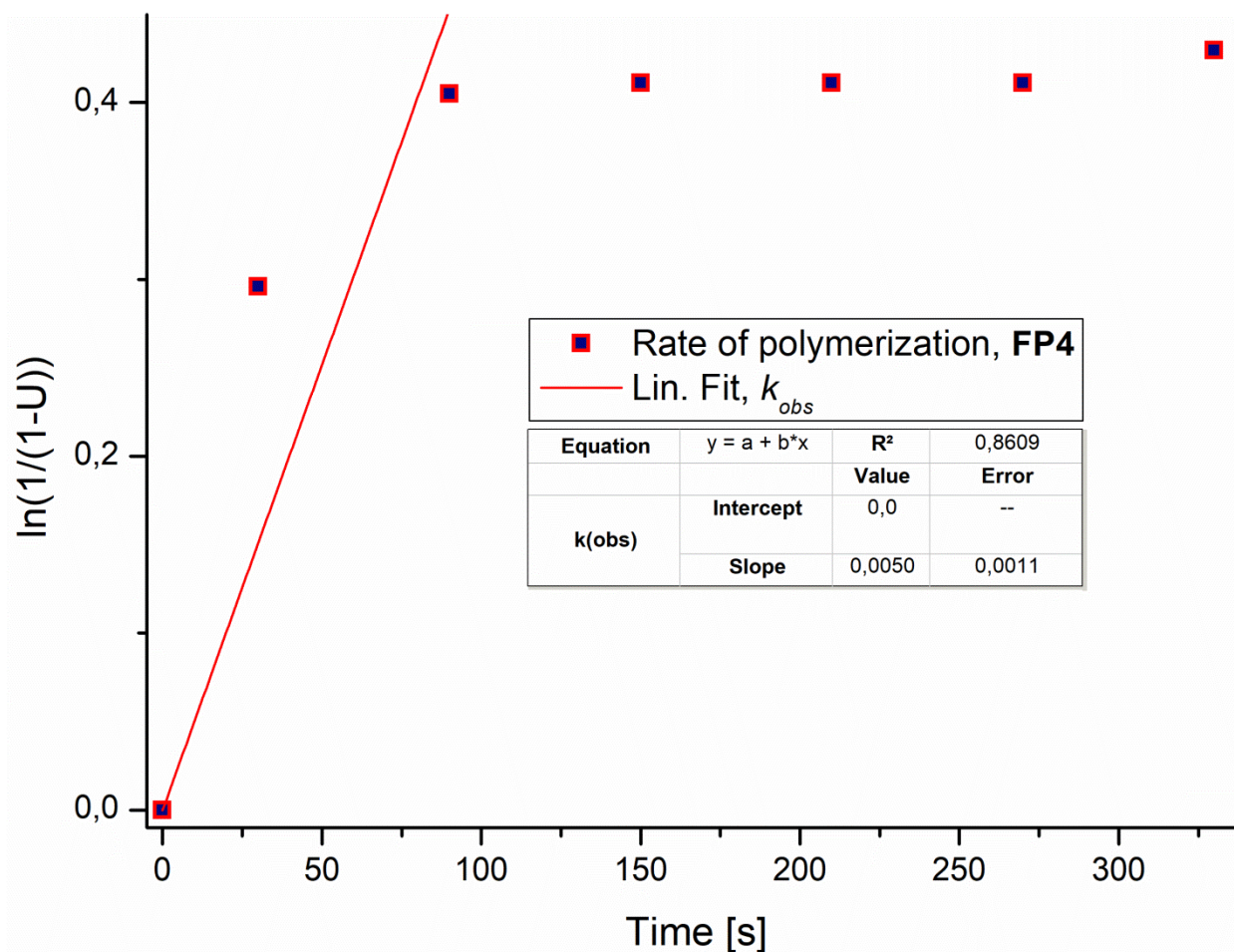
Furanone-DVE-copolymer FP4						
	Furanone		Di(ethylene glycol) divinyl ether		k(obs)	$(5.0 \pm 1.1) \cdot 10^{-3}$ [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	0,83	2,15	0,74	1,08	0,00	0,00
30	0,81	2,10	0,20	0,30	0,26	0,30
90	0,83	2,15	0,00	0,00	0,33	0,40
150	0,82	2,14	0,00	0,00	0,34	0,41
210	0,82	2,14	0,00	0,00	0,34	0,41
270	0,82	2,14	0,00	0,00	0,34	0,41
330	0,81	2,10	0,00	0,00	0,35	0,43



**Fig. S117.** Concentration of monomers over time of the copolymerization of 2(5H)-furanone with di(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 5.5 min.

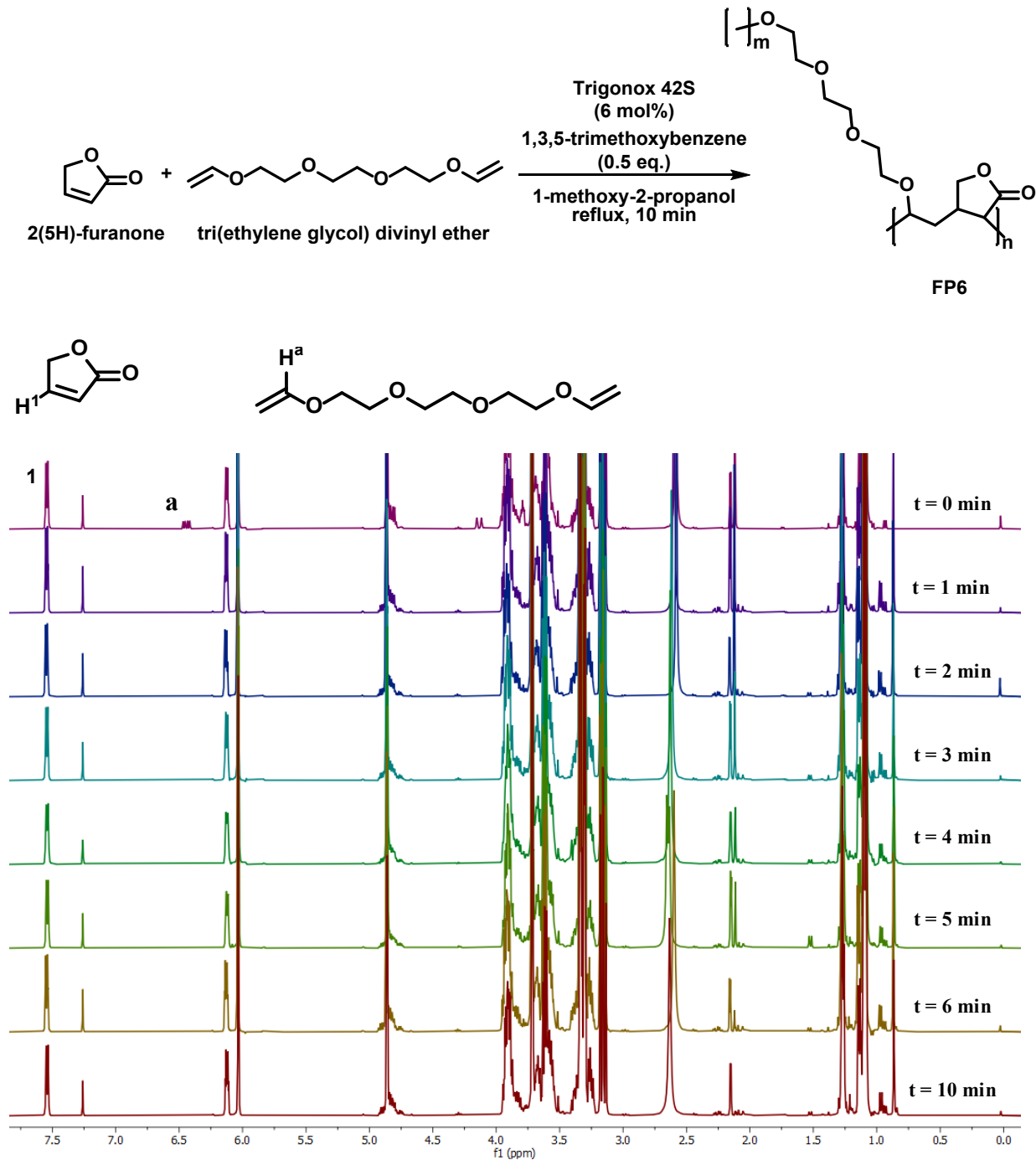


**Fig. S118.** Conversion of polymer **FP4** over time; copolymerization of 2(5H)-furanone with di(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 5.5 min.



**Fig. S119.** Rate of copolymerization of 2(5H)-furanone with di(ethylene glycol) divinyl ether (1:0.5 ratio) to **FP4** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 5.5 min.

## 2(5H)-furanone-tri(ethylene glycol)-di-vinyl-ether-copolymer FP6

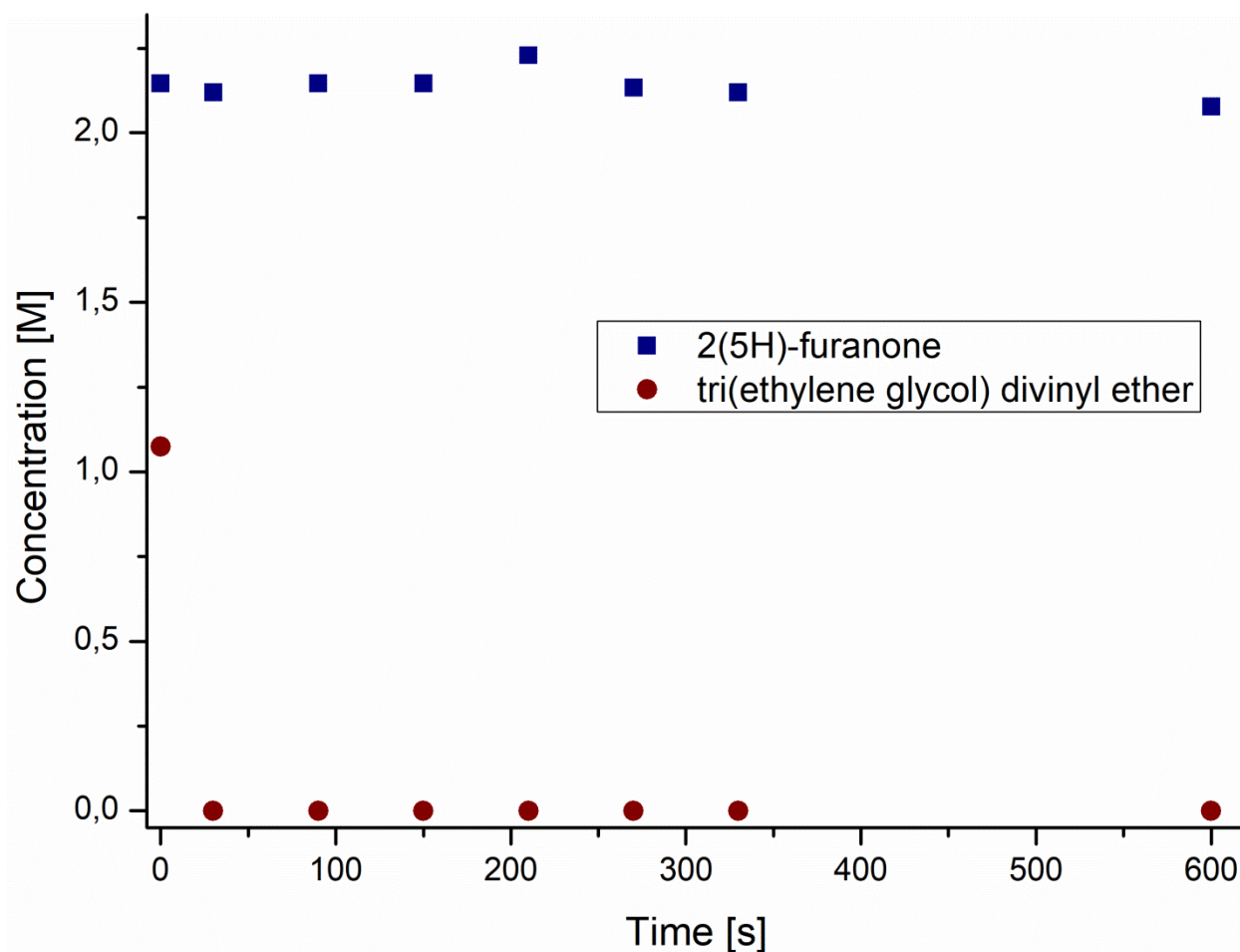


**Fig. S120.** Reaction scheme copolymerization 2(5H)-furanone with tri(ethylene glycol) divinyl ether (1:0.5 ratio), reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for tri(ethylene glycol) divinyl ether), reflux, 10 min (top).  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

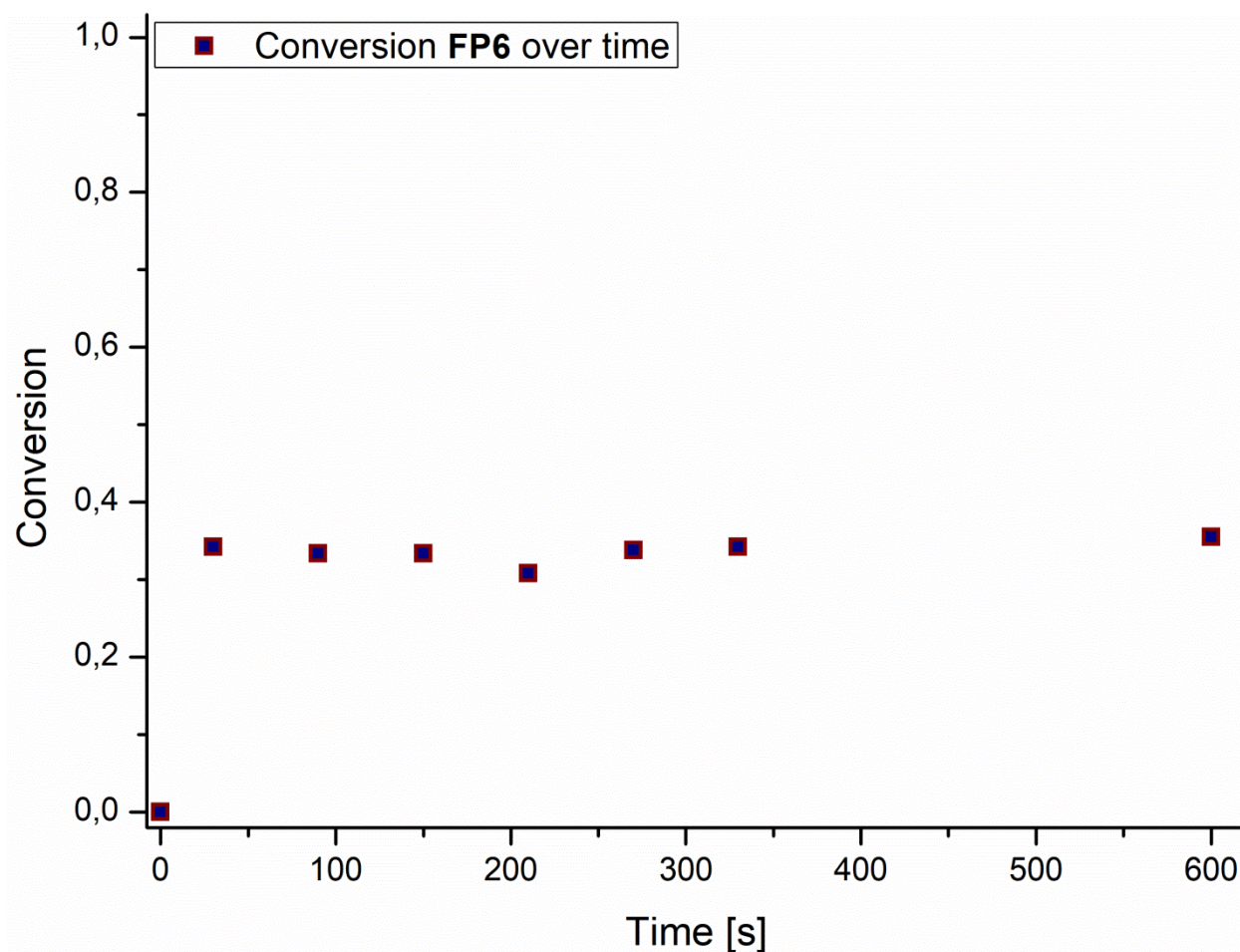
**Table S32** Kinetic studies of the copolymerization of 2(5H)-furanone with tri(ethylene glycol) divinyl ether (1:0.5 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol (1.075 M for tri(ethylene glycol) divinyl ether), reflux, 10 min.

Furanone-TVE-copolymer FP6						
	Furanone		Tri(ethylene glycol) divinyl ether		k(obs)	$(1.4 \pm 0.1) \cdot 10^{-2}$ [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	0,78	2,15	0,60	1,08	0,00	0,00
30	0,77	2,12	0,00	0,00	0,34	0,42
90	0,78	2,15	0,00	0,00	0,33	0,41
150	0,78	2,15	0,00	0,00	0,33	0,41
210	0,81	2,23	0,00	0,00	0,31	0,37
270	0,78	2,13	0,00	0,00	0,34	0,41
330	0,77	2,12	0,00	0,00	0,34	0,42
600	0,76	2,08	0,00	0,00	0,36	0,44

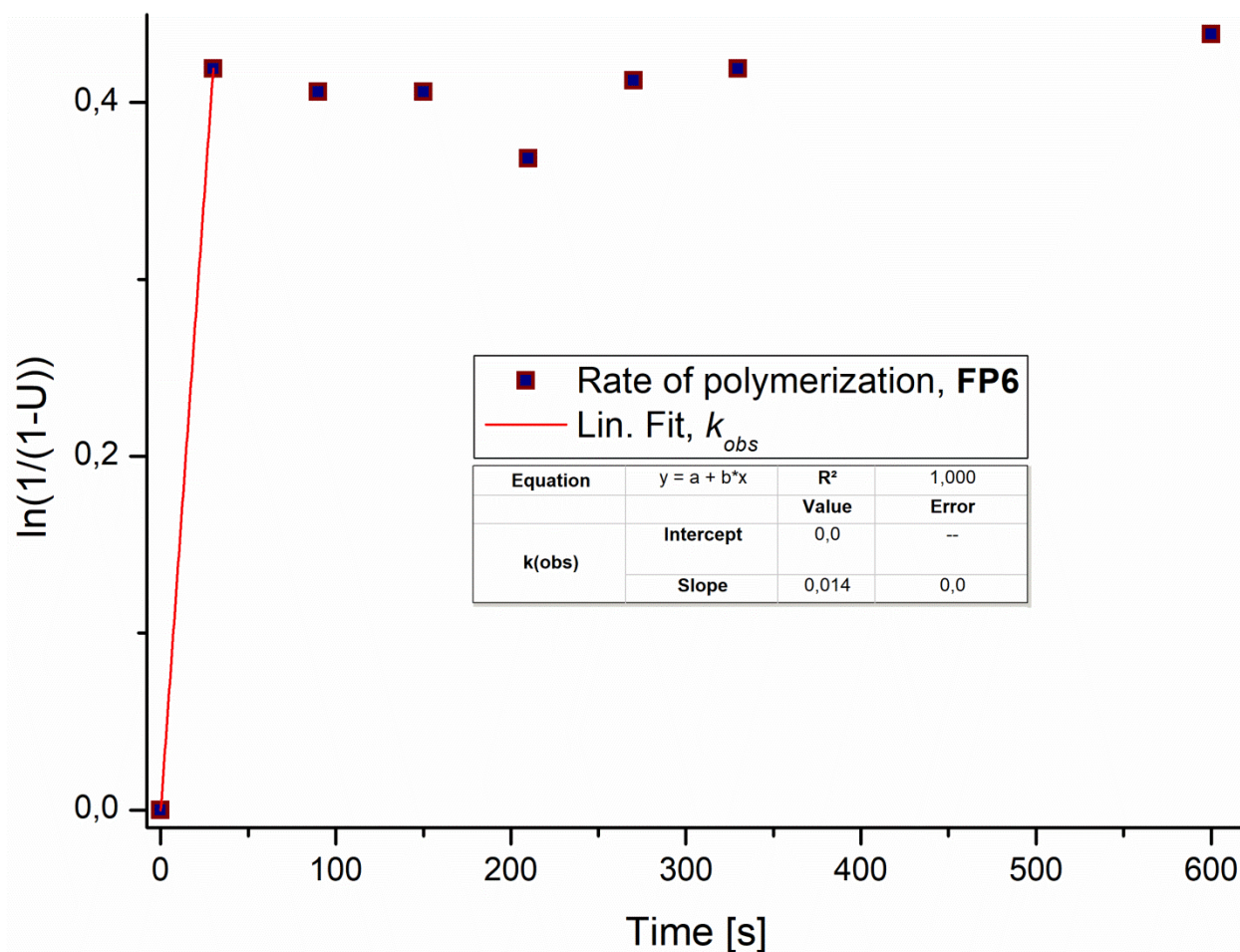




**Fig. S121.** Concentration of monomers over time of the copolymerization of 2(5H)-furanone with tri(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 10 min.



**Fig. S122.** Conversion of polymer **FP6** over time; copolymerization of 2(5H)-furanone with tri(ethylene glycol) divinyl ether (1:0.5 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 10 min.



**Fig. S123.** Rate of copolymerization of 2(5H)-furanone with tri(ethylene glycol) divinyl ether (1:0.5 ratio) to **FP6** over time; followed by <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 10 min.

## Effect of polymer concentration on the reaction kinetics

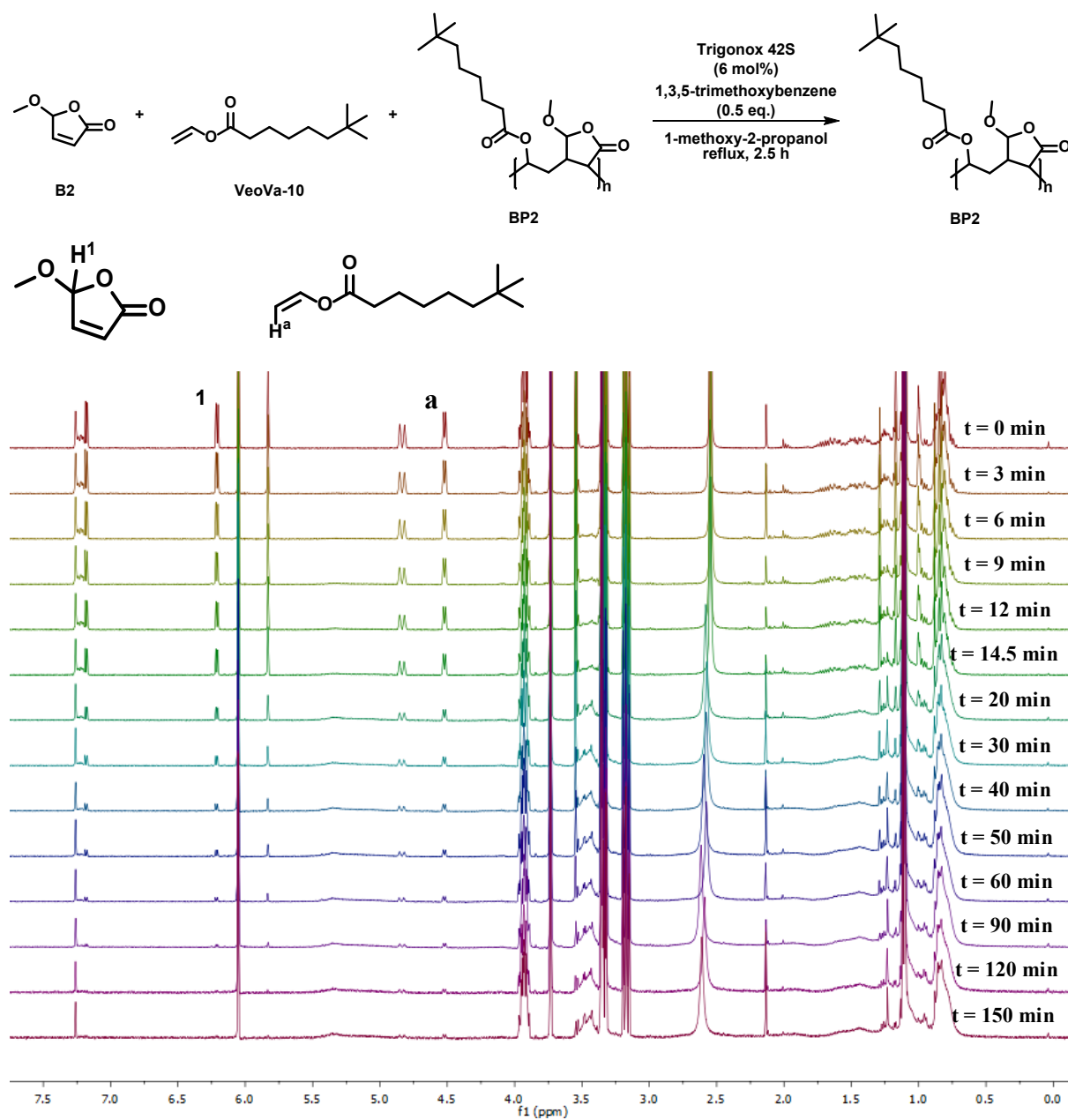
To determine whether the concentration of polymer has an influence on the occurrence of a second rate, resulting in an inhibited conversion, visible in homo-polymerizations **BP1**, **HP1**, **IP1**, **MP1** and in copolymerizations **HP2**, **MP2**, **MMP1**, the reaction rate of the polymerization was followed while additional respective polymer was added at an earlier point during the polymerization. In this way, the concentration of polymer suddenly increases. To prevent inconvenience during the addition of the extra polymer the polymer was added in solution (2.15 M). The concentration for the monomer is therefore halved at the addition. To exclude dilution effects the reaction kinetics were followed for the copolymerizations of **BP2** and **MP2** at (1.075 M).

Although neither a second rate nor an inhibited conversion was found for polymer **BP2**, the experiment was conducted for **BP2**. However upon addition of polymer **BP2** at  $t = 15$  min, a smaller rate constant was found, blue line **Fig. S127**. The reaction was inhibited at 96% conversion. Control experiments under diluted conditions (**Fig. S131**) resulted in a similar rate constant as obtained in the copolymerization of **BP2** (**Fig. S19**).

Since a second rate and inhibited conversion was obtained for polymer **MP2**, the experiment was conducted for **MP2**. Upon addition of polymer **MP2** at  $t = 40$  min, a similar small second rate constant was found, now at an earlier stage in the polymerization (blue line **Fig. S135**), as was also found in the standard copolymerization **MP2** (**Fig. S71**). The reaction was now inhibited at 74% conversion. Control experiments under diluted conditions (**Fig. S139**) resulted in a similar rate constant as obtained in the copolymerization of **MP2** (**Fig. S71**). Control experiments with 12 mol% Trigonox 42S, double concentration initiator, were conducted to exclude an effect caused by higher concentration of initiator since unreacted initiator could be present in the pre-synthesized polymer. These experiments showed the increasing concentration of polymer is the main rationale for a secondary radical process. As proposed, inhibition of polymerization is caused by C-H abstraction by a propagating radical of the labile acetal proton of the formed polymer, however our hypothesis remains inconclusive as inhibition of polymerization was also present in the copolymerization of methylmethoxybutenolide **B6**, bearing a methyl group at the acetal position, **Fig. S83**.

### **5-methoxy-2(5H)-furanone-VeoVa-10-copolymer BP2**

Copolymer **BP2** was synthesized according to **General Procedure A** with a conversion of >99%. The solvent (1-methoxy-2-propanol) was not evaporated to prevent inconvenience during the addition of the polymer. Remaining non-decomposed radical initiator was not removed from the reaction mixture. 1 mL of a 2.15 M solution of **BP2** in 1-methoxy-2-propanol was added during the polymerization at t=15 min. Additional experiments to exclude dilution effects were conducted.

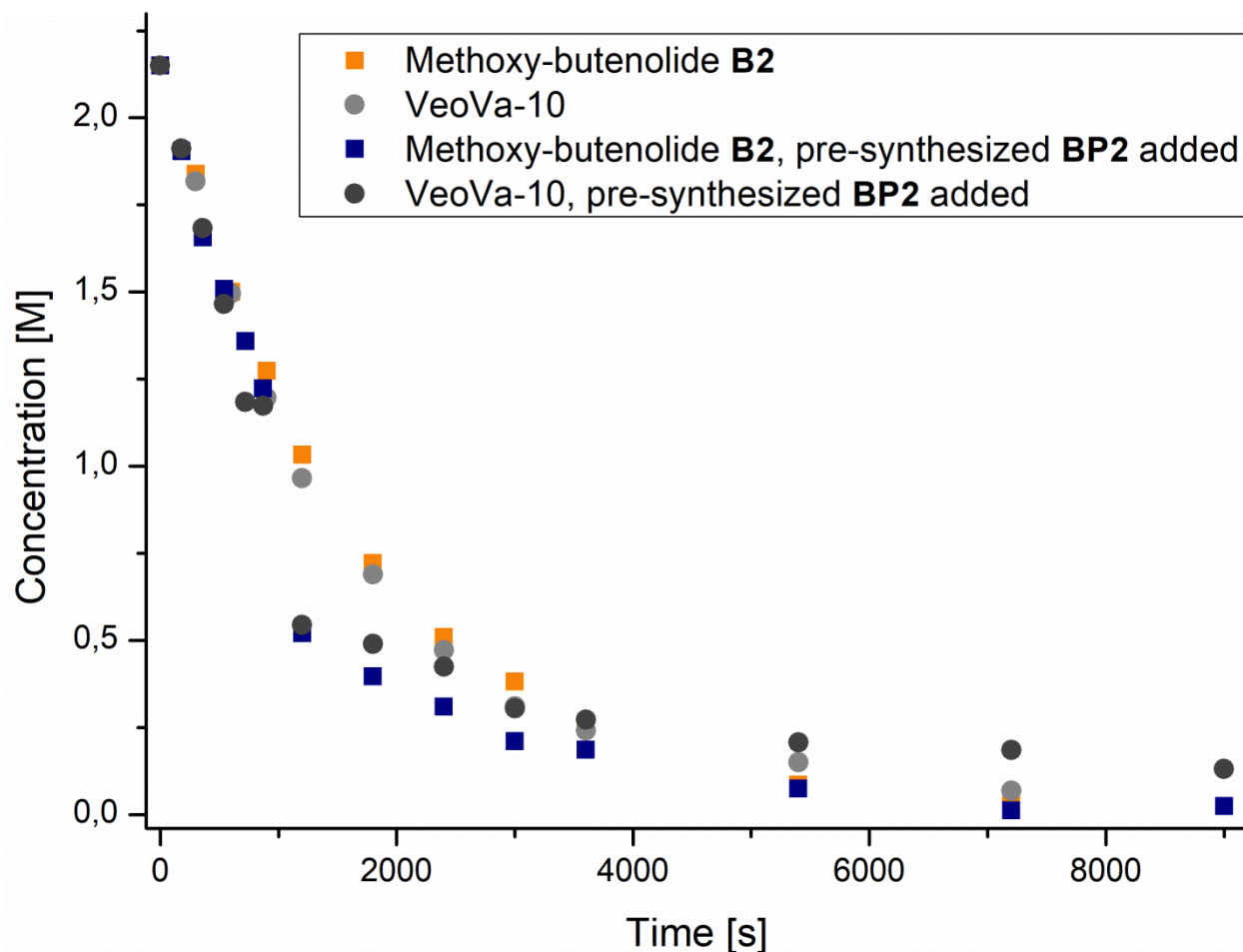


**Fig. S124.** Reaction scheme copolymerization methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) with addition of pre-synthesized methoxybutenolide-VeoVa-10-copolymer **BP2** (1 mL 2.15 M solution in 1-methoxy-2-propanol) added at  $t = 15$  min, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2.5 h (top).  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

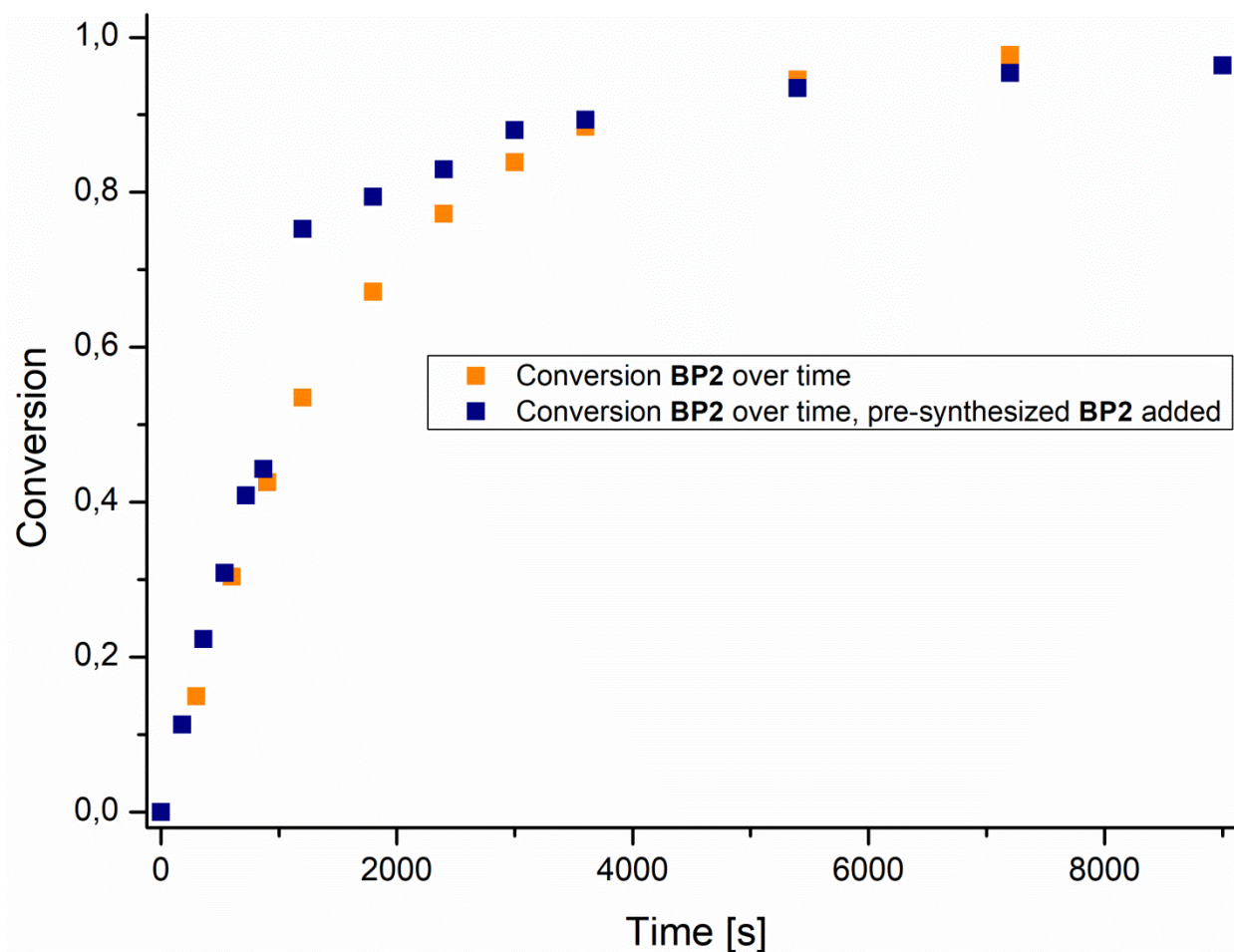


**Table S33.** Kinetic studies of the copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) with addition of pre-synthesized methoxybutenolide-VeoVa-10-copolymer **BP2** (1 mL 2.15 M solution in 1-methoxy-2-propanol) added at  $t = 15$  min, followed by  $^1\text{H NMR}$  spectroscopy. Integrated  $^1\text{H NMR}$  signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2.5 h.

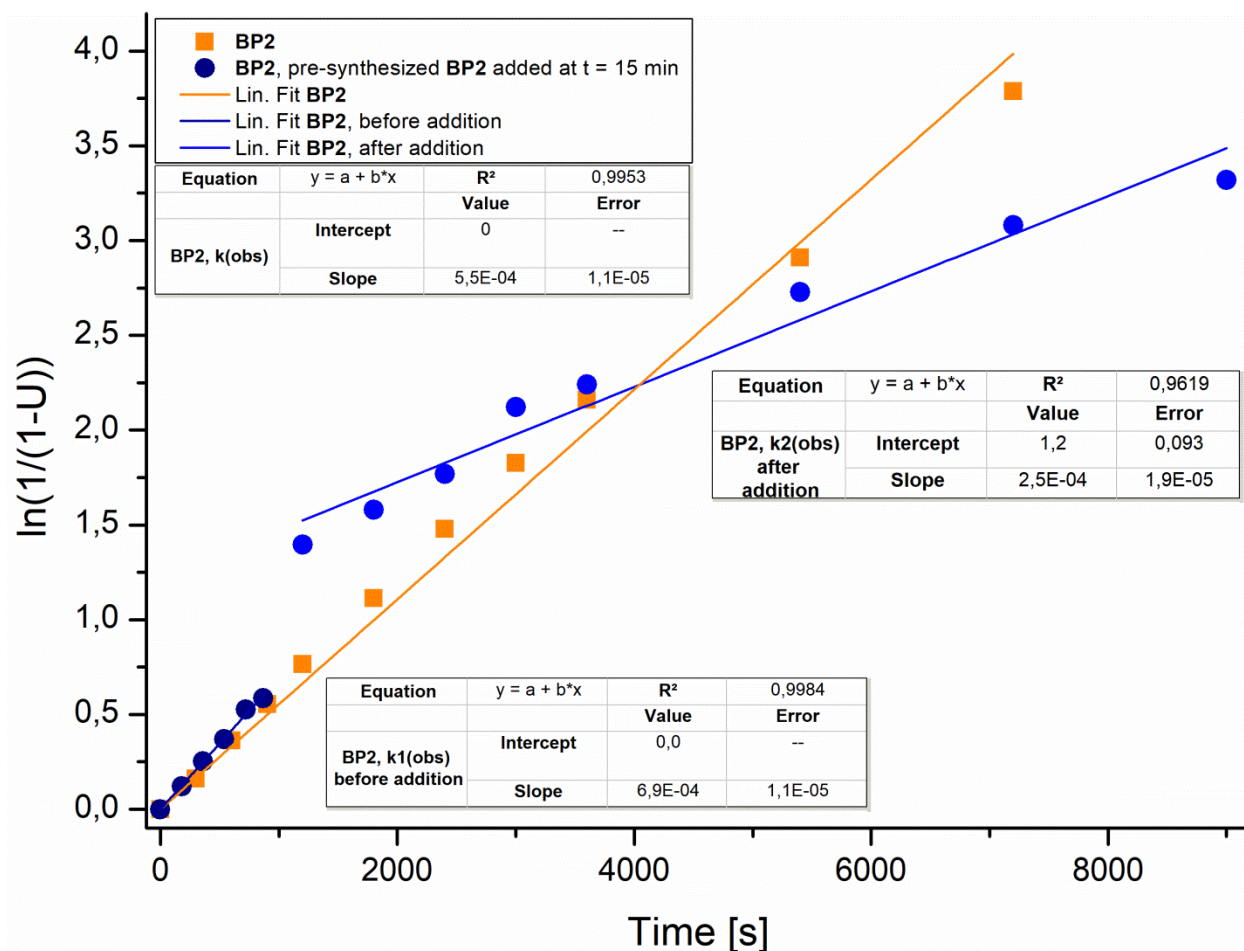
Methoxybutenolide-VeoVa-10-copolymer BP2, additional polymer added					k1(obs)	$(6.9 \pm 0.1) \cdot 10^{-4}$ [s <sup>-1</sup> ]
Methoxybutenolide B2			VeoVa-10		k2(obs)	$(2.5 \pm 0.2) \cdot 10^{-4}$ [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	0,87	2,15	0,99	2,15	0,00	0,00
180	0,77	1,90	0,88	1,91	0,11	0,12
360	0,67	1,66	0,78	1,68	0,22	0,25
540	0,61	1,51	0,68	1,47	0,31	0,37
720	0,55	1,36	0,55	1,18	0,41	0,53
870	0,50	1,22	0,54	1,17	0,44	0,58
1200	0,42	0,52	0,50	0,54	0,75	1,40
1800	0,32	0,40	0,45	0,49	0,79	1,58
2400	0,25	0,31	0,39	0,42	0,83	1,77
3000	0,17	0,21	0,28	0,30	0,88	2,12
3600	0,15	0,19	0,25	0,27	0,89	2,24
5400	0,06	0,07	0,19	0,21	0,93	2,73
7200	0,01	0,01	0,17	0,19	0,95	3,08
9000	0,02	0,02	0,12	0,13	0,96	3,32



**Fig. S125.** Concentration of monomers over time of the copolymerization of methoxybutenolide **B2** (orange square) with VeoVa-10 (grey circle) (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time. Concentration of the monomers over time, with pre-synthesized polymer **BP2** added at  $t = 15$  min, of the copolymerization of methoxybutenolide **B2** (navy blue square) and VeoVa-10 (dark grey circle) followed by  $^1\text{H}$ NMR signals. 1 mL of a 2.15 M solution of **BP2** in 1-methoxy-2-propanol was added during the polymerization at  $t = 15$  min. Samples for  $^1\text{H}$ NMR were taken at certain timestamps and flash frozen ( $-18^\circ\text{C}$ ) and quantified by using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2.5 h.

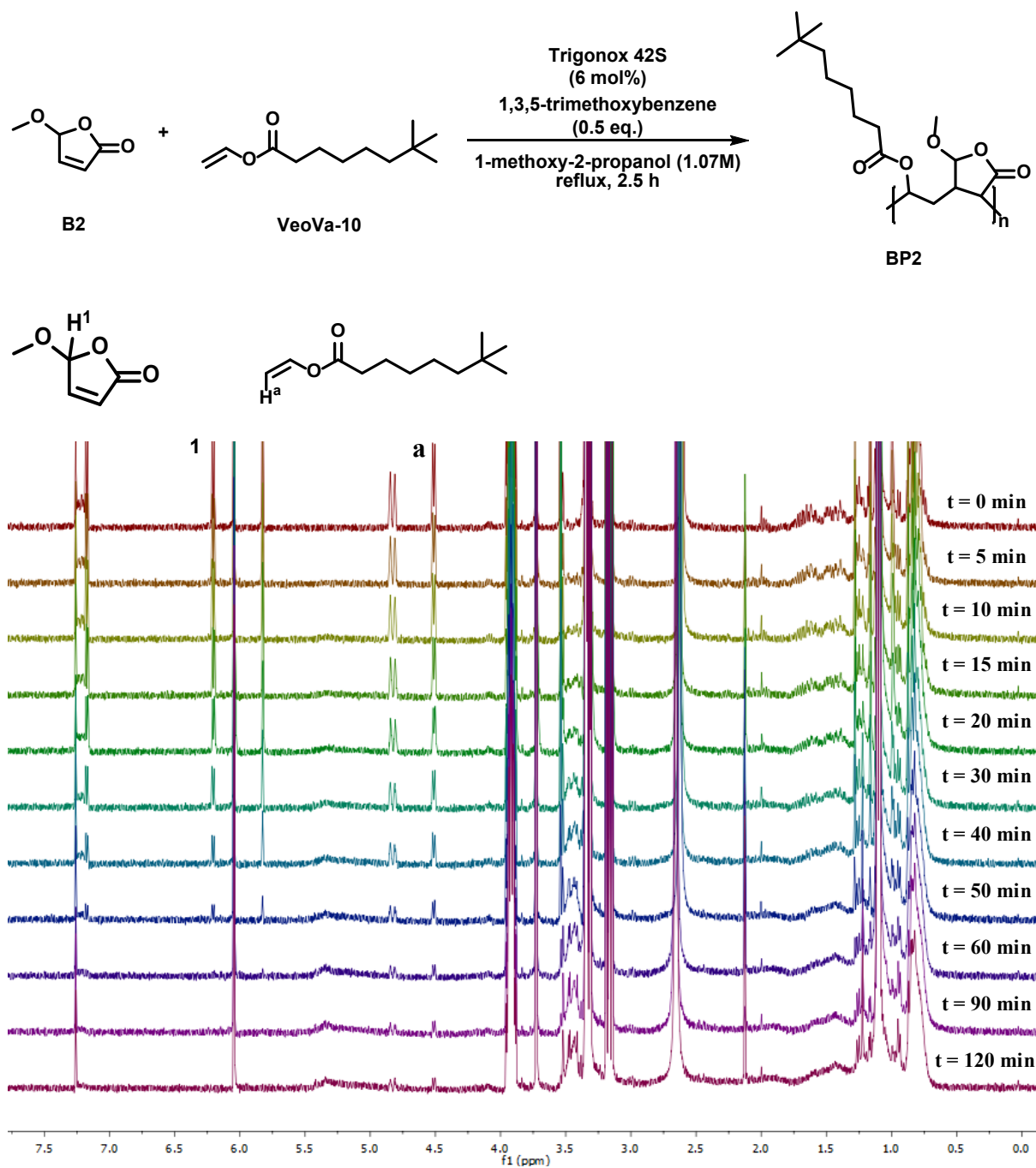


**Fig. S126.** Conversion of polymer **BP2** (orange square) over time; copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time. Conversion of polymer **BP2** (navy blue square) over time, with pre-synthesized polymer **BP2** added at  $t = 15$  min, of the copolymerization of methoxybutenolide **B2** and VeoVa-10 followed by  $^1\text{H}$ NMR signals. 1 mL of a 2.15 M solution of **BP2** in 1-methoxy-2-propanol was added during the polymerization at  $t = 15$  min. Samples for  $^1\text{H}$ NMR were taken at certain timestamps and flash frozen ( $-18^\circ\text{C}$ ) and quantified by using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2.5 h.



**Fig. S127.** Rate of copolymerization and inhibition after addition of pre-synthesized copolymer **BP2**. Copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio, orange) followed by  $^1\text{H}$ NMR signals over time. Copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio, dark blue line) until  $t = 900$  s. Inhibited polymerization of methoxybutenolide **B2** with VeoVa-10 after addition of pre-synthesized methoxybutenolide-VeoVa-10-copolymer **BP2** (1 mL 2.15 M solution in 1-methoxy-2-propanol, >99% conversion) (1:1 ratio, blue line) at  $t = 1200$  s. A lower reaction rate is obtained,  $k_{\text{obs}}^{\text{before}} = 5.5 \cdot 10^{-4} \text{ s}^{-1}$  and  $k_{\text{obs}}^{\text{after}} = 2.5 \cdot 10^{-4} \text{ s}^{-1}$ , for the induced inhibited polymerization at  $t = 1200$  s (blue line). Samples for  $^1\text{H}$ NMR were taken at certain timestamps and flash frozen ( $-18^\circ\text{C}$ ) and quantified by using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 2.5 h.

### 5-methoxy-2(5H)-furanone-VeoVa-10-copolymer BP2, half concentration

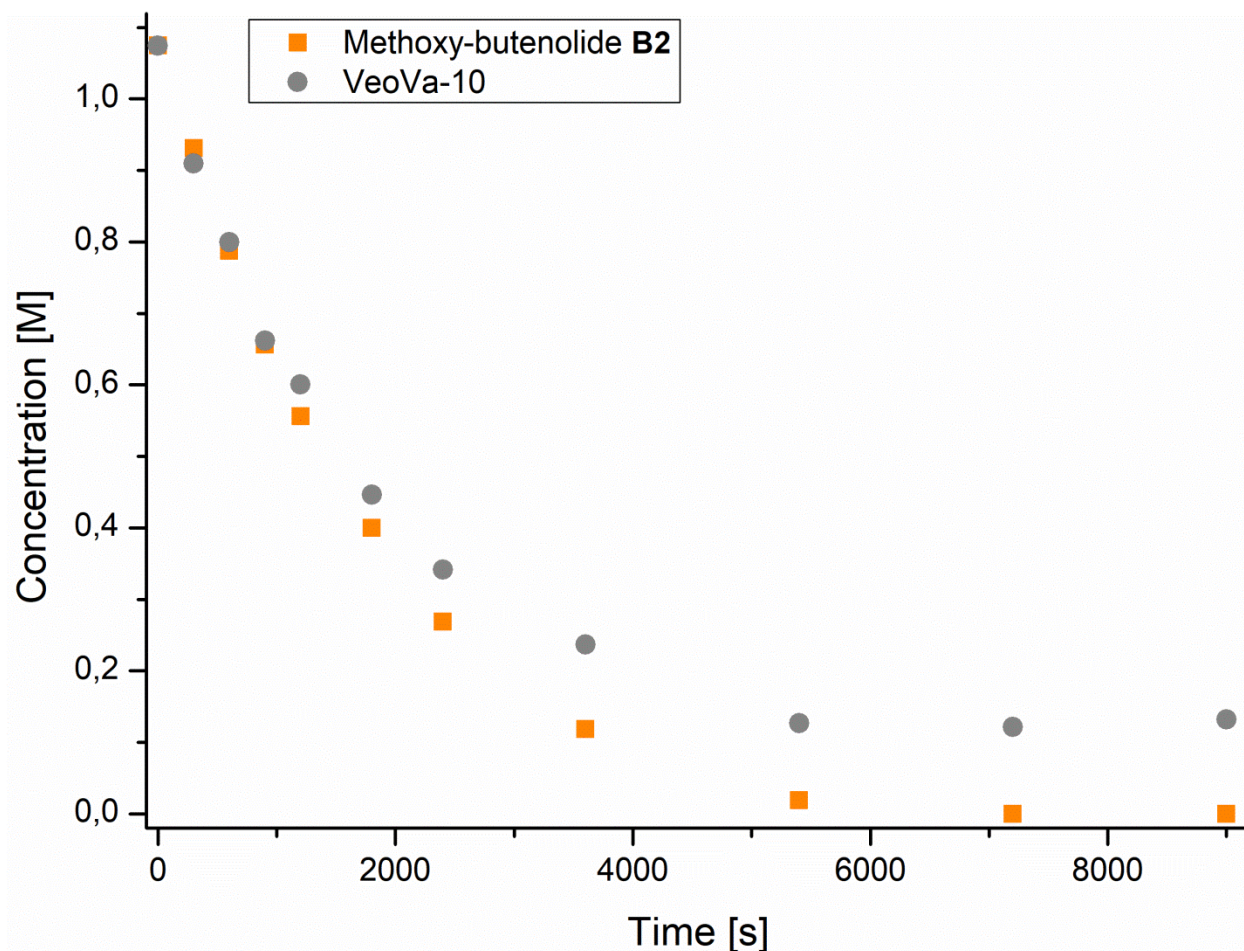


**Fig. S128** Reaction scheme copolymerization methoxybutenolide **B2** with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 1.07 M (2x diluted) in 1-methoxy-2-propanol to exclude dilution effects, reflux, 2.5 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

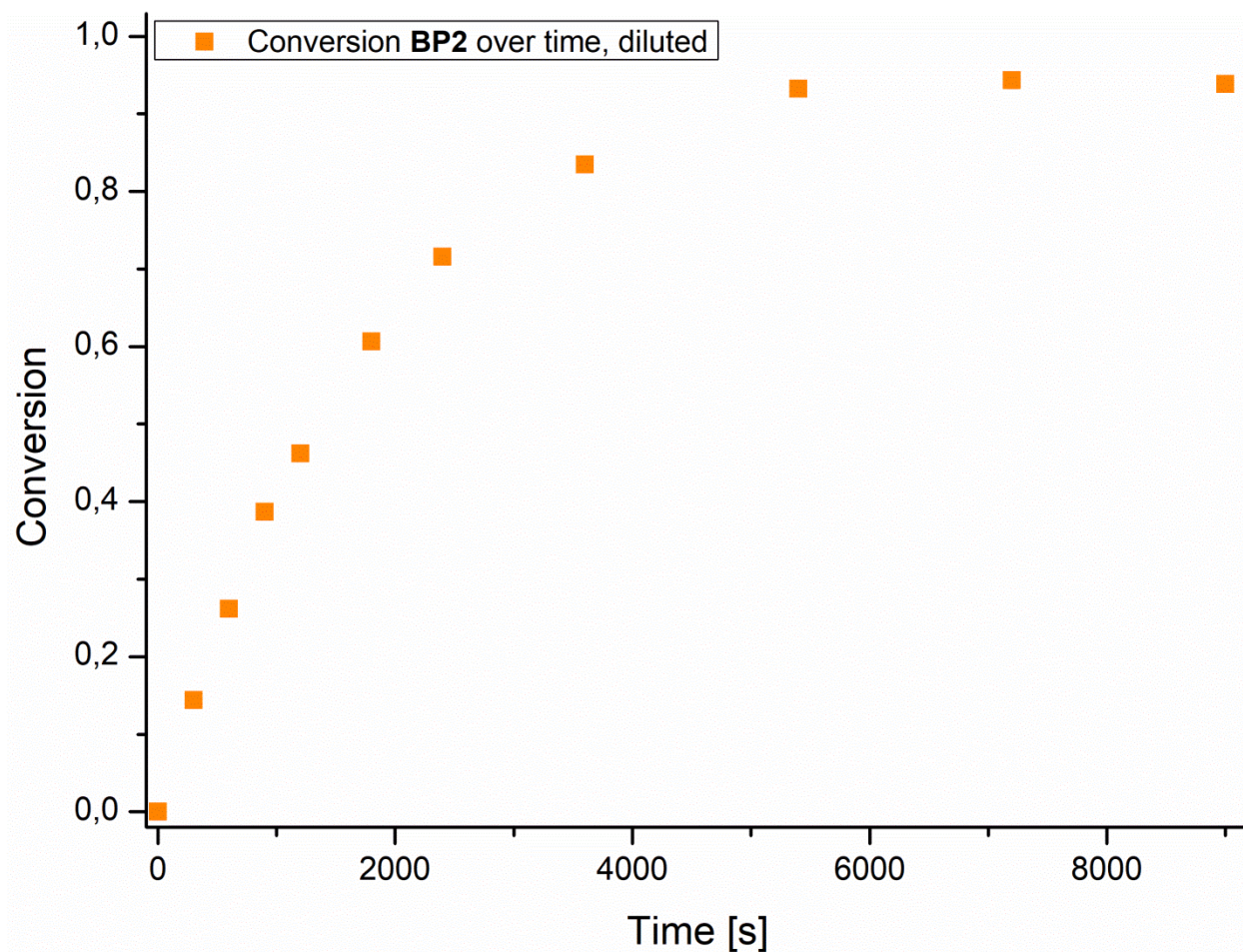
**Table S34.** Kinetic studies of the copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 1.07 M (2x diluted) in 1-methoxy-2-propanol to exclude dilution effects, reflux, 2.5 h.

<b>Methoxybutenolide-VeoVa-10-copolymer BP2, 2x diluted</b>						
	<b>Methoxybutenolide B2</b>		<b>VeoVa-10</b>		<b>k(obs)</b>	<b>(5.0±0.1)·10<sup>-4</sup> [s<sup>-1</sup>]</b>
<b>Time [s]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Integral</b>	<b>Concentration [mol/L]</b>	<b>Conversion</b>	<b>ln(1/[1-U])</b>
0	0,86	1,07	0,98	1,07	0,00	0,00
300	0,75	0,93	0,83	0,91	0,14	0,16
600	0,63	0,79	0,73	0,80	0,26	0,30
900	0,53	0,66	0,60	0,66	0,39	0,49
1200	0,45	0,56	0,55	0,60	0,46	0,62
1800	0,32	0,40	0,41	0,45	0,61	0,93
2400	0,22	0,27	0,31	0,34	0,72	1,26
3600	0,10	0,12	0,22	0,24	0,83	1,80
5400	0,02	0,02	0,12	0,13	0,93	2,69
7200	0,00	0,00	0,11	0,12	0,94	2,88
9000	0,00	0,00	0,12	0,13	0,94	2,79

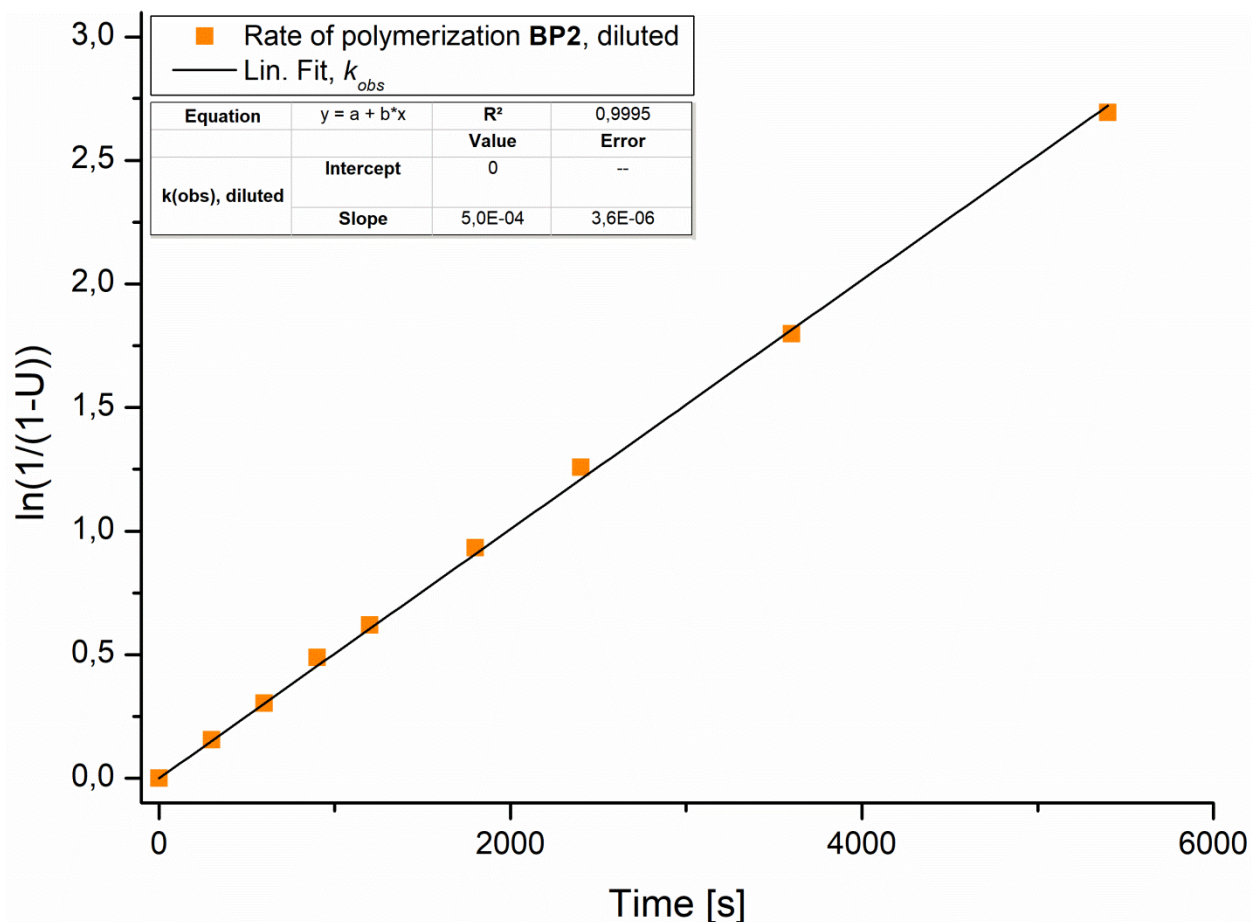




**Fig. S129.** Concentration of monomers over time of the copolymerization of methoxy-butenolide **B2** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 1.07 M (2x diluted) in 1-methoxy-2-propanol to exclude dilution effects, reflux, 2.5 h.



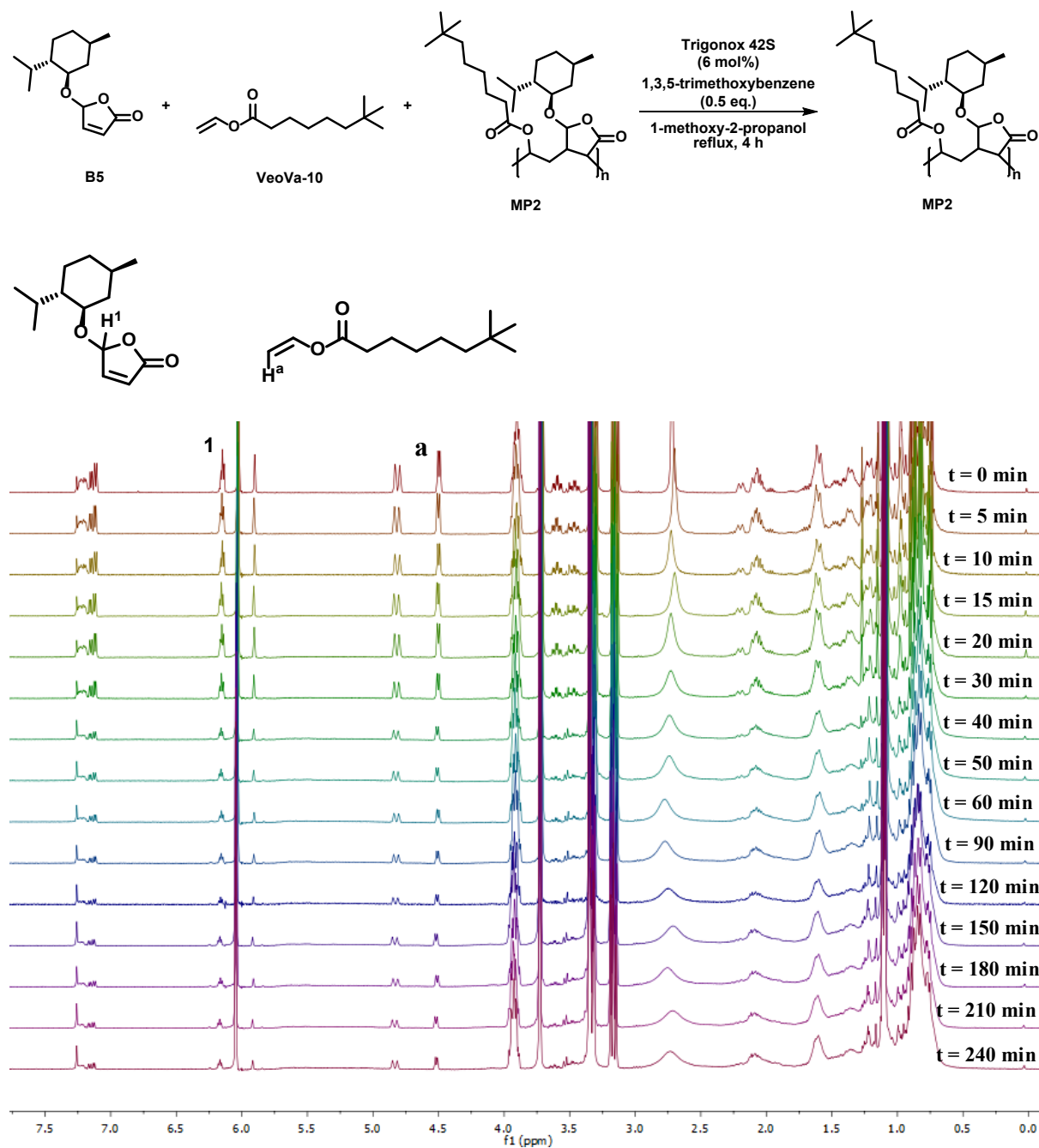
**Fig. S130.** Conversion of polymer **BP2** over time; copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 1.07 M (2x diluted) in 1-methoxy-2-propanol to exclude dilution effects, reflux, 2.5 h.



**Fig. S131.** Rate of copolymerization of methoxybutenolide **B2** with VeoVa-10 (1:1 ratio) to **BP2** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 1.07 M (2x diluted) in 1-methoxy-2-propanol to exclude dilution effects, reflux, 2.5 h.

### **5-menthyloxy-2(5H)-furanone-VeoVa-10-copolymer MP2**

Copolymer **MP2** was synthesized according to **General Procedure A** with a conversion of 92%. The solvent (1-methoxy-2-propanol) was not evaporated to prevent inconvenience during the addition of the polymer. Remaining non-decomposed radical initiator was not removed from the reaction mixture. 1 mL of a 2.15 M solution of **MP2** in 1-methoxy-2-propanol was added at t = 40 min. Additional experiments to exclude dilution effects were conducted. Additional experiments to exclude effects of higher concentrations of radical initiator were conducted.



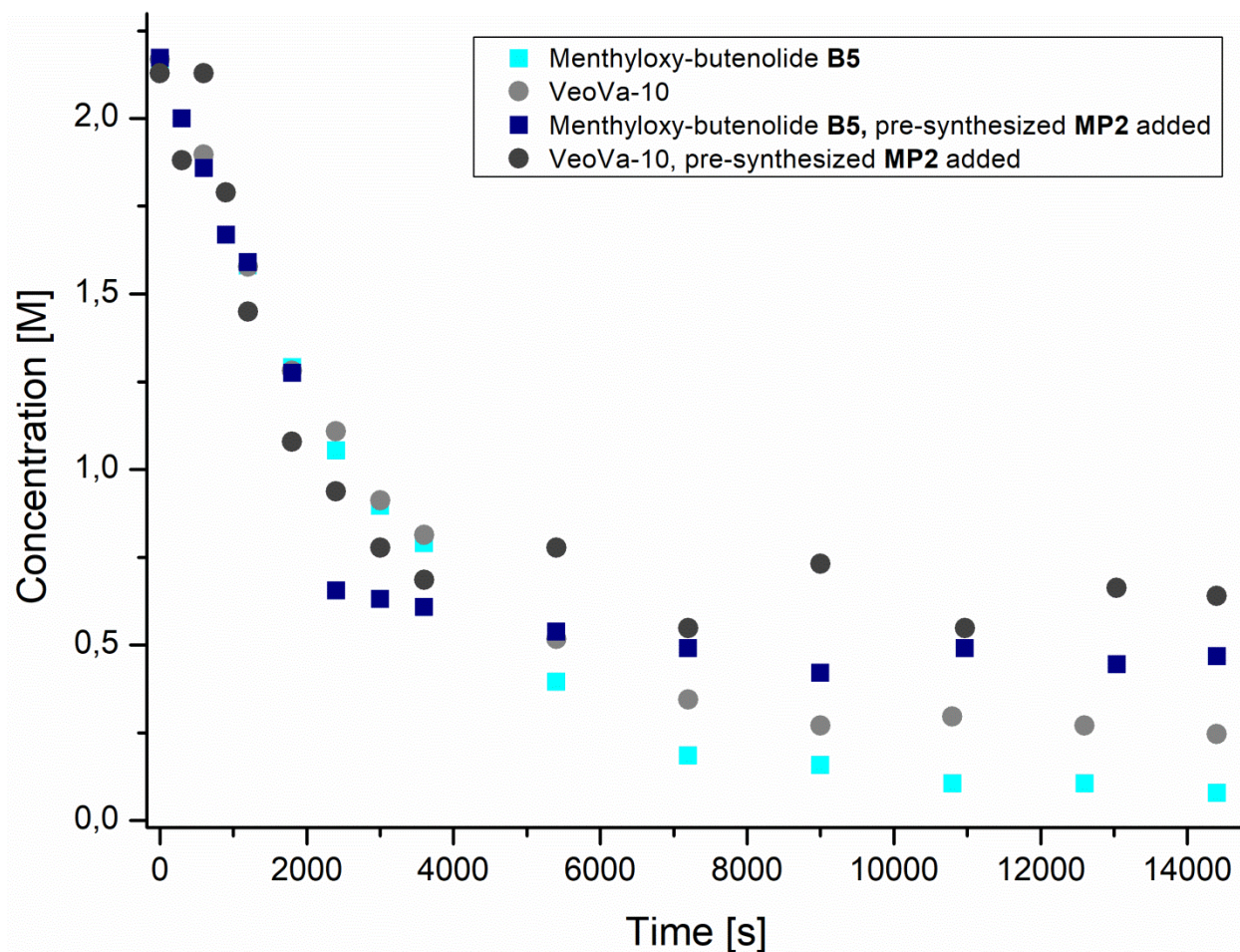
**Fig. S132.** Reaction scheme copolymerization menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) with addition of pre-synthesized menthyloxybutenolide-VeoVa-10-copolymer **MP2** (1 mL 2.15 M solution in 1-methoxy-2-propanol) added at  $t = 40$  min, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h (top).  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).



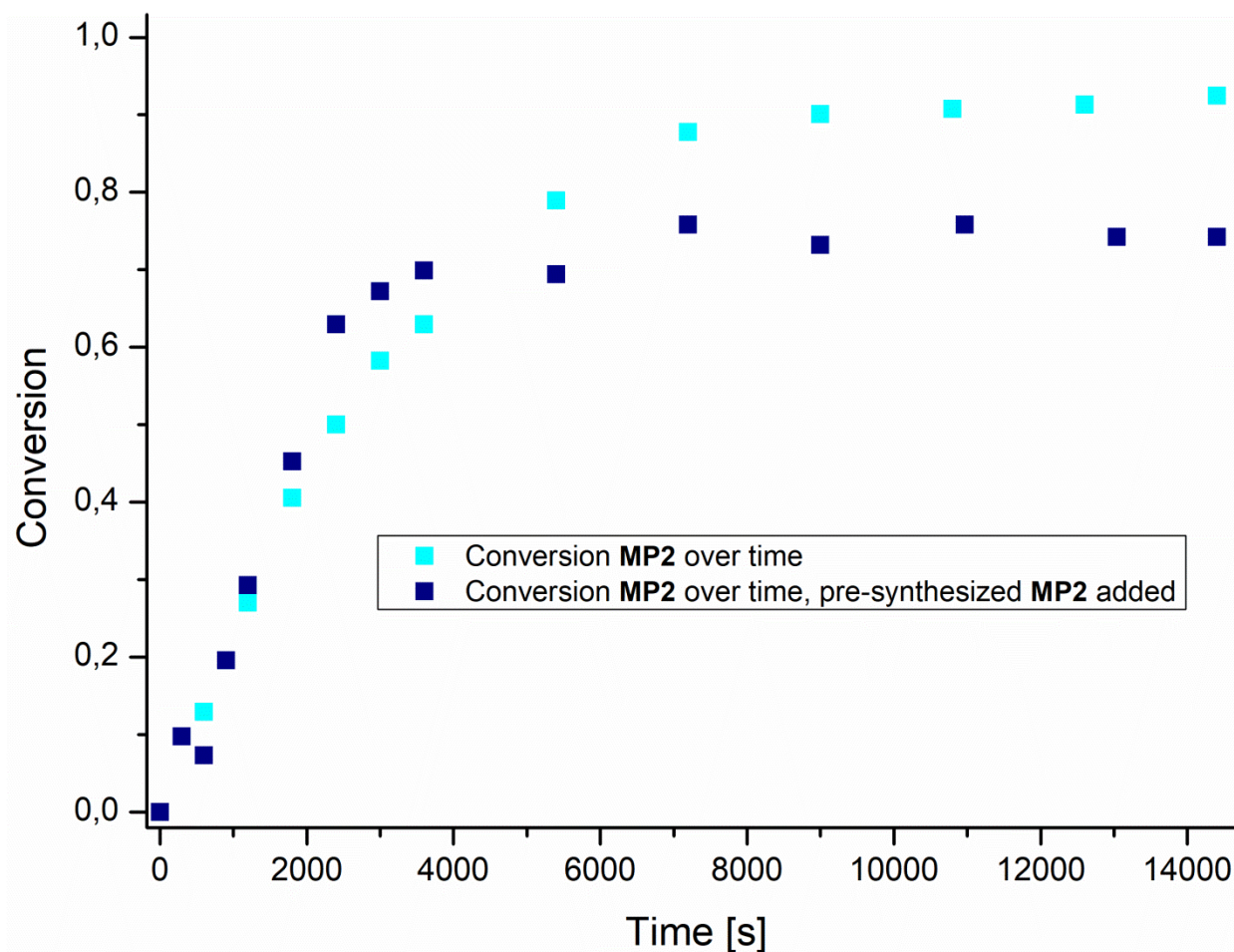
**Table S35.** Kinetic studies of the copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) with addition of pre-synthesized menthyloxybutenolide-VeoVa-10-copolymer **MP2** (1 mL 2.15 M solution in 1-methoxy-2-propanol) added at  $t = 40$  min, followed by  $^1\text{H NMR}$  spectroscopy. Integrated  $^1\text{H NMR}$  signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.

Menthyloxybutenolide-VeoVa-10-copolymer MP2, Additional polymer added					k1(obs)	$(3.0 \pm 0.2) \cdot 10^{-4}$ [s <sup>-1</sup> ]
Menthyloxybutenolide B5		VeoVa-10			k2(obs)	$(2.6 \pm 0.8) \cdot 10^{-5}$ [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	0,70	2,17	0,71	2,13	0,00	0,00
300	0,64	2,00	0,63	1,88	0,10	0,10
600	0,60	1,86	0,71	2,13	0,07	0,08
900	0,54	1,67	0,60	1,79	0,20	0,22
1200	0,51	1,59	0,49	1,45	0,29	0,35
1800	0,41	1,28	0,36	1,08	0,45	0,60
2400	0,40	0,66	0,59	0,94	0,63	0,99
3000	0,38	0,63	0,49	0,78	0,67	1,12
3600	0,37	0,61	0,44	0,69	0,70	1,20
5400	0,33	0,54	0,49	0,78	0,69	1,18
7200	0,30	0,49	0,35	0,55	0,76	1,42
9000	0,26	0,42	0,46	0,73	0,73	1,32
10969	0,30	0,49	0,35	0,55	0,76	1,42
13036	0,27	0,44	0,42	0,66	0,74	1,36
14400	0,28	0,47	0,41	0,64	0,74	1,36

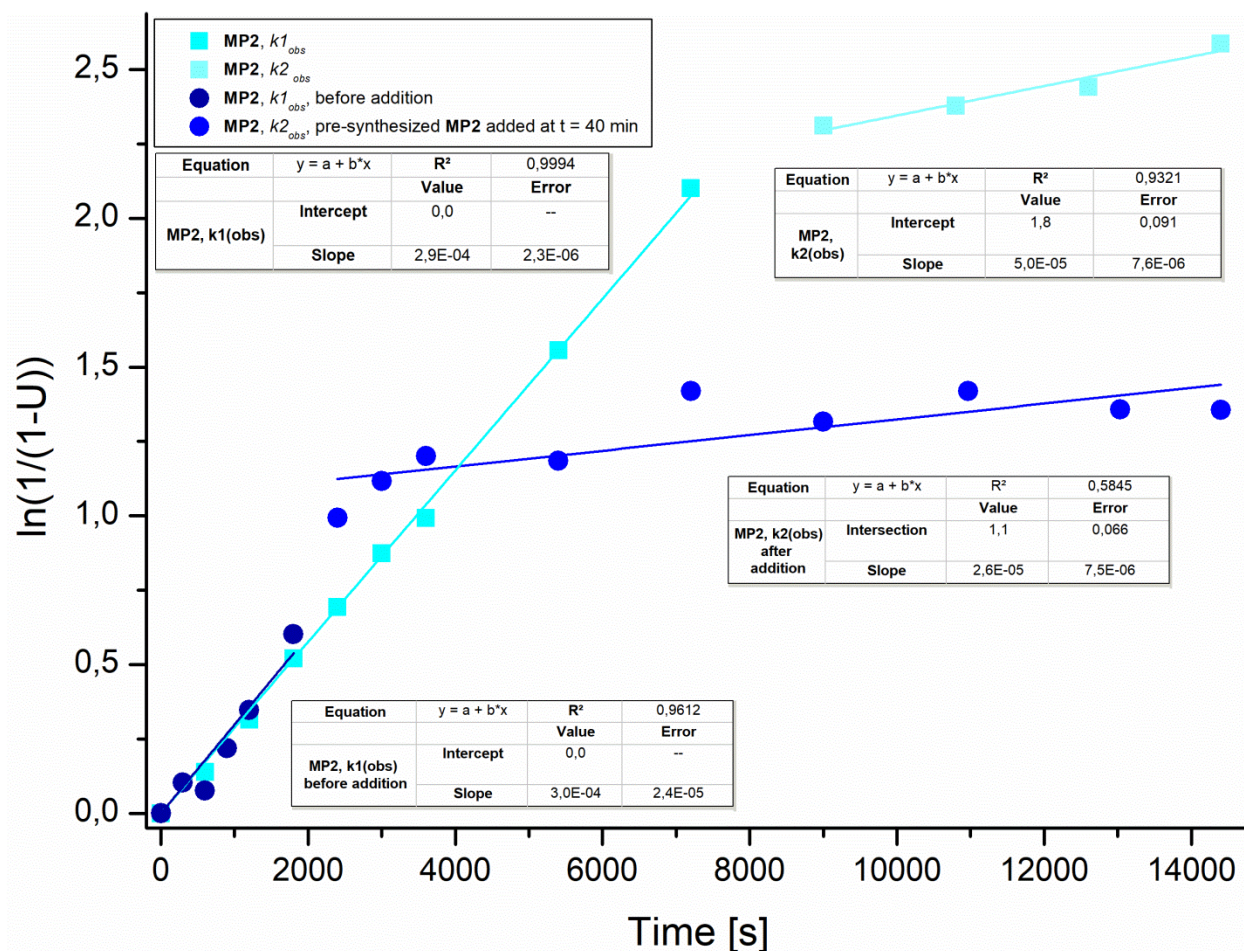




**Fig. S133.** Concentration of monomers over time of the copolymerization of menthyloxybutenolide **B5** (cyan square) with VeoVa-10 (grey circle) (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time. Concentration of the monomers over time, with pre-synthesized polymer **MP2** added at  $t = 40$  min, of the copolymerization of menthyloxybutenolide **B5** (navy blue square) and VeoVa-10 (dark grey circle) followed by  $^1\text{H}$ NMR signals. 1 mL of a 2.15 M solution of **MP2** in 1-methoxy-2-propanol was added during the polymerization at  $t = 40$  min. Samples for  $^1\text{H}$ NMR were taken at certain timestamps and flash frozen ( $-18^\circ\text{C}$ ) and quantified by using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.



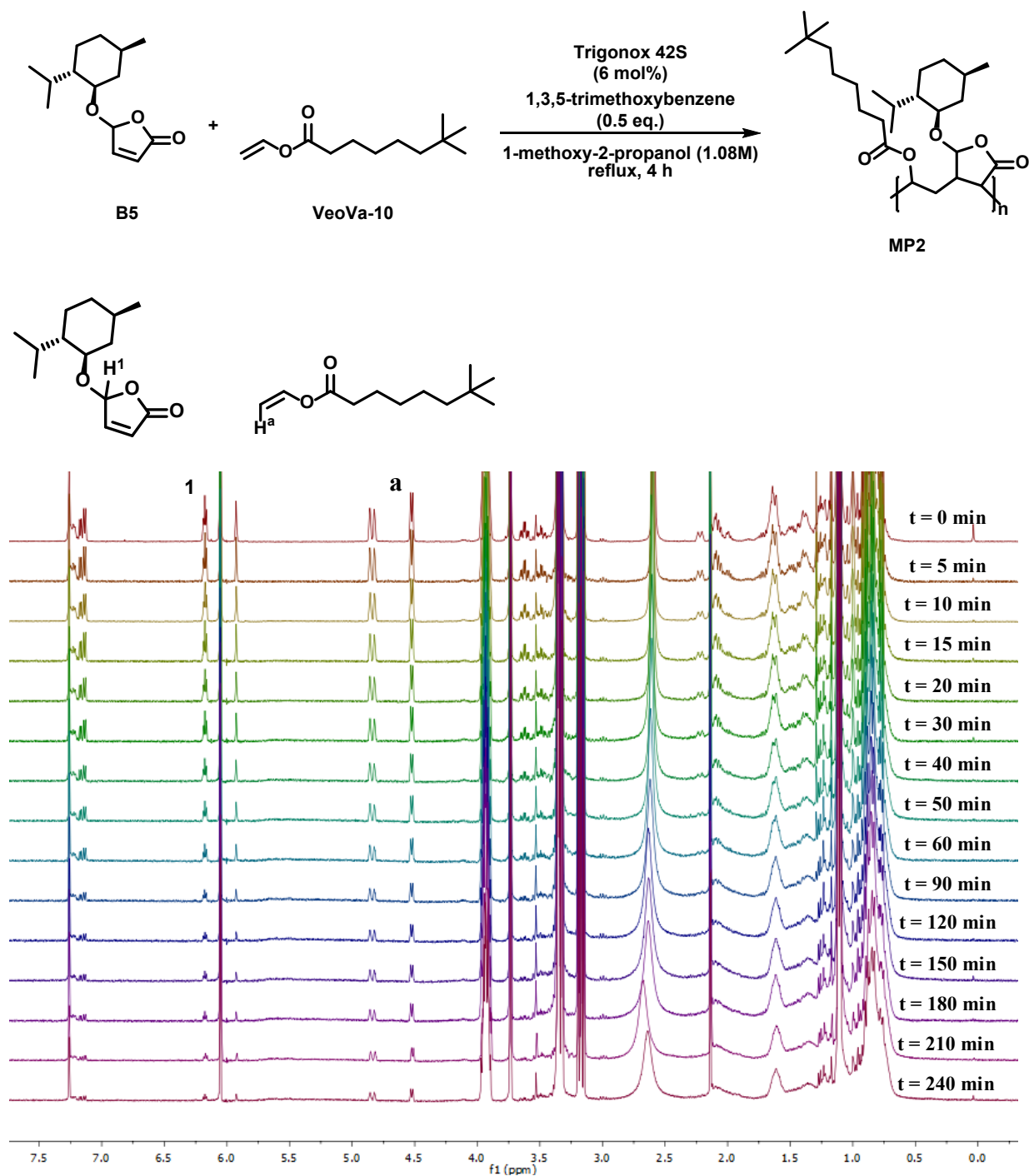
**Fig. S134.** Conversion of polymer **MP2** (cyan square) over time; copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time. Conversion of polymer **MP2** (navy blue square) over time, with pre-synthesized polymer **MP2** added at  $t = 40$  min, of the copolymerization of menthyloxybutenolide **B5** and VeoVa-10 followed by  $^1\text{H}$  NMR signals. 1 mL of a 2.15 M solution of **MP2** in 1-methoxy-2-propanol was added during the polymerization at  $t = 40$  min. Samples for  $^1\text{H}$  NMR were taken at certain timestamps and flash frozen ( $-18^\circ\text{C}$ ) and quantified by using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.



**Fig. S135.** Rate of copolymerization and inhibition after addition of pre-synthesized copolymer **MP2**. Inhibited polymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio, cyan line) at 92% conversion,  $t = 9000$  s. Polymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio, dark blue line) until  $t = 1800$  s. Inhibited polymerization of menthyloxybutenolide **B5** with VeoVa-10 after addition of pre-synthesized menthyloxybutenolide-VeoVa-10-copolymer **MP2** (1 mL 2.15 M solution in 1-methoxy-2-propanol, 92% conversion) (1:1 ratio, blue line) at  $t = 2400$  s. Similar reaction rates are obtained,  $k2_{obs}^{before} = 5.0 \cdot 10^{-5} \text{ s}^{-1}$  and  $k2_{obs}^{after} = 2.6 \cdot 10^{-5} \text{ s}^{-1}$ , for the inhibited polymerization at  $t = 9000$  s (cyan line) and the induced inhibited polymerization at  $t = 2400$  s (blue line). Samples for  $^1\text{H NMR}$  were taken at certain timestamps and flash frozen ( $-18^\circ\text{C}$ ) and quantified by using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.



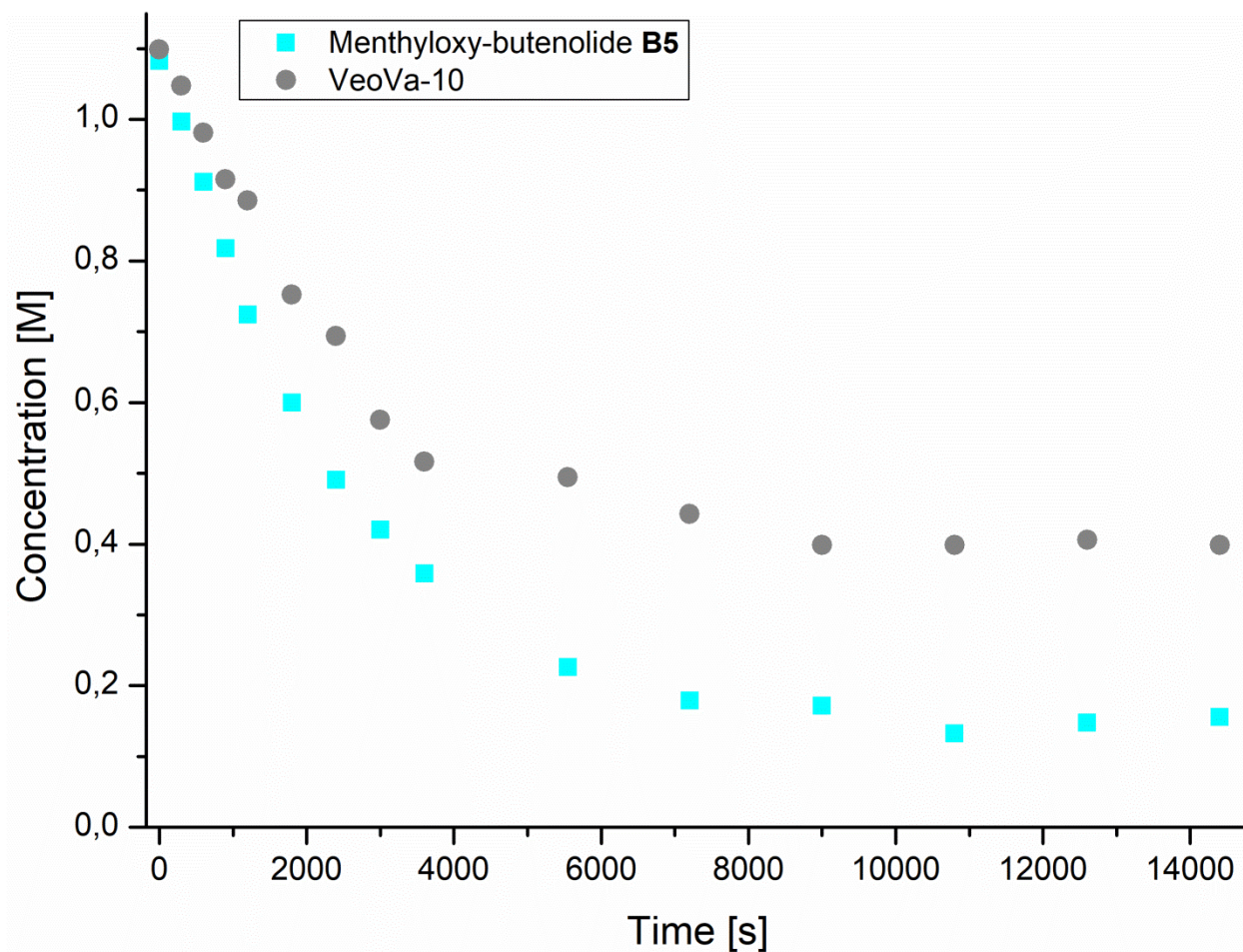
5-menthyloxy-2(5H)-furanone-VeoVa-10-copolymer MP2, half concentration



**Fig. S136.** Reaction scheme copolymerization menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 1.08 M (2x diluted) in 1-methoxy-2-propanol to exclude dilution effects, reflux, 4 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

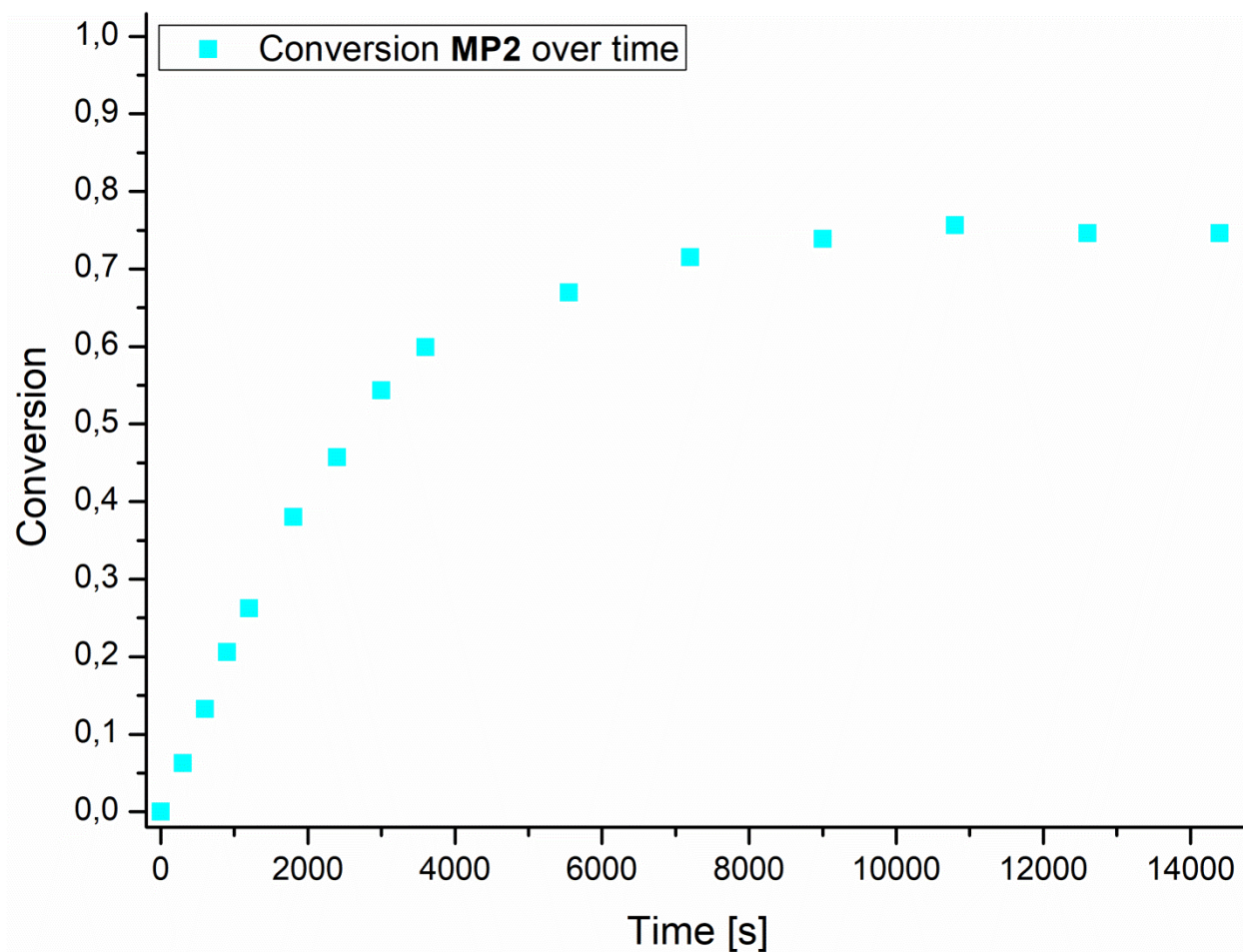
**Table S36.** Kinetic studies of the copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (6 mol%), 1.08 M (2x diluted) in 1-methoxy-2-propanol to exclude dilution effects, reflux, 4 h.

Menthyloxybutenolide-VeoVa-10-copolymer MP2, 2x diluted					k1(obs)	$(2.6 \pm 0.1) \cdot 10^{-4}$ [s <sup>-1</sup> ]
Menthyloxybutenolide <b>B5</b>		VeoVa-10		k2(obs)	$(2.8 \pm 1.0) \cdot 10^{-5}$ [s <sup>-1</sup> ]	
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	$\ln(1/[1-U])$
0	0,70	1,08	0,74	1,10	0,00	0,00
300	0,64	1,00	0,70	1,05	0,06	0,07
600	0,59	0,91	0,66	0,98	0,13	0,14
900	0,53	0,82	0,61	0,91	0,21	0,23
1200	0,47	0,72	0,59	0,89	0,26	0,30
1800	0,39	0,60	0,50	0,75	0,38	0,48
2400	0,32	0,49	0,46	0,69	0,46	0,61
3000	0,27	0,42	0,39	0,58	0,54	0,78
3600	0,23	0,36	0,35	0,52	0,60	0,91
5549	0,15	0,23	0,33	0,49	0,67	1,11
7200	0,12	0,18	0,30	0,44	0,72	1,26
9000	0,11	0,17	0,27	0,40	0,74	1,34
10800	0,09	0,13	0,27	0,40	0,76	1,41
12600	0,10	0,15	0,27	0,41	0,75	1,37
14400	0,10	0,16	0,27	0,40	0,75	1,37

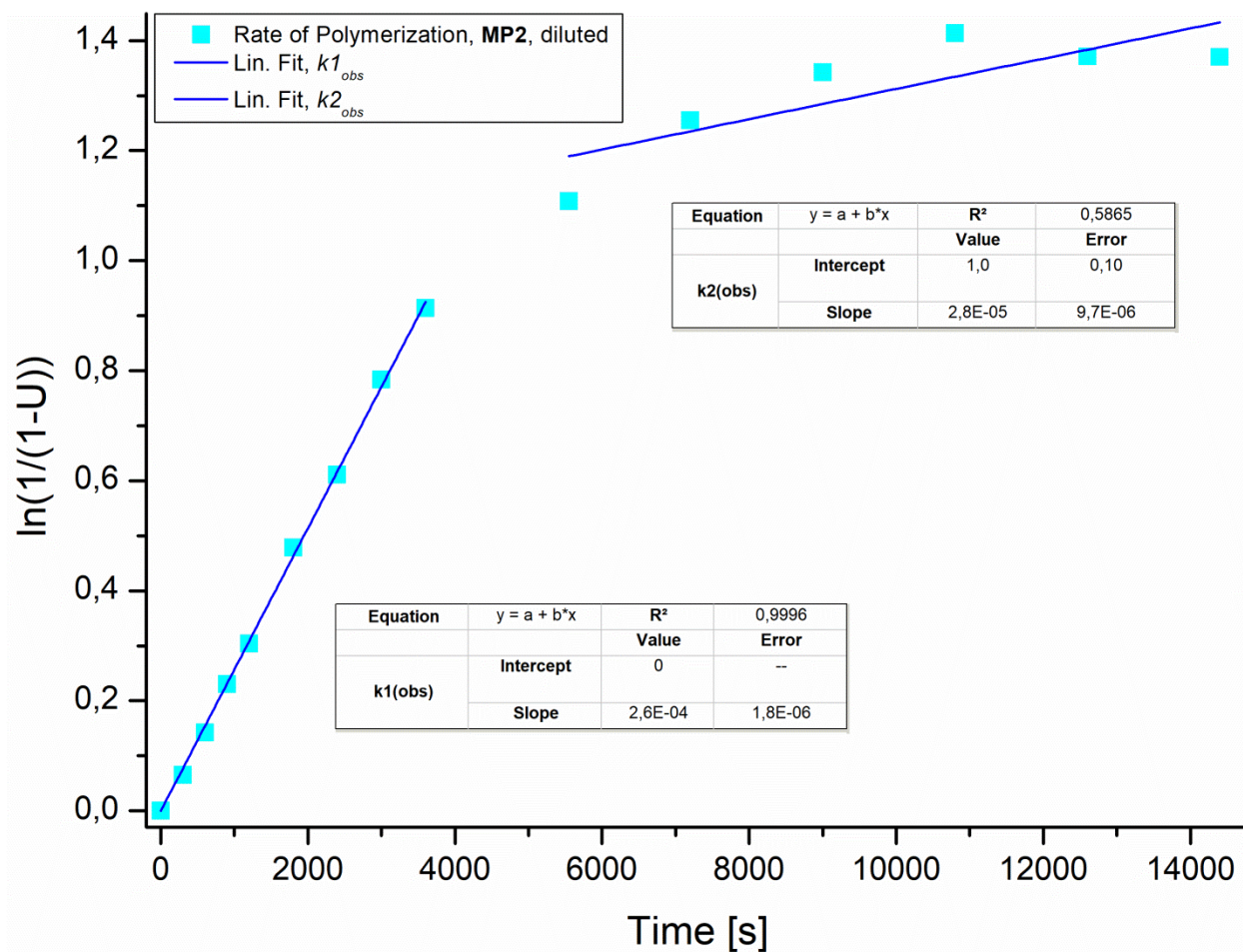


**Fig. S137.** Concentration of monomers over time of the copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 1.08 M (2x diluted) in 1-methoxy-2-propanol to exclude dilution effects, reflux, 4 h.



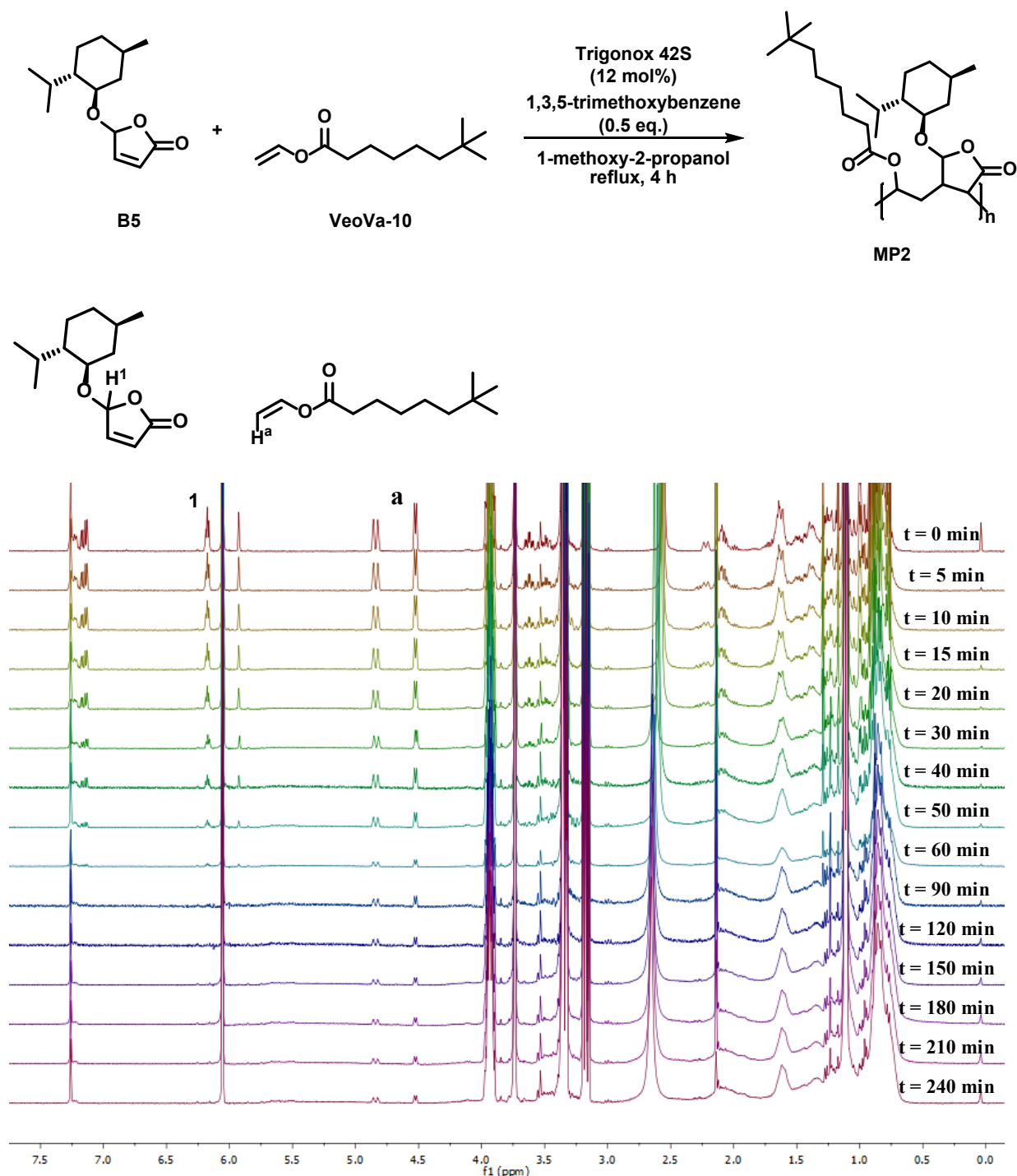


**Fig. S138.** Conversion of polymer **MP2** over time; copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 1.08 M (2x diluted) in 1-methoxy-2-propanol to exclude dilution effects, reflux, 4 h.



**Fig. S139.** Rate of copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) to **MP2** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 1.08 M (2x diluted) in 1-methoxy-2-propanol to exclude dilution effects, reflux, 4 h.

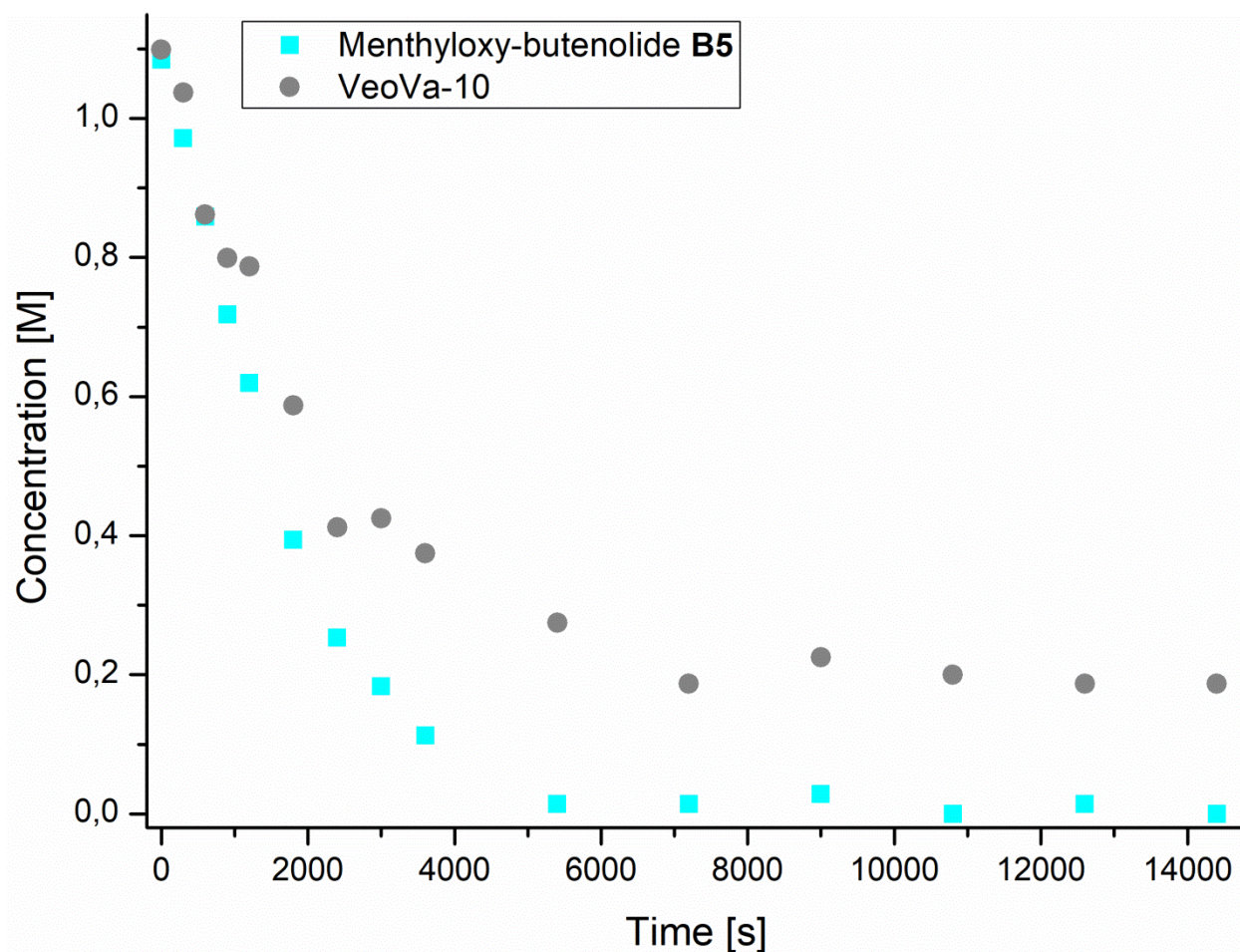
5-methyloxy-2(5H)-furanone-VeoVa-10-copolymer MP2, double concentration initiator



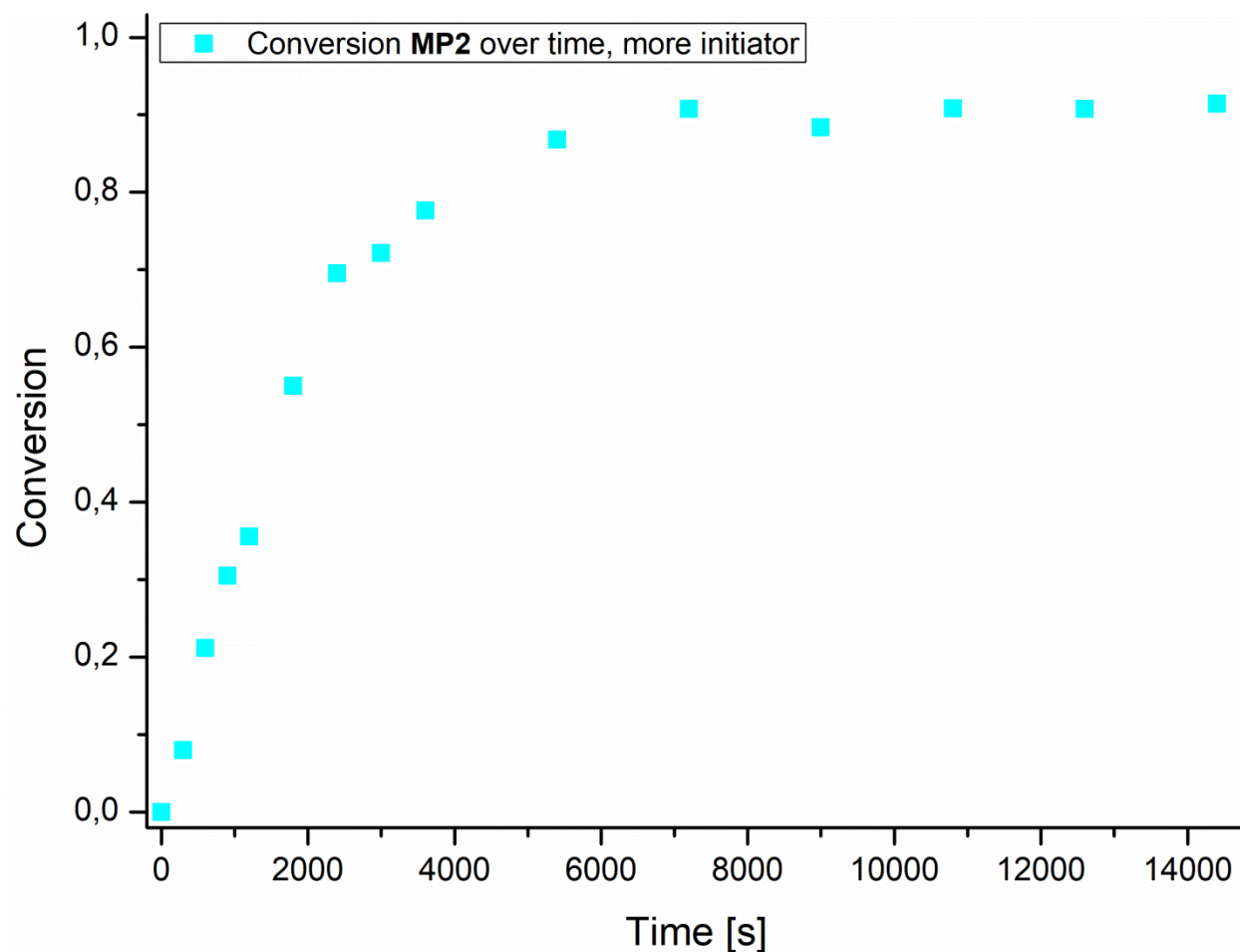
**Fig. S140.** Reaction scheme copolymerization menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio), reaction conditions: Trigonox 42S (12 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h (top). <sup>1</sup>H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

**Table S37.** Kinetic studies of the copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio), followed by <sup>1</sup>H NMR spectroscopy. Integrated <sup>1</sup>H NMR signals over time determined by integration against the internal standard 1,3,5-trimethoxybenzene (0.5 eq.). Rate constant ( $k_{obs}$ ) determined by slope of trendline ( $y = ax$ ) of  $\ln(1/(1-U))$  values. Reaction conditions: Trigonox 42S (12 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.

Menthyloxybutenolide-VeoVa-10-copolymer MP2, 12 mol% Trigonox 42S					k1(obs)	(4.3±0.1)·10 <sup>-4</sup> [s <sup>-1</sup> ]
Menthyloxybutenolide B5		VeoVa-10			k2(obs)	(3.8±1.7)·10 <sup>-5</sup> [s <sup>-1</sup> ]
Time [s]	Integral	Concentration [mol/L]	Integral	Concentration [mol/L]	Conversion	ln(1/[1-U])
0	0,77	1,08	0,86	1,10	0,00	0,00
300	0,69	0,97	0,82	1,04	0,08	0,08
600	0,61	0,86	0,68	0,86	0,21	0,24
900	0,51	0,72	0,63	0,80	0,30	0,36
1200	0,44	0,62	0,62	0,79	0,36	0,44
1800	0,28	0,39	0,46	0,59	0,55	0,80
2400	0,18	0,25	0,32	0,41	0,70	1,19
3000	0,13	0,18	0,33	0,42	0,72	1,28
3600	0,08	0,11	0,29	0,37	0,78	1,50
5400	0,01	0,01	0,22	0,27	0,87	2,02
7200	0,01	0,01	0,15	0,19	0,91	2,38
9000	0,02	0,03	0,18	0,22	0,88	2,16
10800	0,00	0,00	0,16	0,20	0,91	2,39
12600	0,01	0,01	0,15	0,19	0,91	2,38
14400	0,00	0,00	0,15	0,19	0,91	2,46

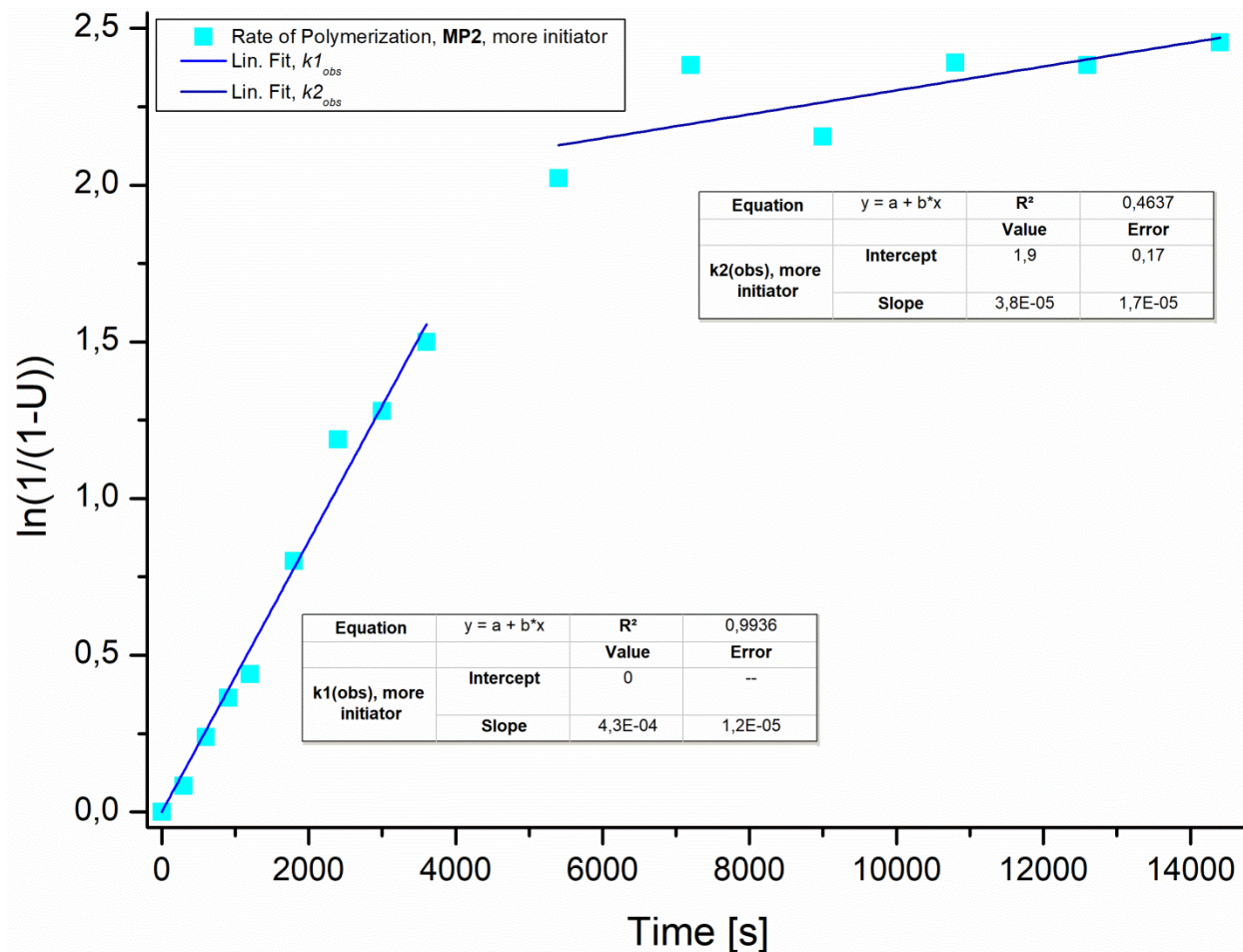


**Fig. S141.** Concentration of monomers over time of the copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (12 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.



**Fig. S142.** Conversion of polymer **MP2** over time; copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) followed by  $^1\text{H}$ NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (12 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.





**Fig. S143.** Rate of copolymerization of menthyloxybutenolide **B5** with VeoVa-10 (1:1 ratio) to **MP2** over time; followed by  $^1\text{H}$  NMR signals over time by taking samples and flash freezing ( $-18^\circ\text{C}$ ) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (12 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 4 h.

## Summary kinetic studies (co)polymerization

**Table S38.** Summary kinetic studies (co)polymerization reactions. Reaction conditions: monomer 1 – monomer 2 (1:1 ratio) (in case of di(ethylene glycol) divinyl ether (1:0.5 ratio), Trigonox 42S (6 mol%) (in case of homopolymerization 3 mol%), 2.15 M in 1-methoxy-2-propanol (in case of homopolymerization 4.3 M in 1-methoxy-2-propanol), reflux, 6 min–4 h. a) Maximum conversion measured due to gel-solid transition. b) Reaction kinetics only measured until 6 min. c) Reaction kinetics only measured until 2 h. d) Reaction kinetics only measured until 1 h. e) Reaction rate mostly based on monomer 2.

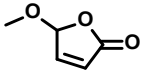
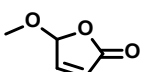
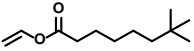
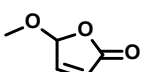
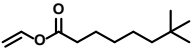
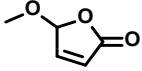
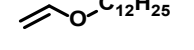
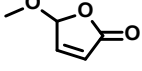
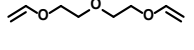
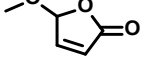
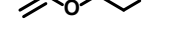
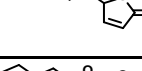
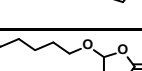
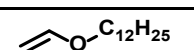
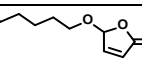
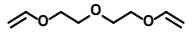
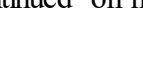

Polymer	Monomer 1	Monomer 2	Conversion (%)	$k(1)_{\text{obs}} (s^{-1})$	$k(2)_{\text{obs}} (s^{-1})$
BP1		/	53	$(1.4 \pm 0.1) \cdot 10^{-4}$	$(1.3 \pm 0.4) \cdot 10^{-5}$
BP2 (Raman)			>99	$(7.4 \pm 0.1) \cdot 10^{-4}$	-
BP2 (NMR)			98	$(5.5 \pm 0.1) \cdot 10^{-4}$	-
BP3			95	$(1.4 \pm 0.1) \cdot 10^{-3}$	$(8.5 \pm 0.1) \cdot 10^{-5}$
BP4			69 <sup>a</sup>	$(3.3 \pm 0.1) \cdot 10^{-3}$	-
BP5			99	$(2.5 \pm 0.1) \cdot 10^{-3}$	$(2.6 \pm 0.1) \cdot 10^{-4}$
HP1		/	51	$(9.2 \pm 0.1) \cdot 10^{-5}$	$(1.6 \pm 0.1) \cdot 10^{-5}$
HP2			92	$(3.6 \pm 0.1) \cdot 10^{-4}$	$(1.4 \pm 2.6) \cdot 10^{-5}$
HP3			>99	$(2.1 \pm 0.1) \cdot 10^{-3}$	-
HP4			88 <sup>a</sup>	$(3.5 \pm 0.1) \cdot 10^{-3}$	-

Table S38. continued on next page

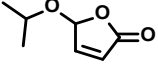
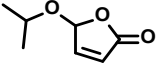
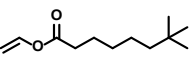
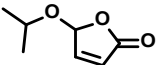
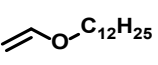
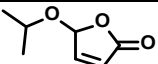
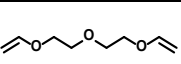
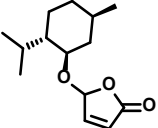
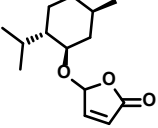

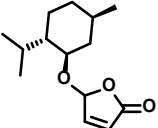
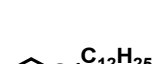
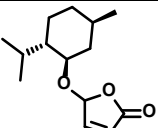

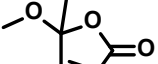
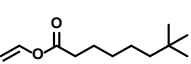
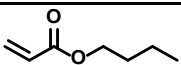
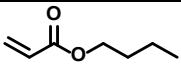
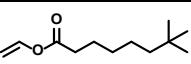
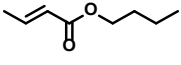
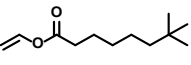
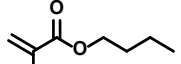
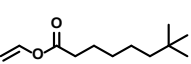
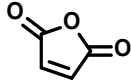
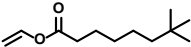
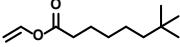

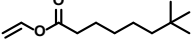

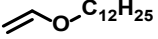

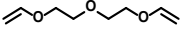

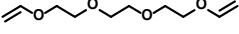
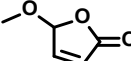
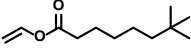
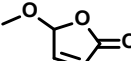
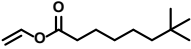
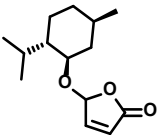
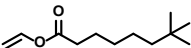
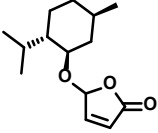
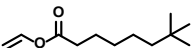
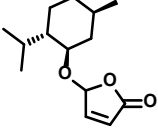
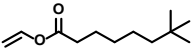
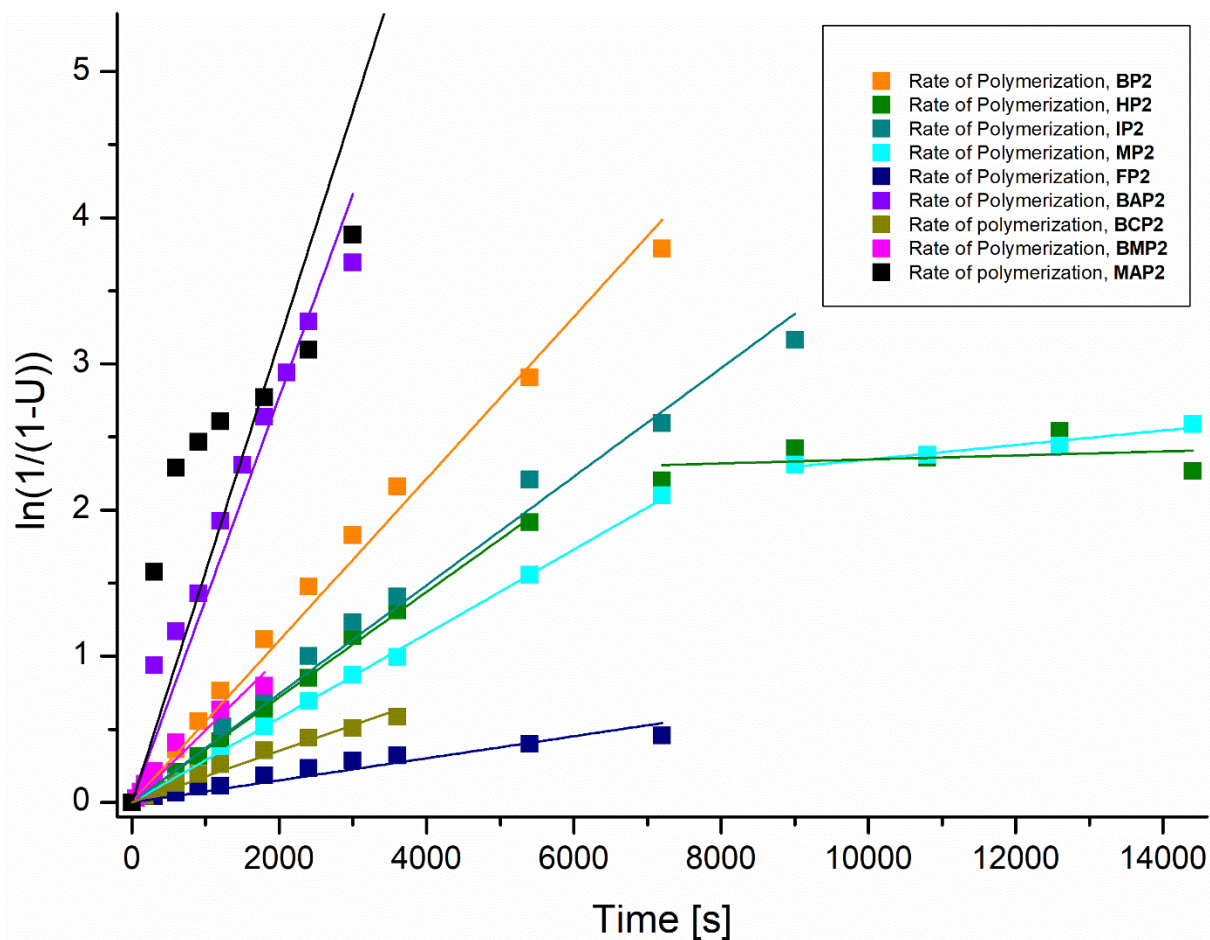
Polymer	Monomer 1	Monomer 2	Conversion (%)	$k(1)_{\text{obs}} (\text{s}^{-1})$	$k(2)_{\text{obs}} (\text{s}^{-1})$
IP1		/	37	$(1.1 \pm 0.1) \cdot 10^{-4}$	$(3.7 \pm 0.2) \cdot 10^{-5}$
IP2			96	$(3.7 \pm 0.1) \cdot 10^{-4}$	-
IP3			>99	$(2.0 \pm 0.1) \cdot 10^{-3}$	-
IP4			91 <sup>a</sup>	$(1.8 \pm 0.1) \cdot 10^{-3}$	-
MP1		/	30	$(9.2 \pm 0.2) \cdot 10^{-5}$	-
MP2			92	$(2.9 \pm 0.1) \cdot 10^{-4}$	$(5.0 \pm 0.8) \cdot 10^{-5}$
MP3			>99	$(1.1 \pm 0.1) \cdot 10^{-3}$	-
MP4			>99	$(3.2 \pm 0.3) \cdot 10^{-3}$	-
MMP2			45	$(1.3 \pm 0.1) \cdot 10^{-4}$	-
BAP1		/	90 <sup>b</sup>	$(7.0 \pm 0.3) \cdot 10^{-3}$	-
BAP2			98	$(1.4 \pm 0.1) \cdot 10^{-3}$	-
BCP2			44 <sup>c</sup>	$(1.8 \pm 0.1) \cdot 10^{-4}$	-
BMP2			55	$(4.9 \pm 0.3) \cdot 10^{-4}$	-

Table S38 continued on next page

Polymer	Monomer 1	Monomer 2	Conversion (%)	$k(1)_{\text{obs}} (\text{s}^{-1})$	$k(2)_{\text{obs}} (\text{s}^{-1})$
MAP2			>99	$(1.6 \pm 0.2) \cdot 10^{-3}$	-
VP1		/	>99	$(2.0 \pm 0.1) \cdot 10^{-3}$	-
FP2			37 <sup>c</sup>	$(7.5 \pm 0.4) \cdot 10^{-5}$	-
FP3			58 <sup>d</sup>	$(2.7 \pm 0.1) \cdot 10^{-4}$	-
FP4			35 <sup>e</sup>	$(5.0 \pm 1.1) \cdot 10^{-3}$	-
FP6			36 <sup>e</sup>	$(1.4 \pm 0.1) \cdot 10^{-2}$	-
BP2 (add. BP2)			96	$(6.9 \pm 0.1) \cdot 10^{-4}$	$(2.5 \pm 0.2) \cdot 10^{-4}$
BP2 (BP2 dil.)			94	$(5.0 \pm 0.1) \cdot 10^{-4}$	-
MP2 (add. MP2)			74	$(3.0 \pm 0.2) \cdot 10^{-4}$	$(2.6 \pm 0.8) \cdot 10^{-5}$
MP2 (MP2 dil.)			75	$(2.6 \pm 0.1) \cdot 10^{-4}$	$(2.8 \pm 1.0) \cdot 10^{-5}$
MP2 (12% ini.)			91	$(4.3 \pm 0.1) \cdot 10^{-4}$	$(3.8 \pm 1.7) \cdot 10^{-5}$

The copolymerizations, performed under identical conditions, of various monomers with VeoVa-10 was summarized in **Fig. S144**. This figure depicts the relative reactivity of alkoxybutenolides to acrylate type analogues. The various alkoxybutenolide monomers show, as expected, a lower reactivity than butyl acrylate (**BAP2**), butylmethacrylate (**BMP2**) and maleic anhydride (**MAP2**). The reactivity is comparable to that of butyl crotonate (**BCP2**), featuring a *trans* internal alkene, and dramatically higher than 2(5H)-furanone, containing no acetal functionality (**Fig. 7B**).



**Fig. S144** Comparison of rates of copolymerizations with VeoVa-10 as monomer 2. Copolymer coding: **FP2** = 2(5H)-furanone copolymer, **BAP2** = butyl acrylate copolymer, **BMP2** = butyl methacrylate copolymer, **BCP2** = butyl crotonate copolymer, **MAP2** = maleic anhydride copolymer. Reaction conditions: monomer 1 – VeoVa-10 (1:1 ratio), Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h – 4 h.

## Polymer Properties, GPC traces and DSC

The molecular weights and glass transition temperatures  $T_g$  were measured for the different polymers of the copolymerization of alkoxybutenolides **B2–5** with VeoVa-10 and dodecyl vinyl ether and for the homo- and co-polymerization of butyl acrylate and butyl acrylate with VeoVa-10, respectively.

GPC conditions: Agilent Polypore, THF/acetic acid (99/1), 1 mL/min, RI detector, 50  $\mu$ L injection. Calibrated on polystyrene.

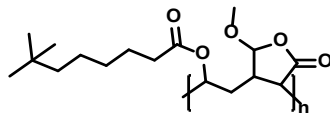
DSC method: The glass transition temperature ( $T_g$ ) is being determined with the DSC Q2000 of TA Instruments in the modulation mode.

After drying the sample for 24h at 80°C in an oven, a DSC cup filled with the sample and an empty DSC reference cup are heated in the Differential Scanning Calorimeter (DSC) in a modulated way according to ASTM method D3418.

DSC modulation conditions: MDSC schedule -150°C/100°C with 1 °C every 40 seconds, 3 cycles (two heating cycles and one cooling), Heating: 5 °C/min, Cooling 10°C/min. Second heating cycle gives most accurate  $T_g$  value.



## 5-methoxy-2(5H)-furanone-VeoVa-10-copolymer BP2

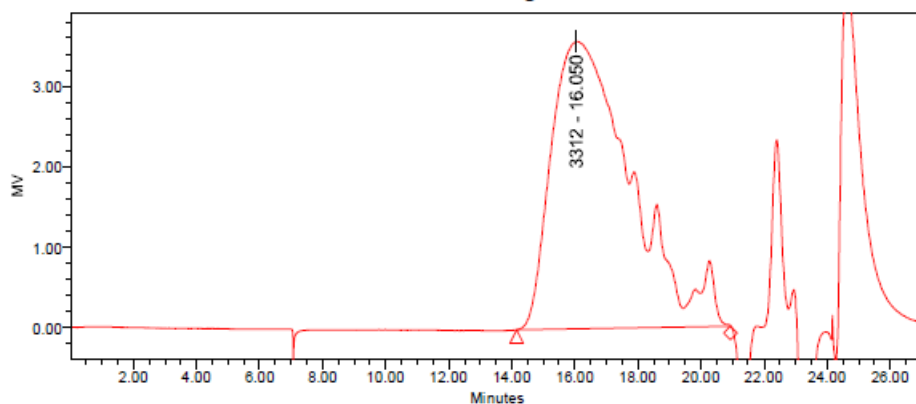


### Akzo Nobel Coatings Analytical Lab Sassenheim

sample name: GPC377: 3-037  
 date acquired: 1/15/2020 2:43:13 PM CET  
 date processed: 1/16/2020 2:53:24 PM CET  
 proc. method: GPC\_Alliance\_noref\_polypore  
 Reported by: lizet

GPC conditions  
 column: GPC\_polypore  
 eluent: THF/HAc (99/1)  
 flow: 1 ml/min  
 detector: RI detector  
 inj. vol.: 50.00 uL

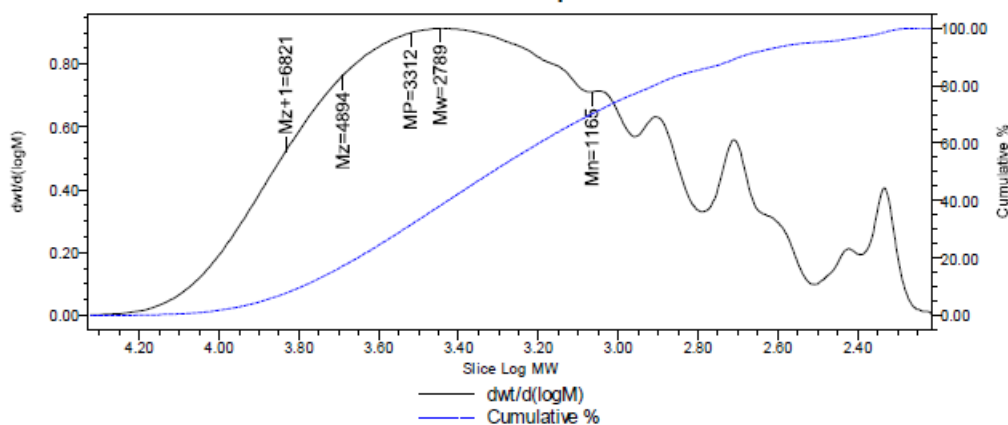
#### Chromatogram



#### GPC Results

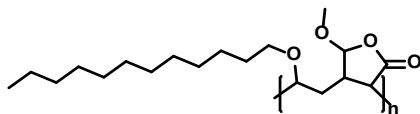
Monstemaam	tr	Mn	Mw	Mz	D	MP	% Area
1 GPC377: 3-037	16.05	1165	2789	4894	2.39	3312	100.00

#### Distribution plot



**Fig. S145.** Structure and GPC results, chromatogram, results and distribution plot, of copolymer methoxybutenolide-VeoVa-10-copolymer **BP2**.

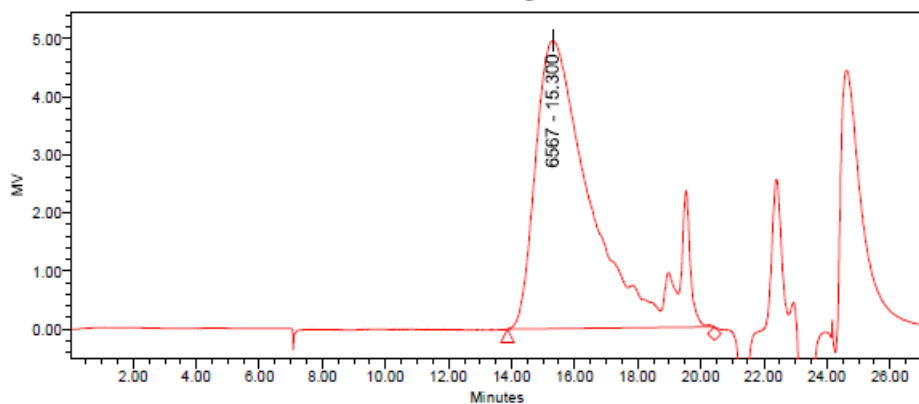
### 5-methoxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer BP3



**Akzo Nobel Coatings  
Analytical Lab Sassenheim**

sample name:	GPC377: 2-035	GPC conditions
date acquired:	1/15/2020 2:15:03 PM CET	column: GPC_polypore
date processed:	1/16/2020 2:51:29 PM CET	eluent: THF/HAc (99/1)
proc. method:	GPC_Alliance_noref_polypore	flow: 1 ml/min
Reported by:	lizet	detector: RI detector
		inj. vol.: 50.00 uL

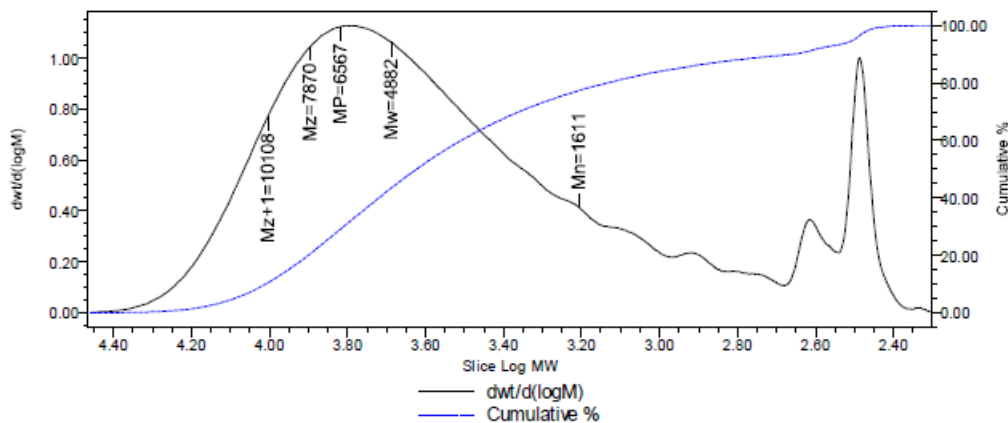
#### Chromatogram



#### GPC Results

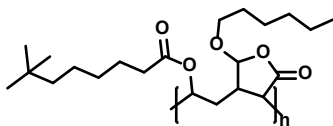
	Monstemaam	tr	Mn	Mw	Mz	D	MP	% Area
1	GPC377: 2-035	15.30	1611	4882	7870	3.03	6567	100.00

#### Distribution plot



**Fig. S146.** Structure and GPC results, chromatogram, results and distribution plot, of copolymer methoxybutenolide-dodecyl-vinyl-ether-copolymer **BP3**.

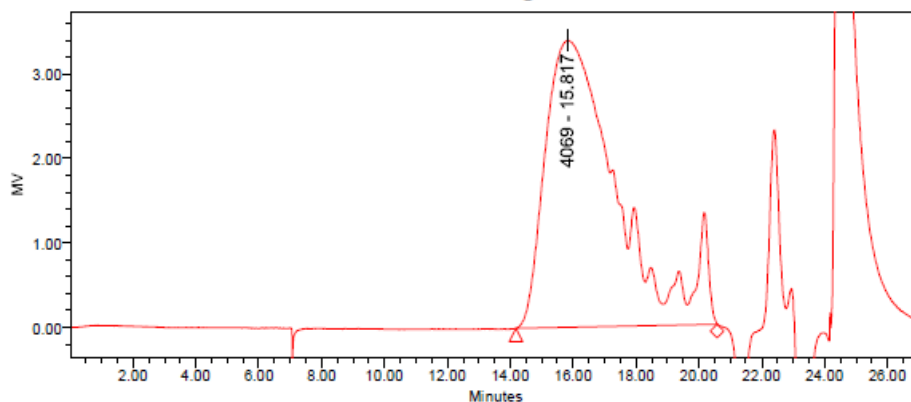
## 5-hexyloxy-2(5H)-furanone-VeoVa-10-copolymer HP2



**Akzo Nobel Coatings  
Analytical Lab Sassenheim**

sample name:	GPC377: 8-026	GPC conditions
date acquired:	1/15/2020 4:07:59 PM CET	column: GPC_polypore
date processed:	1/16/2020 2:54:05 PM CET	eluent: THF/HAc (99/1)
proc. method:	GPC_Alliance_noref_polypore	flow: 1 ml/min
Reported by:	lizet	detector: RI detector
		inj. vol.: 50.00 uL

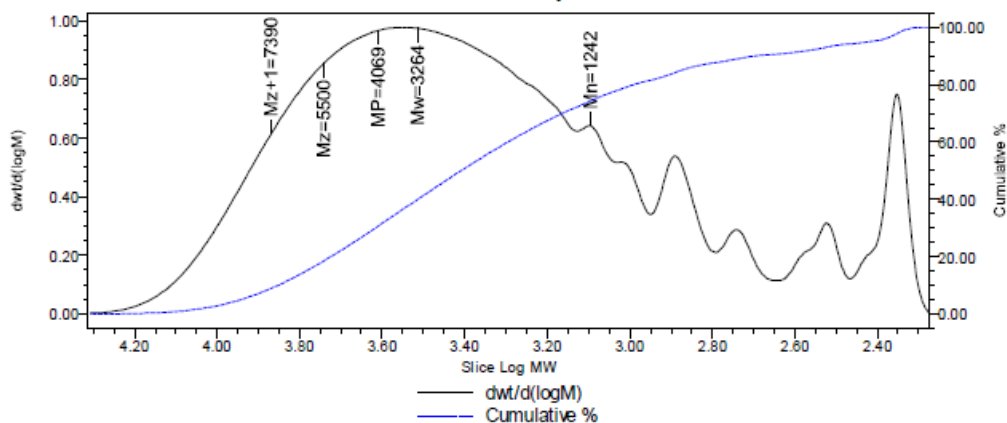
### Chromatogram



### GPC Results

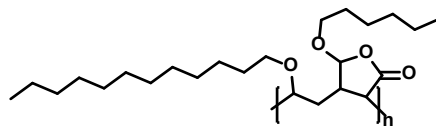
Monstemaam	tr	Mn	Mw	Mz	D	MP	% Area
1 GPC377: 8-026	15.82	1242	3264	5500	2.63	4069	100.00

### Distribution plot



**Fig. S147.** Structure and GPC results, chromatogram, results and distribution plot, of copolymer hexyloxybutenolide-VeoVa-10-copolymer **HP2**.

### 5-hexyloxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer HP3

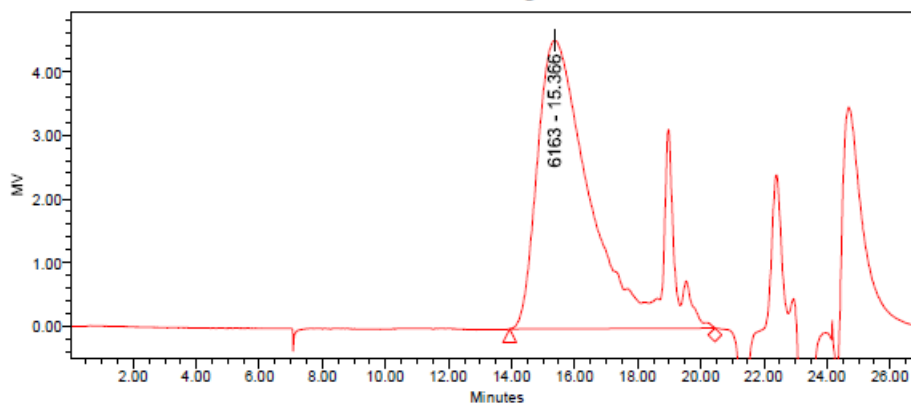


#### Akzo Nobel Coatings Analytical Lab Sassenheim

sample name: GPC377: 9-027  
 date acquired: 1/15/2020 4:36:09 PM CET  
 date processed: 1/16/2020 2:54:33 PM CET  
 proc. method: GPC\_Alliance\_noref\_polypore  
 Reported by: lizet

GPC conditions  
 column: GPC polypore  
 eluent: THF/HAc (99/1)  
 flow: 1 ml/min  
 detector: RI detector  
 inj. vol.: 50.00 uL

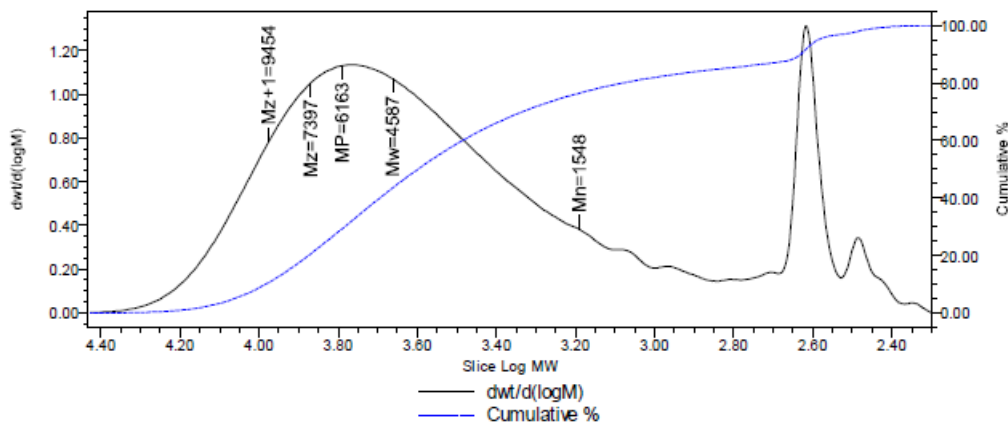
#### Chromatogram



#### GPC Results

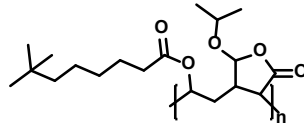
Monstemaam	tr	Mn	Mw	Mz	D	MP	% Area
1 GPC377: 9-027	15.37	1548	4587	7397	2.96	6163	100.00

#### Distribution plot



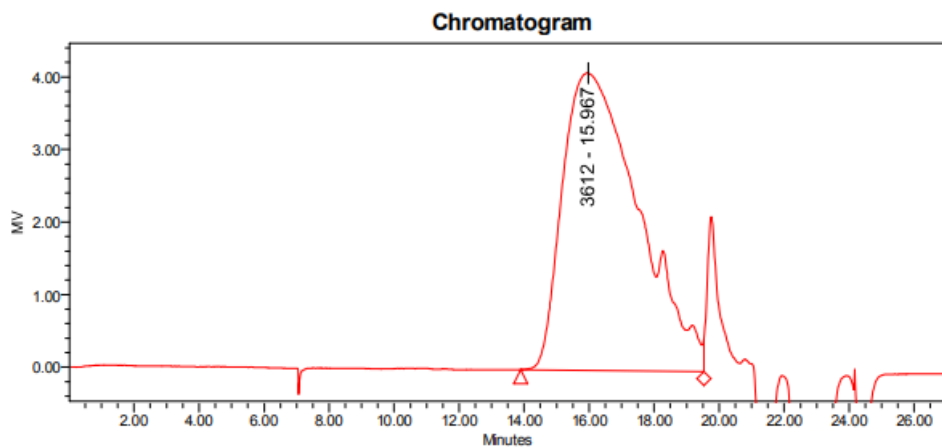
**Fig. S148.** Structure and GPC results, chromatogram, results and distribution plot, of copolymer hexyloxybutenolide-dodecyl-vinyl-ether-copolymer **HP3**.

## 5-isopropoxy-2(5H)-furanone-VeoVa-10-copolymer IP2



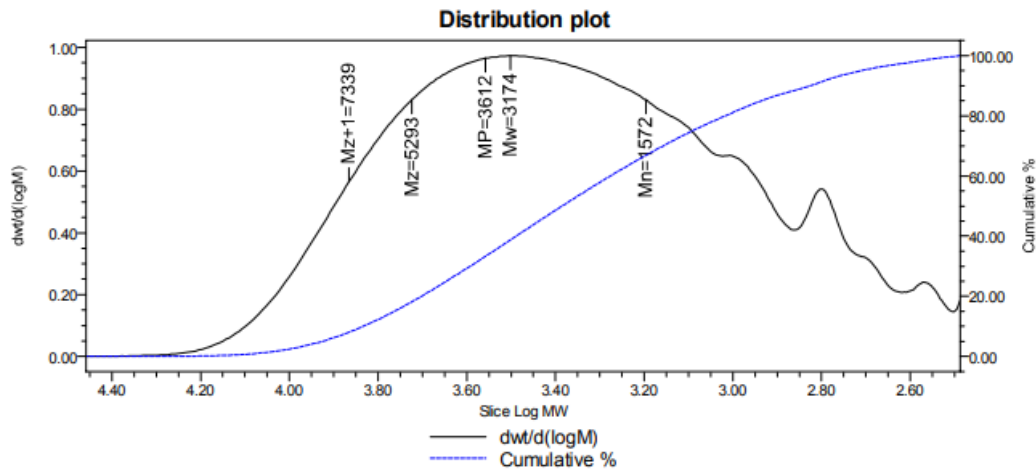
**Akzo Nobel Coatings**  
**Analytical Lab Sassenheim**

sample name:	GPC0444:RG-vial74	GPC conditions
date acquired:	6/3/2020 6:52:41 PM CEST	column: GPC_polypore
date processed:	6/4/2020 1:22:58 PM CEST	eluent: THF/FAC (99/1)
proc. method:	GPC_Alliance_noref_polypore	flow: 1 ml/min
Reported by:	Chemist	detector: RI detector
		inj. vol.: 50.00 uL



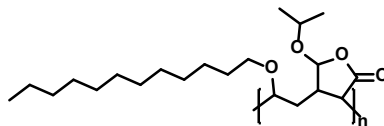
**GPC Results**

	Monsternaam	tr	Mn	Mw	Mz	D	MP	% Area
1	GPC0444:RG-vial74	15.97	1572	3174	5293	2.02	3612	100.00



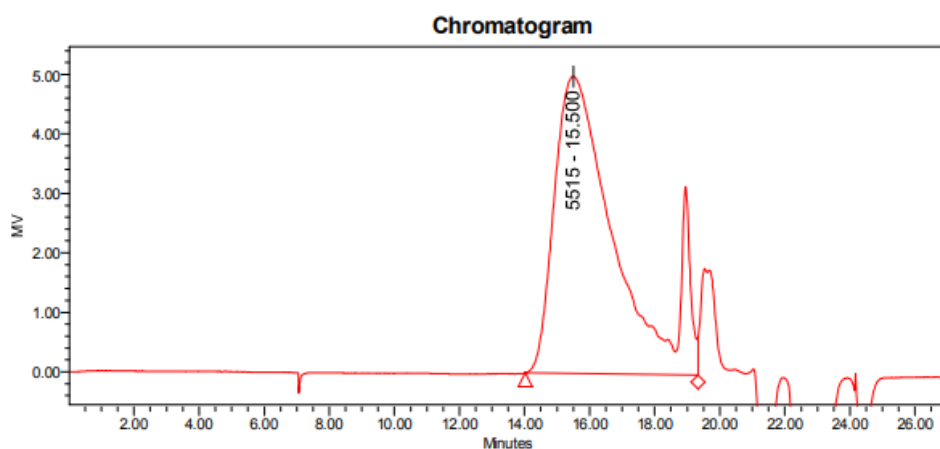
**Fig. S149.** Structure and GPC results, chromatogram, results and distribution plot, of copolymer isopropoxybutenolide-VeoVa-10-copolymer IP2.

## 5-isopropoxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer IP3



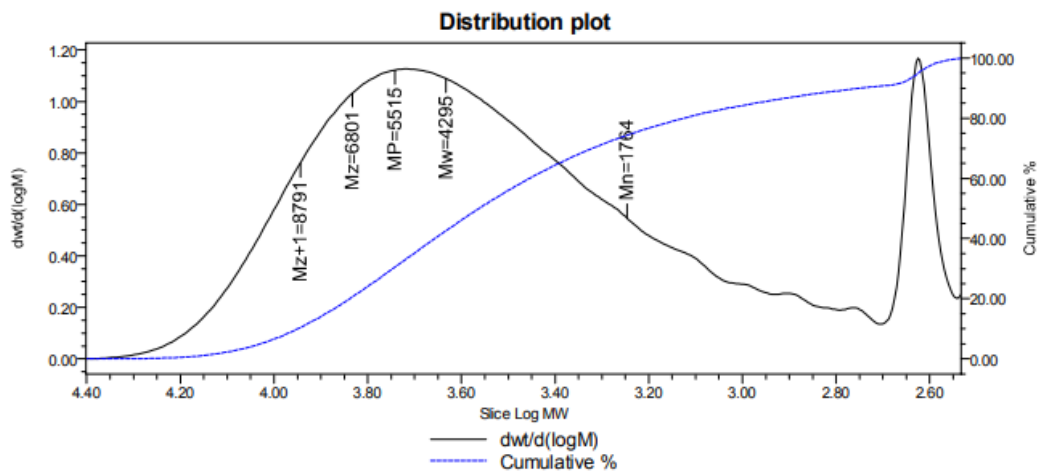
**Akzo Nobel Coatings  
Analytical Lab Sassenheim**

sample name:	GPC0444:RG-vial80	GPC conditions
date acquired:	6/3/2020 7:20:51 PM CEST	column: GPC polypore
date processed:	6/4/2020 1:22:47 PM CEST	eluent: THF/FAc (99/1)
proc. method:	GPC_Alliance_noref_polypore	flow: 1 ml/min
Reported by:	Chemist	detector: RI detector
		inj. vol.: 50.00 uL



**GPC Results**

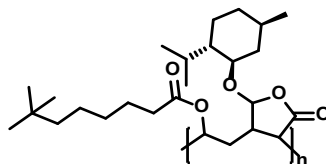
	Monsternaam	tr	Mn	Mw	Mz	D	MP	% Area
1	GPC0444:RG-vial80	15.50	1764	4295	6801	2.43	5515	100.00



**Fig. S150.** Structure and GPC results, chromatogram, results and distribution plot, of copolymer isopropoxybutenolide-dodecyl-vinyl-ether-copolymer **IP3**.



## 5-menthyloxy-2(5H)-furanone-VeoVa-10-copolymer MP2

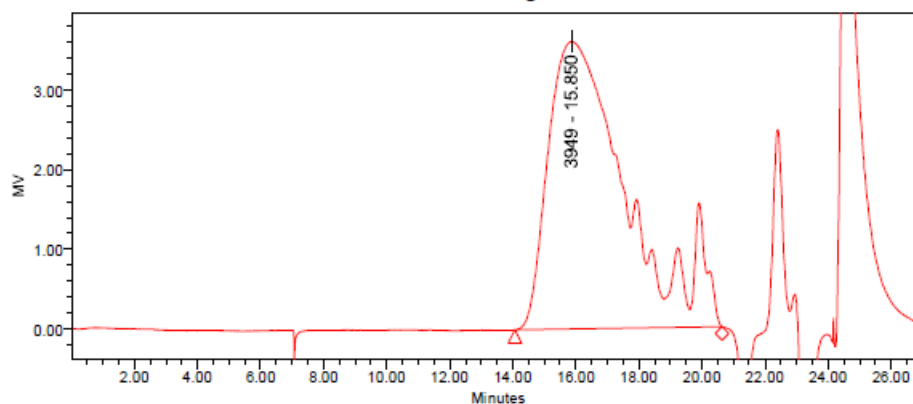


**Akzo Nobel Coatings  
Analytical Lab Sassenheim**

sample name: GPC377: 5-024  
 date acquired: 1/15/2020 3:11:32 PM CET  
 date processed: 1/16/2020 2:53:40 PM CET  
 proc. method: GPC\_Alliance\_noref\_polypore  
 Reported by: lizet

GPC conditions  
 column: GPC\_polypore  
 eluent: THF/HAc (99/1)  
 flow: 1 ml/min  
 detector: RI detector  
 inj. vol.: 50.00 uL

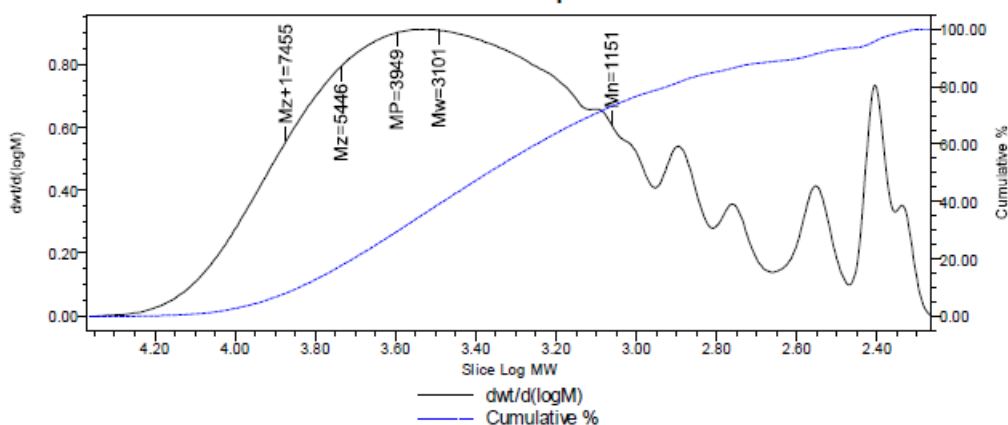
### Chromatogram



### GPC Results

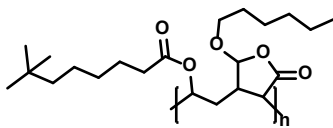
	Monstemaam	tr	Mn	Mw	Mz	D	MP	% Area
1	GPC377: 5-024	15.85	1151	3101	5446	2.69	3949	100.00

### Distribution plot



**Fig. S151.** Structure and GPC results, chromatogram, results and distribution plot, of copolymer menthyloxybutenolide-VeoVa-10-copolymer **MP2**.

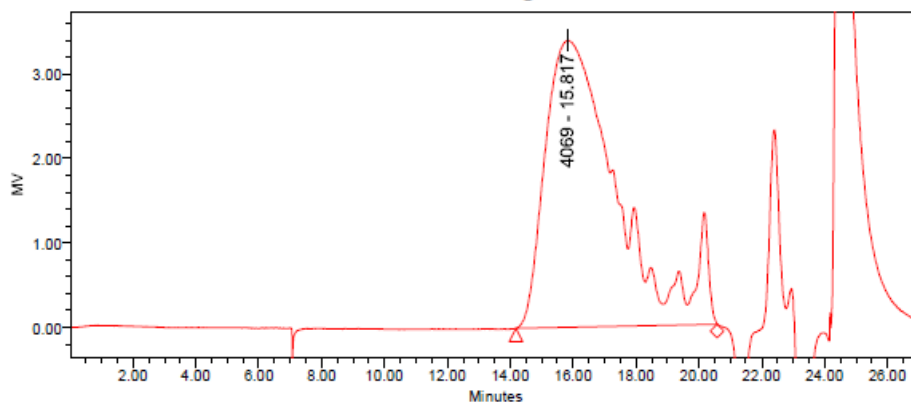
## 5-hexyloxy-2(5H)-furanone-VeoVa-10-copolymer HP2



**Akzo Nobel Coatings  
Analytical Lab Sassenheim**

sample name:	GPC377: 8-026	GPC conditions
date acquired:	1/15/2020 4:07:59 PM CET	column: GPC_polypore
date processed:	1/16/2020 2:54:05 PM CET	eluent: THF/HAc (99/1)
proc. method:	GPC_Alliance_noref_polypore	flow: 1 ml/min
Reported by:	lizet	detector: RI detector
		inj. vol.: 50.00 uL

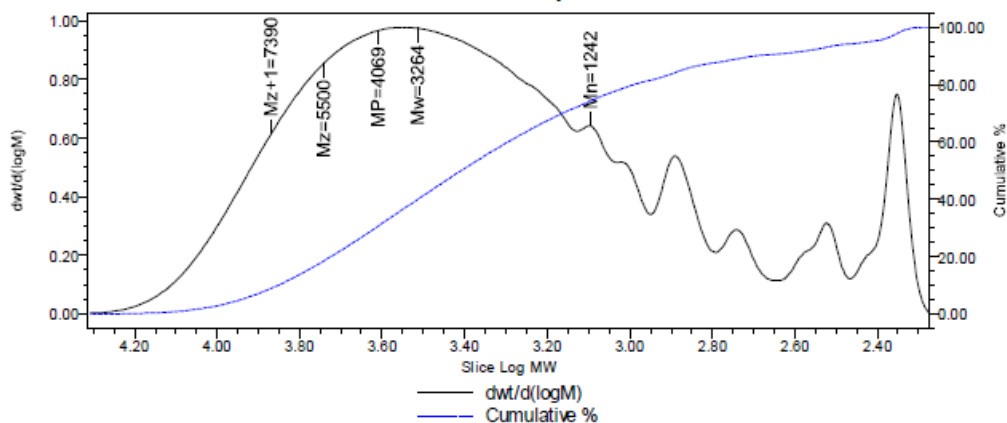
### Chromatogram



### GPC Results

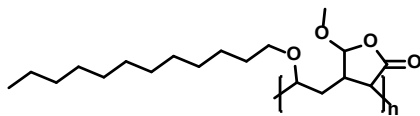
Monstemaam	tr	Mn	Mw	Mz	D	MP	% Area
1 GPC377: 8-026	15.82	1242	3264	5500	2.63	4069	100.00

### Distribution plot



**Fig. S147.** Structure and GPC results, chromatogram, results and distribution plot, of copolymer hexyloxybutenolide-VeoVa-10-copolymer **HP2**.

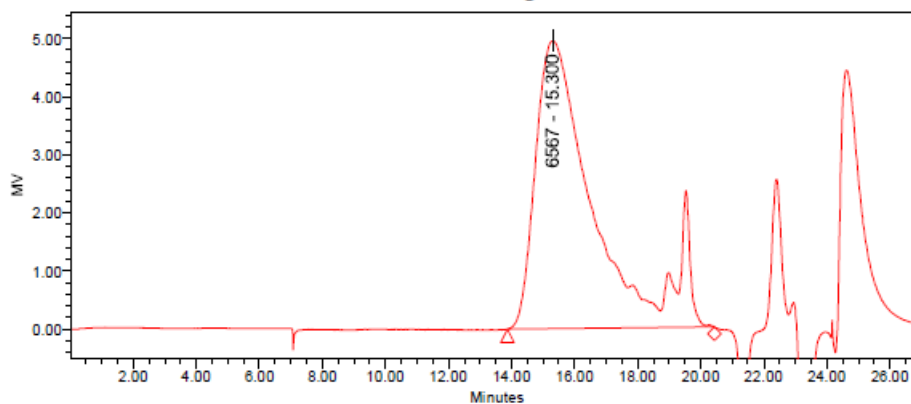
**5-methoxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer BP3**



**Akzo Nobel Coatings  
Analytical Lab Sassenheim**

sample name:	GPC377: 2-035	GPC conditions
date acquired:	1/15/2020 2:15:03 PM CET	column: GPC_polypore
date processed:	1/16/2020 2:51:29 PM CET	eluent: THF/HAc (99/1)
proc. method:	GPC_Alliance_noref_polypore	flow: 1 ml/min
Reported by:	lizet	detector: RI detector
		inj. vol.: 50.00 uL

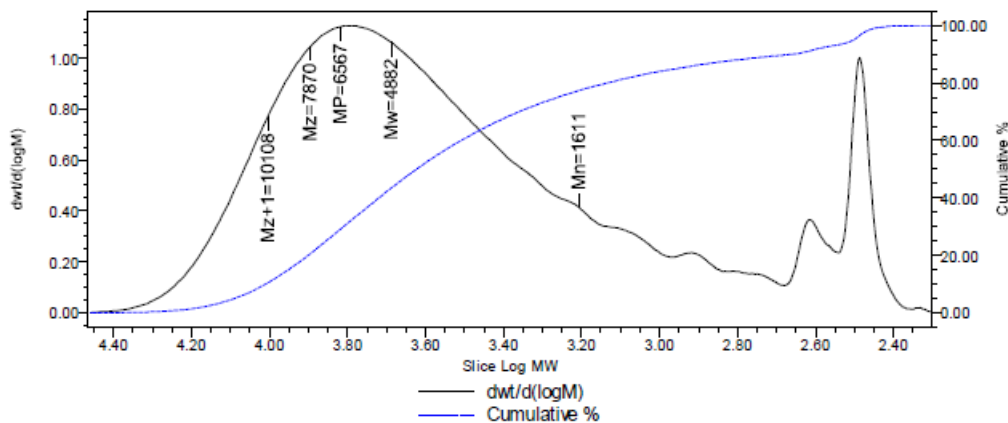
**Chromatogram**



**GPC Results**

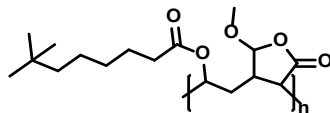
	Monstemaam	tr	Mn	Mw	Mz	D	MP	% Area
1	GPC377: 2-035	15.30	1611	4882	7870	3.03	6567	100.00

**Distribution plot**



**Fig. S146.** Structure and GPC results, chromatogram, results and distribution plot, of copolymer methoxybutenolide-dodecyl-vinyl-ether-copolymer **BP3**.

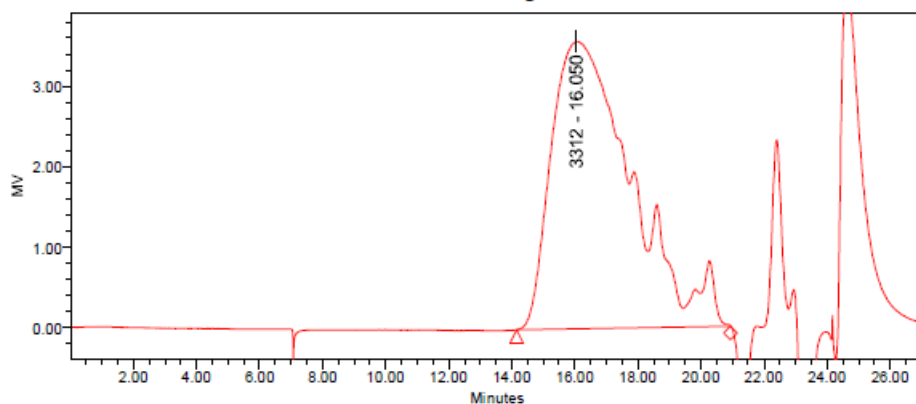
## 5-methoxy-2(5H)-furanone-VeoVa-10-copolymer BP2



### Akzo Nobel Coatings Analytical Lab Sassenheim

sample name:	GPC377: 3-037	GPC conditions
date acquired:	1/15/2020 2:43:13 PM CET	column: GPC_polypore
date processed:	1/16/2020 2:53:24 PM CET	eluent: THF/HAc (99/1)
proc. method:	GPC_Alliance_noref_polypore	flow: 1 ml/min
Reported by:	lizet	detector: RI detector
		inj. vol.: 50.00 uL

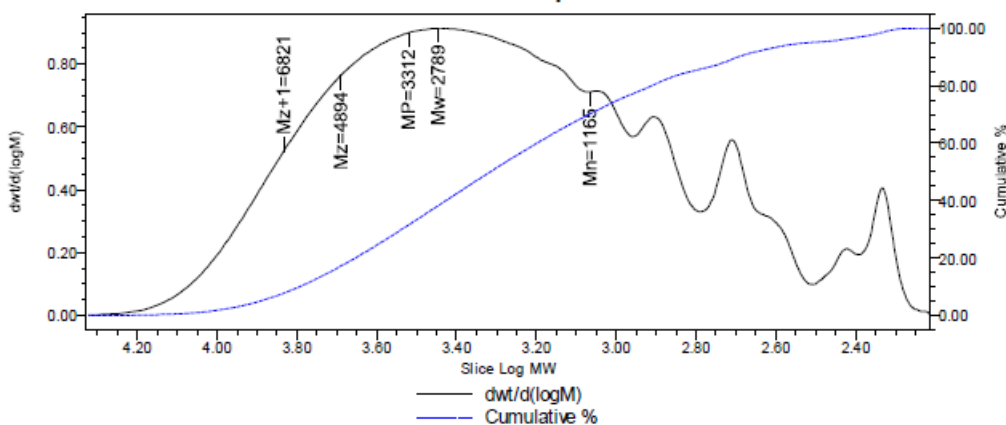
#### Chromatogram



#### GPC Results

Monstemaam	tr	Mn	Mw	Mz	D	MP	% Area
1 GPC377: 3-037	16.05	1165	2789	4894	2.39	3312	100.00

#### Distribution plot



**Fig. S145.** Structure and GPC results, chromatogram, results and distribution plot, of copolymer methoxybutenolide-VeoVa-10-copolymer **BP2**.

## Polymer Properties, GPC traces and DSC

The molecular weights and glass transition temperatures  $T_g$  were measured for the different polymers of the copolymerization of alkoxybutenolides **B2–5** with VeoVa-10 and dodecyl vinyl ether and for the homo- and co-polymerization of butyl acrylate and butyl acrylate with VeoVa-10, respectively.

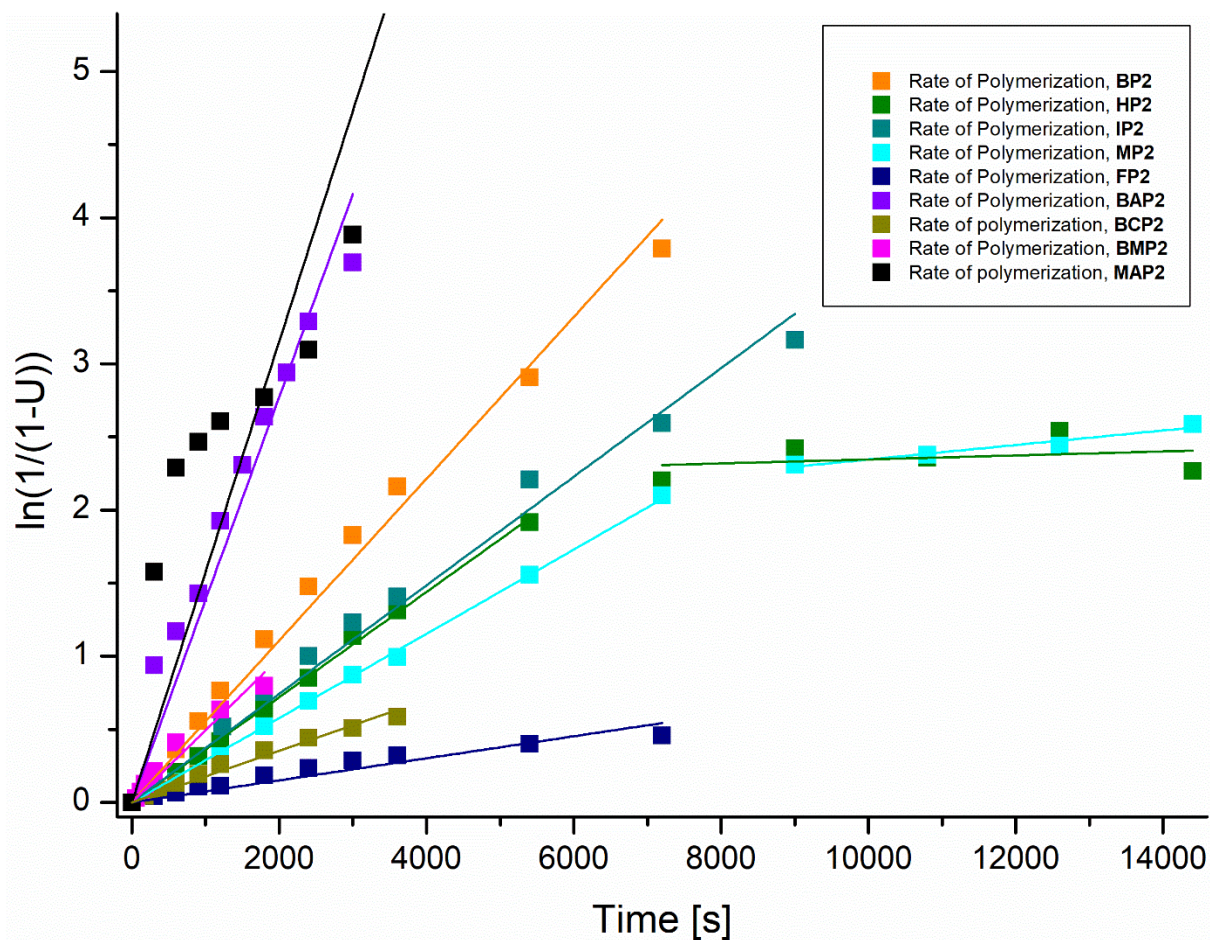
GPC conditions: Agilent Polypore, THF/acetic acid (99/1), 1 mL/min, RI detector, 50  $\mu$ L injection. Calibrated on polystyrene.

DSC method: The glass transition temperature ( $T_g$ ) is being determined with the DSC Q2000 of TA Instruments in the modulation mode.

After drying the sample for 24h at 80°C in an oven, a DSC cup filled with the sample and an empty DSC reference cup are heated in the Differential Scanning Calorimeter (DSC) in a modulated way according to ASTM method D3418.

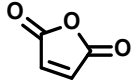
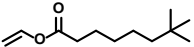
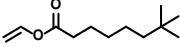

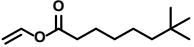

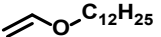

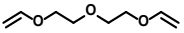

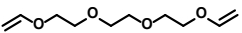
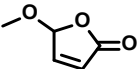
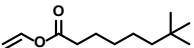
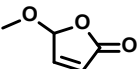
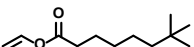
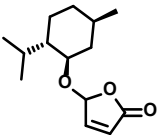
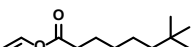
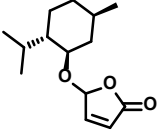
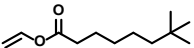
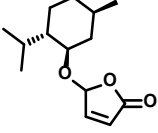
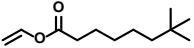
DSC modulation conditions: MDSC schedule -150°C/100°C with 1 °C every 40 seconds, 3 cycles (two heating cycles and one cooling), Heating: 5 °C/min, Cooling 10°C/min. Second heating cycle gives most accurate  $T_g$  value.

The copolymerizations, performed under identical conditions, of various monomers with VeoVa-10 was summarized in **Fig. S144**. This figure depicts the relative reactivity of alkoxybutenolides to acrylate type analogues. The various alkoxybutenolide monomers show, as expected, a lower reactivity than butyl acrylate (**BAP2**), butylmethacrylate (**BMP2**) and maleic anhydride (**MAP2**). The reactivity is comparable to that of butyl crotonate (**BCP2**), featuring a *trans* internal alkene, and dramatically higher than 2(5H)-furanone, containing no acetal functionality (**Fig. 7B**).



**Fig. S144** Comparison of rates of copolymerizations with VeoVa-10 as monomer 2. Copolymer coding: **FP2** = 2(5H)-furanone copolymer, **BAP2** = butyl acrylate copolymer, **BMP2** = butyl methacrylate copolymer, **BCP2** = butyl crotonate copolymer, **MAP2** = maleic anhydride copolymer. Reaction conditions: monomer 1 – VeoVa-10 (1:1 ratio), Trigonox 42S (6 mol%), 2.15 M in 1-methoxy-2-propanol, reflux, 1 h – 4 h.



Polymer	Monomer 1	Monomer 2	Conversion (%)	$k(1)_{\text{obs}} (\text{s}^{-1})$	$k(2)_{\text{obs}} (\text{s}^{-1})$
MAP2			>99	$(1.6 \pm 0.2) \cdot 10^{-3}$	-
VP1		/	>99	$(2.0 \pm 0.1) \cdot 10^{-3}$	-
FP2			37 <sup>c</sup>	$(7.5 \pm 0.4) \cdot 10^{-5}$	-
FP3			58 <sup>d</sup>	$(2.7 \pm 0.1) \cdot 10^{-4}$	-
FP4			35 <sup>e</sup>	$(5.0 \pm 1.1) \cdot 10^{-3}$	-
FP6			36 <sup>e</sup>	$(1.4 \pm 0.1) \cdot 10^{-2}$	-
BP2 (add. BP2)			96	$(6.9 \pm 0.1) \cdot 10^{-4}$	$(2.5 \pm 0.2) \cdot 10^{-4}$
BP2 (BP2 dil.)			94	$(5.0 \pm 0.1) \cdot 10^{-4}$	-
MP2 (add. MP2)			74	$(3.0 \pm 0.2) \cdot 10^{-4}$	$(2.6 \pm 0.8) \cdot 10^{-5}$
MP2 (MP2 dil.)			75	$(2.6 \pm 0.1) \cdot 10^{-4}$	$(2.8 \pm 1.0) \cdot 10^{-5}$
MP2 (12% ini.)			91	$(4.3 \pm 0.1) \cdot 10^{-4}$	$(3.8 \pm 1.7) \cdot 10^{-5}$

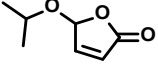
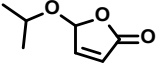
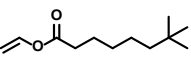
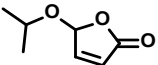
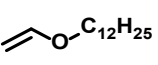
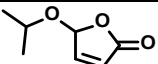
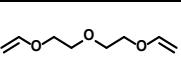
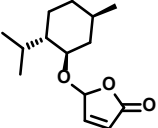
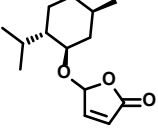

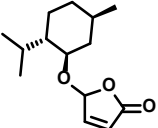
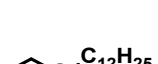
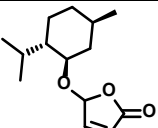

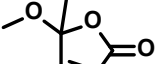
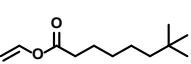
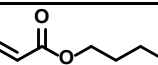
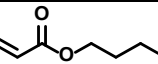
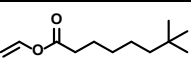
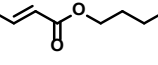
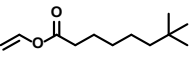
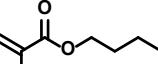
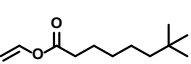
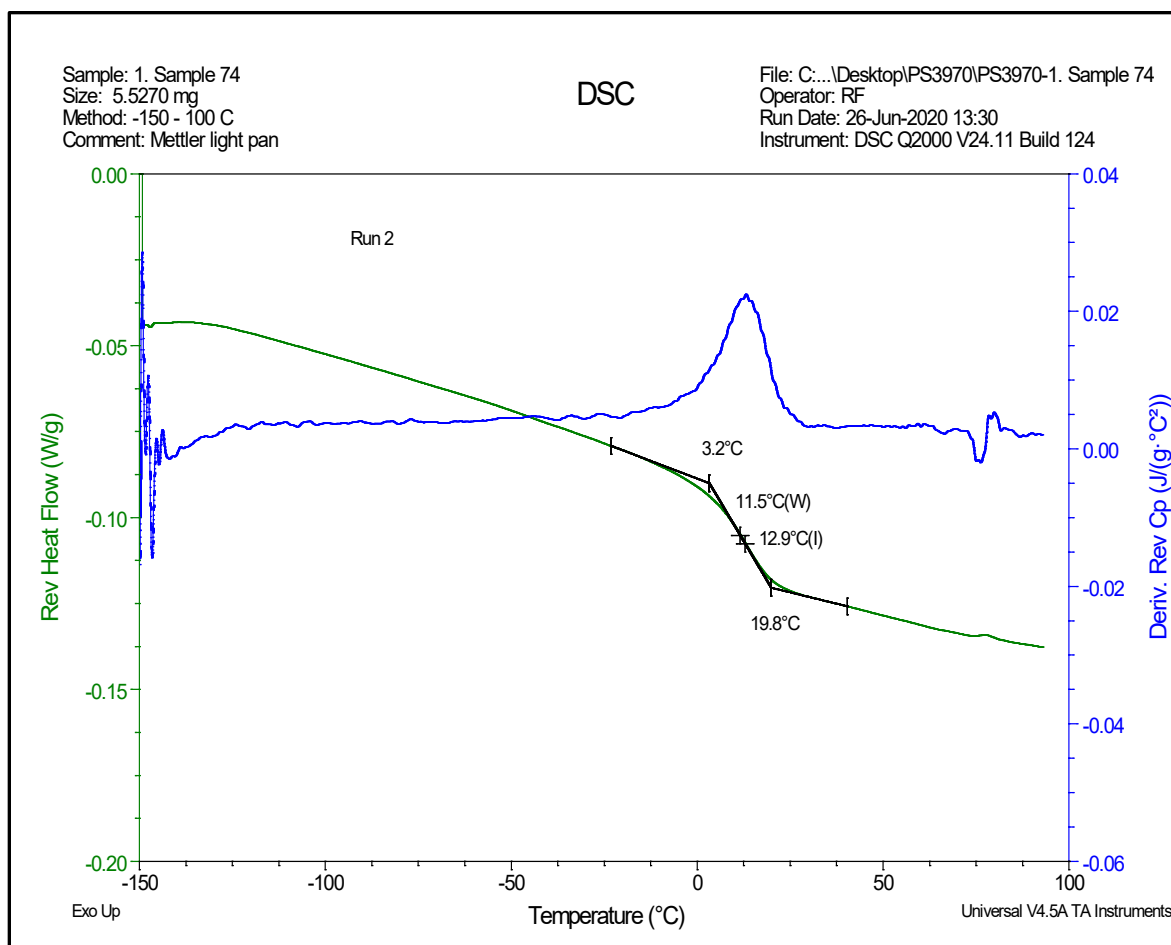
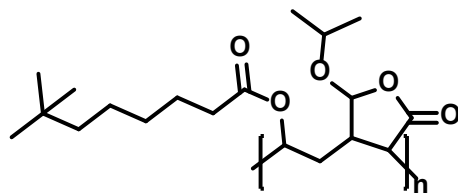
Polymer	Monomer 1	Monomer 2	Conversion (%)	$k(1)_{\text{obs}} (\text{s}^{-1})$	$k(2)_{\text{obs}} (\text{s}^{-1})$
IP1		/	37	$(1.1 \pm 0.1) \cdot 10^{-4}$	$(3.7 \pm 0.2) \cdot 10^{-5}$
IP2			96	$(3.7 \pm 0.1) \cdot 10^{-4}$	-
IP3			>99	$(2.0 \pm 0.1) \cdot 10^{-3}$	-
IP4			91 <sup>a</sup>	$(1.8 \pm 0.1) \cdot 10^{-3}$	-
MP1		/	30	$(9.2 \pm 0.2) \cdot 10^{-5}$	-
MP2			92	$(2.9 \pm 0.1) \cdot 10^{-4}$	$(5.0 \pm 0.8) \cdot 10^{-5}$
MP3			>99	$(1.1 \pm 0.1) \cdot 10^{-3}$	-
MP4			>99	$(3.2 \pm 0.3) \cdot 10^{-3}$	-
MMP2			45	$(1.3 \pm 0.1) \cdot 10^{-4}$	-
BAP1		/	90 <sup>b</sup>	$(7.0 \pm 0.3) \cdot 10^{-3}$	-
BAP2			98	$(1.4 \pm 0.1) \cdot 10^{-3}$	-
BCP2			44 <sup>c</sup>	$(1.8 \pm 0.1) \cdot 10^{-4}$	-
BMP2			55	$(4.9 \pm 0.3) \cdot 10^{-4}$	-

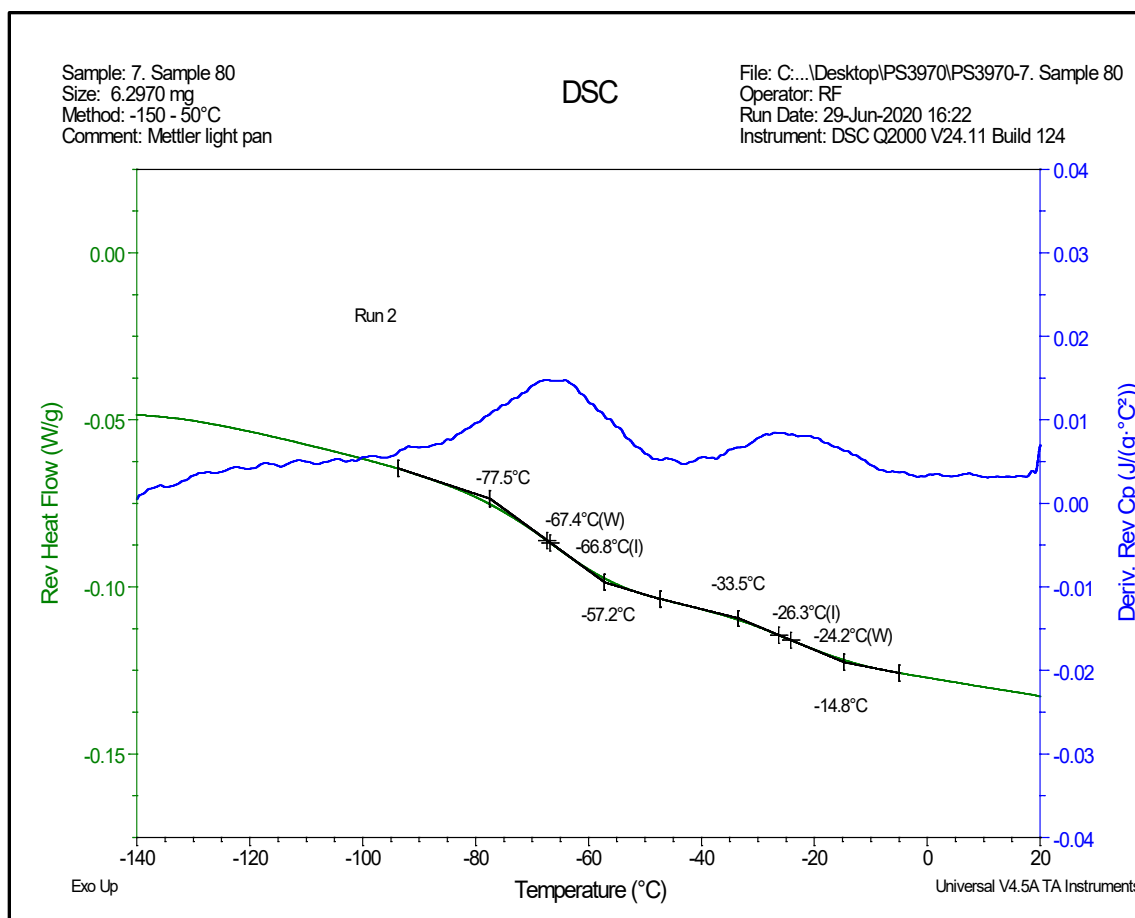
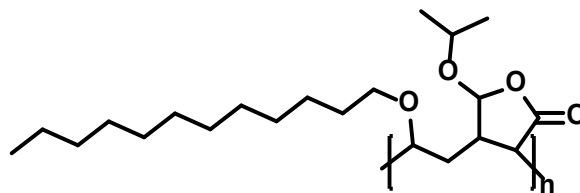
Table S38 continued on next page

# 5-isopropoxy-2(5H)-furanone-VeoVa-10-copolymer IP2



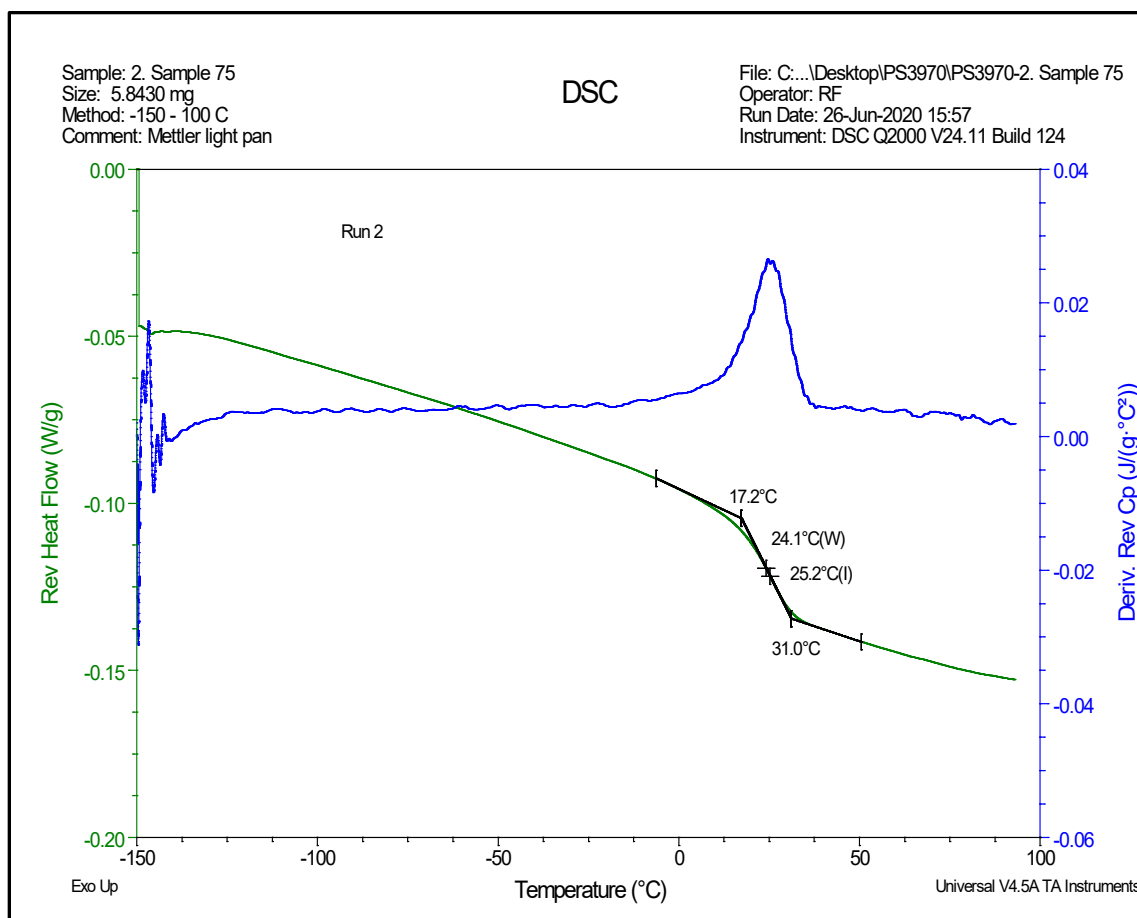
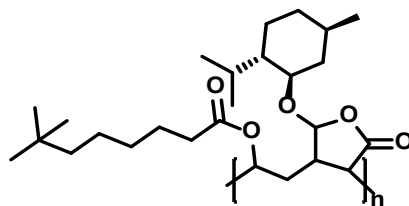
**Fig. S159.** Structure and DSC results of copolymer isopropoxybutenolide-VeoVa-10-copolymer **IP2**. Glass transition temperature of 12 °C.

### 5-isopropoxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer IP3



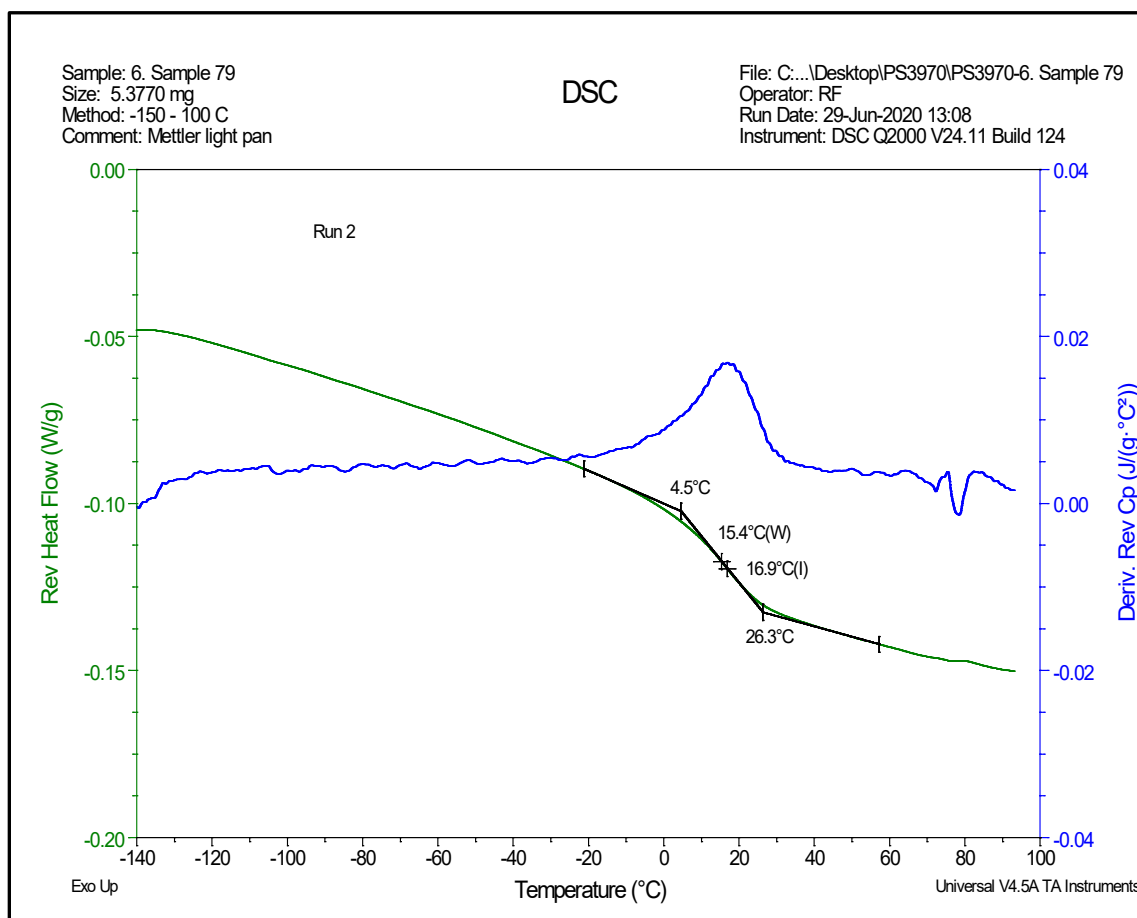
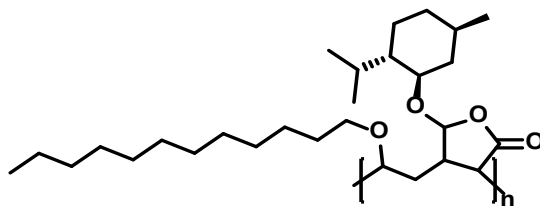
**Fig. S160.** Structure and DSC results of copolymer isopropoxybutenolide-dodecyl-vinyl-ether-copolymer IP3. Glass transition temperature of -67 °C. A second peak is visible at -25 °C, possibly due to a difference in composition of some of the polymers due to a slight mismatch in reactivity, see Fig. S57.

5-menthyloxy-2(5H)-furanone-VeoVa-10-copolymer MP2



**Fig. S161.** Structure and DSC results of copolymer menthyloxyoxybutenolide-VeoVa-10-copolymer **MP2**. Glass transition temperature of 24 °C.

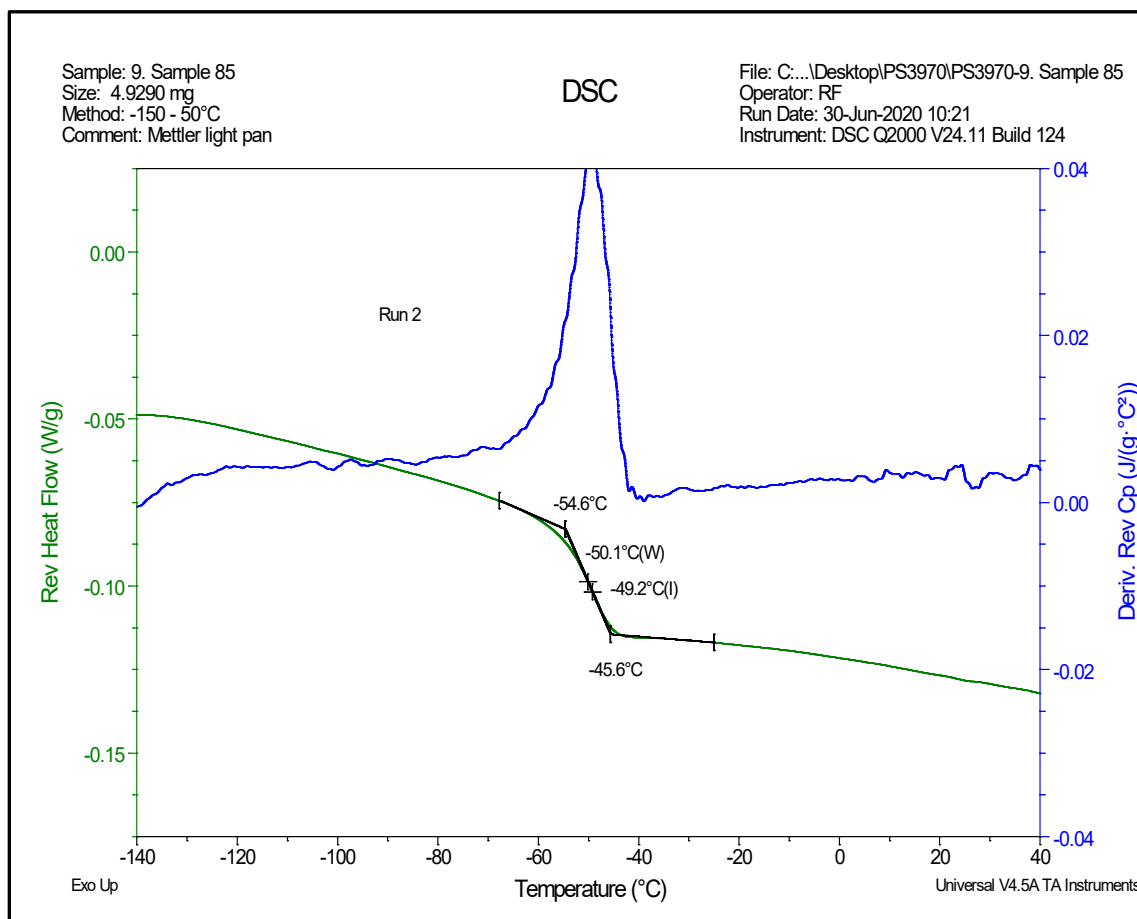
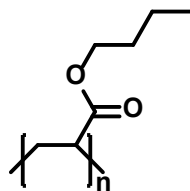
5-menthyloxy-2(5H)-furanone-dodecyl-vinyl-ether-copolymer MP3



**Fig. S162.** Structure and DSC results of copolymer menthyloxybutenolide-dodecyl-vinyl-ether-copolymer **MP3**. Glass transition temperature of 16 °C.

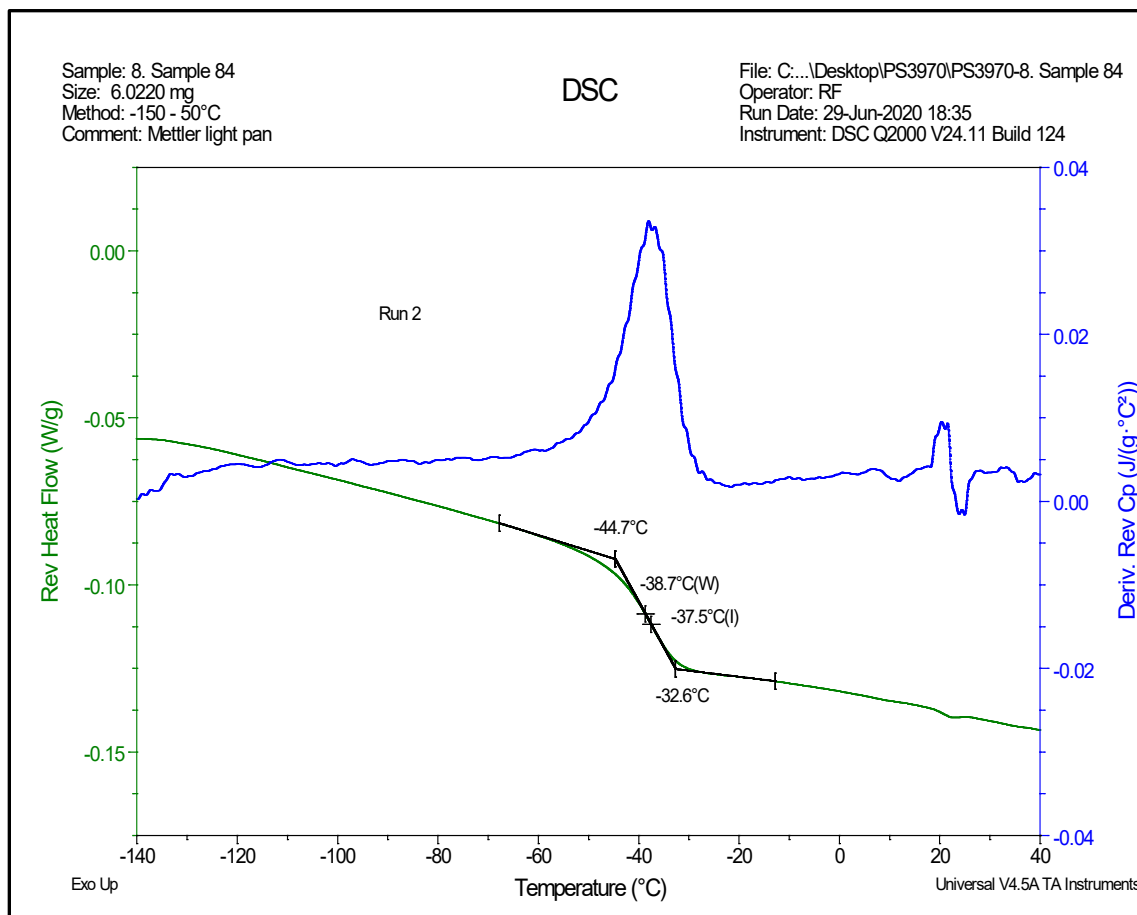
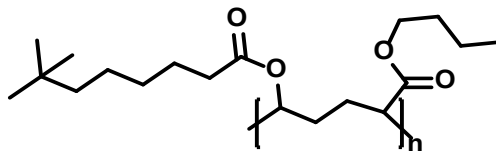


# poly-butyl-acrylate BAP1



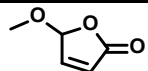
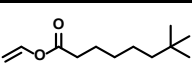
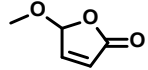
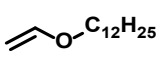
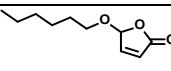
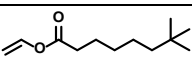
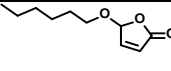
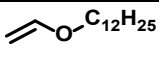
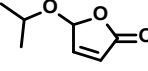
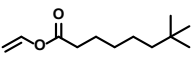
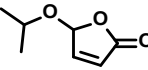
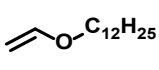
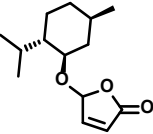
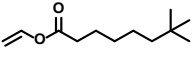
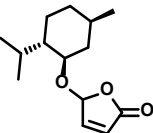
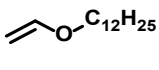
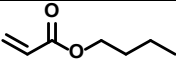
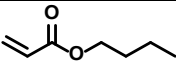
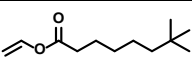
**Fig. S163.** Structure and DSC results of butyl-acrylate-homopolymer **BAP1**. Glass transition temperature of -39 °C.

**butyl-acrylate-VeoVa-10-copolymer BAP2**



**Fig. S164.** Structure and DSC results of copolymer butyl-acrylate-VeoVa-10-copolymer **BAP2**. Glass transition temperature of -50 °C.

**Table S39.** Properties of butenolide polymers. Polymer properties of alkoxybutenolide-based polymers **BP2**, **BP3**, **HP2**, **HP3**, **IP2**, **IP3**, **MP2**, **MP3** and butyl acrylate polymers, homopolymer **BAP1** and copolymer with VeoVa-10 **BAP2** for comparison; molecular weights, length and glass transition temperature ( $T_g$ ). a) Reaction conditions: 1:1 ratio of monomers, Trigonox 42S (6 mol%) (in case of homopolymerization 3 mol%), 2.15 M in 1-methoxy-2-propanol (in case of homopolymerization 4.3 M in 1-methoxy-2-propanol, reflux, 10 min – 4 h. b) Polydispersity ( $D$ ) is calculated by dividing  $M_w$  by  $M_n$ . c) Average amount of units in the polymer chain ( $n$ ) is Calculated through dividing number average molecular weight ( $M_n$ ) by average mass of unit (mass monomer 1 + mass monomer 2).

Polymer <sup>a</sup>	Monomer 1	Monomer 2	$M_n$ (g/mol)	$M_w$ (g/mol)	$D^b$	$n^c$	$T_g$ (°C)
BP2			1165	2789	2.39	8.93	12
BP3			1611	4882	3.03	14.69	-62
HP2			1242	3264	2.63	8.54	-27
HP3			1548	4587	2.96	11.57	-72
IP2			1572	3174	2.02	9.32	12
IP3			1764	4295	2.43	12.12	-67
MP2			1151	3101	2.69	7.11	24
MP3			1584	4711	2.97	10.46	16
BAP1		/	4022	15860	3.94	123.72	-39
BAP2			2806	10766	3.84	33.00	-50

## Coating Formation and Properties

### Coating Formation

The coatings of alkoxybutenolides **B2–5** with di(ethylene glycol) divinyl ether as crosslinker were formed according to **General Procedure B**.

A Byk applicator (50-200 $\mu$ m) was used for the preparation of the film.



**Fig. S165.** Byk applicator for film formation.

The coating was cured by UVA-light ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ) at a distance of 10 cm for 5 minutes.

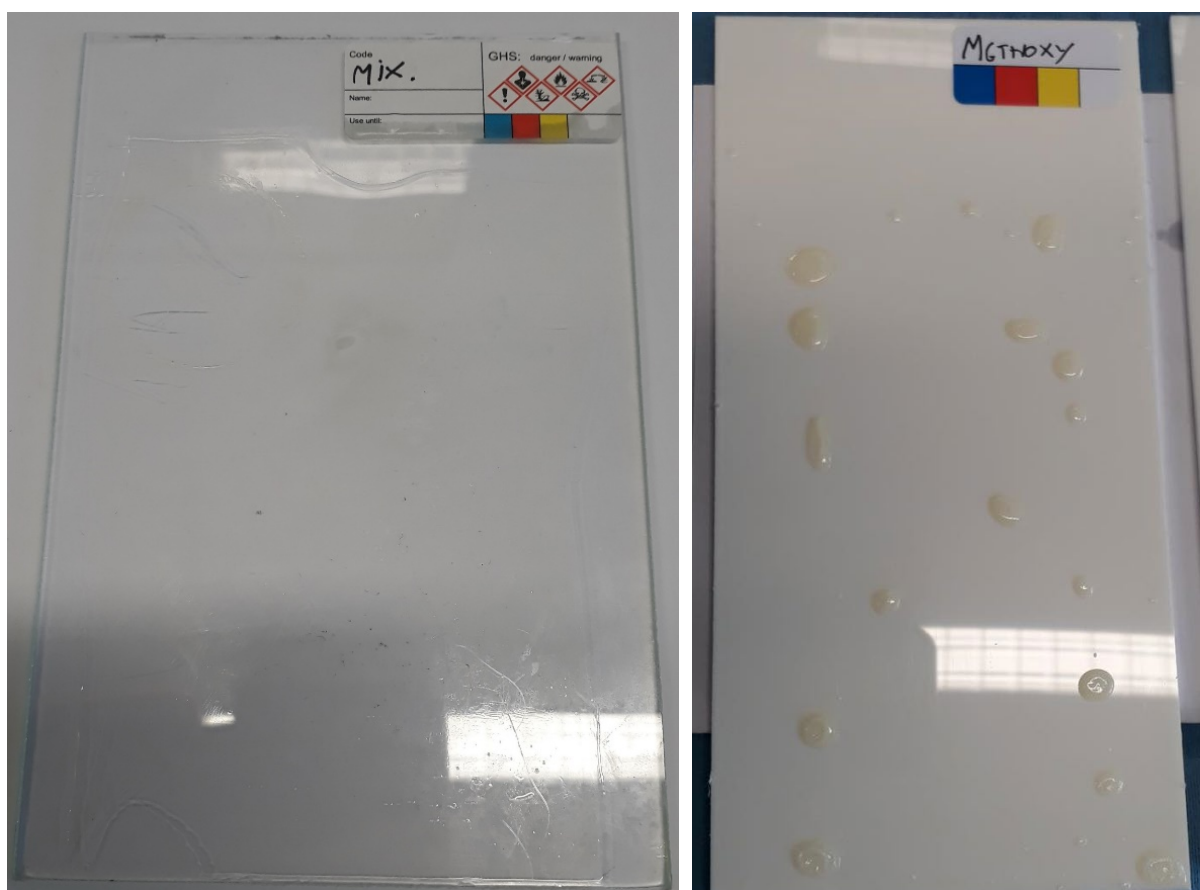


**Fig. S166.** Irradiation setup, LED Beacon above glass plate with uniform film of reaction mixture (alkoxybutenolide **B2–5** – di(ethylene glycol) divinyl ether (1:0.5 ratio) and 3 mol% of Omnirad 819 (bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (left), irradiation setup in action ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ) (right).



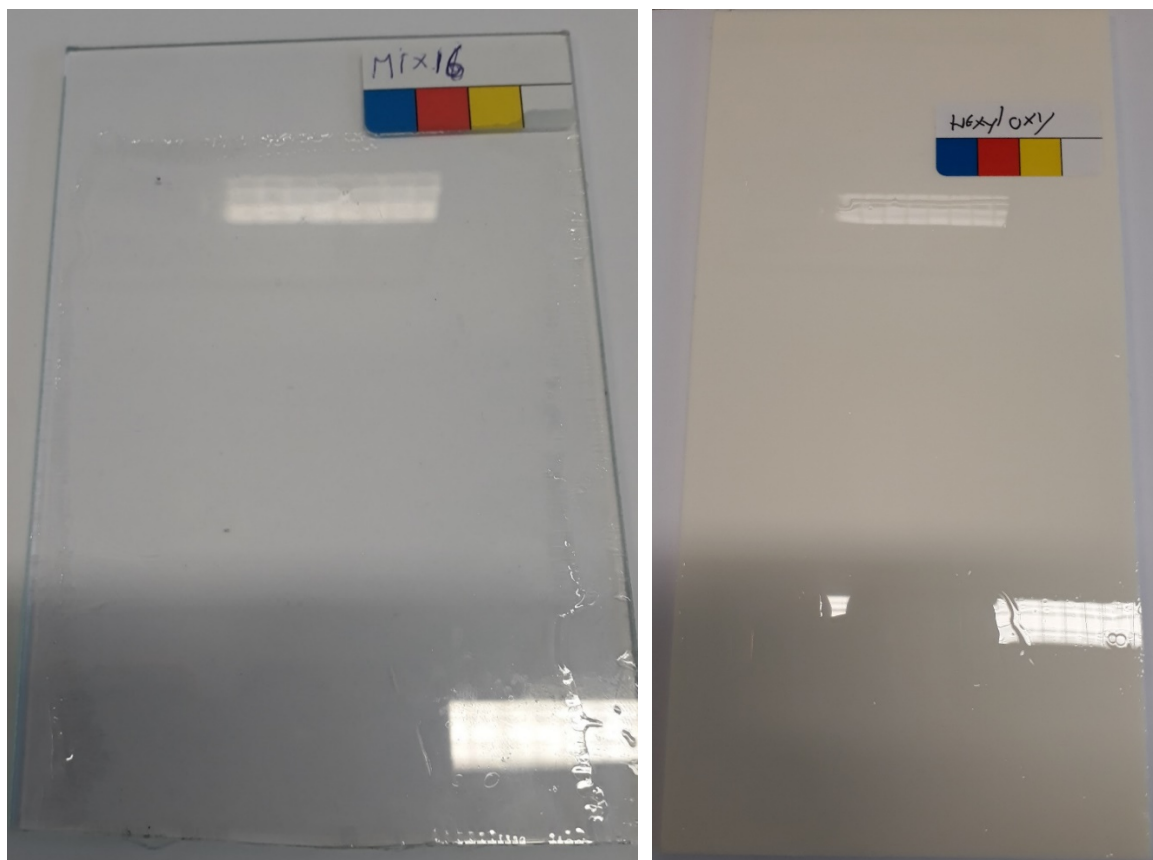
**Fig. S167.** Homogeneous reaction mixture consisting of monomers alkoxybutenolide **B2-5** – di(ethylene glycol) divinyl ether (1:0.5 ratio) and 3 mol% of Omnirad 819 (bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide) before application (left). Resulting alkoxybutenolide coating after UV-curing for 5 min ( $\lambda_{\text{irr}} = 395$  nm) (right).

All butenolide coatings (methoxy- **BP4**, hexyloxy- **HP4**, isopropoxy- **IP4** and menthyloxy- **MP4**) are excellent candidates for glass surfaces, as demonstrated in **Figs. S167–S172**. However only of **HP4** and **MP4**, a film could be applied on a hydrophobic surface of polypropylene, **Figs. S169, S171**. As methoxybutenolide **B2** and isopropoxybutenolide **B4** are more hydrophilic butenolides, instead of a film, droplets of the mixture (alkoxybutenolide, di(ethylene glycol) divinyl ether (1:0.5 ratio) and Omnirad 819 (3 mol%)) were observed upon application on the hydrophobic polypropylene surface, **Figs. S168, S170**. Immediate breaking and shattering of the droplets (**BP4** and **IP4**) and was observed upon UV-curing, presumably due to shrinking-induced stress. In the case of **MP4**, although application on the hydrophobic polypropylene surface was achieved, also immediate breaking and shattering of the film was observed. On the contrary, the softer, more hydrophobic, butenolide coating **HP4** could, aside from glass, also be applied on polypropylene, resulting in a hard uniform coating, without breaking upon UV-curing.

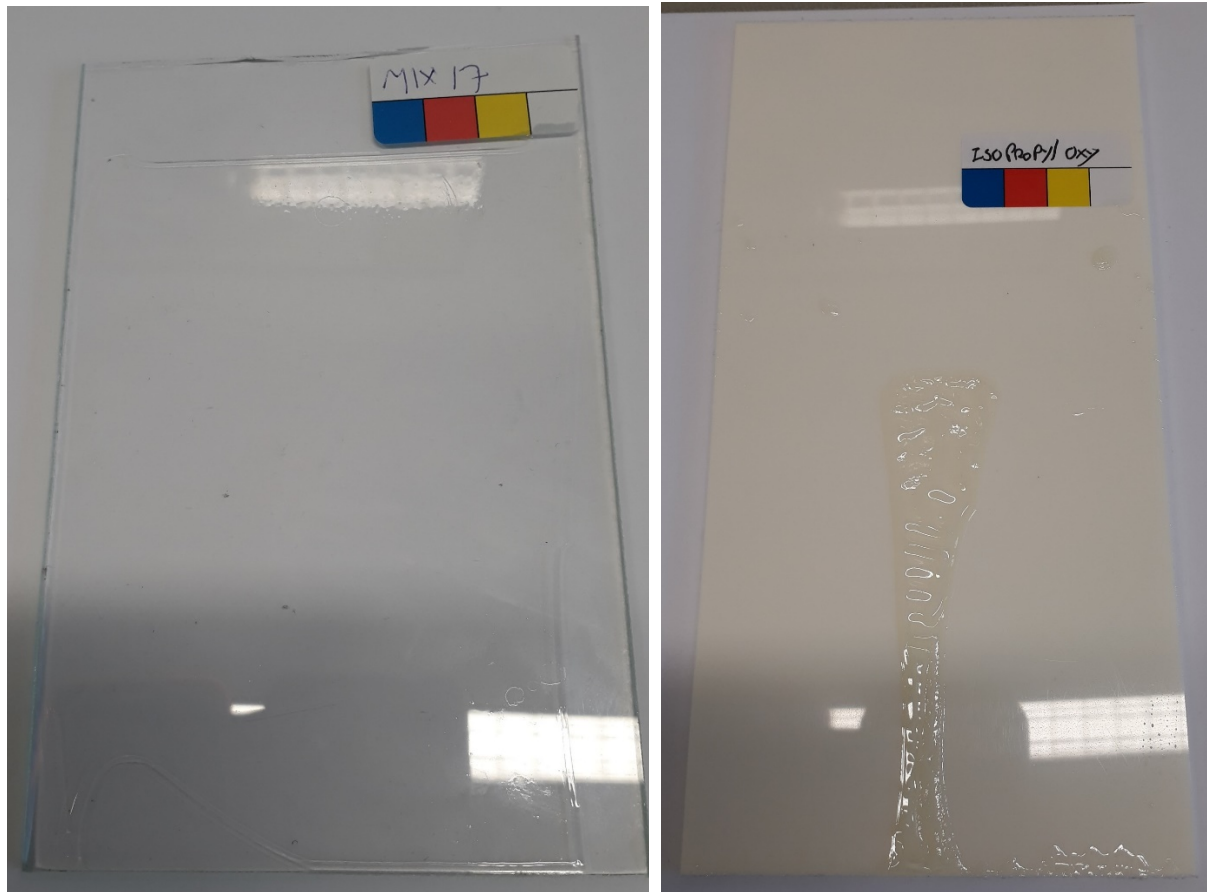


**Fig. S168.** Methoxybutenolide coating **BP4** (100  $\mu\text{m}$ ) on glass surface (left). **BP4** application on polypropylene. Droplet formation due to mismatch in hydrophobicity. Immediate breaking and shattering of droplets upon UV irradiation (right). Coating formation conditions: alkoxybutenolide – di(ethylene glycol) divinyl ether (1:0.5 ratio), Omnirad 819 (3 mol%), UV irradiation ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ), 5 min.

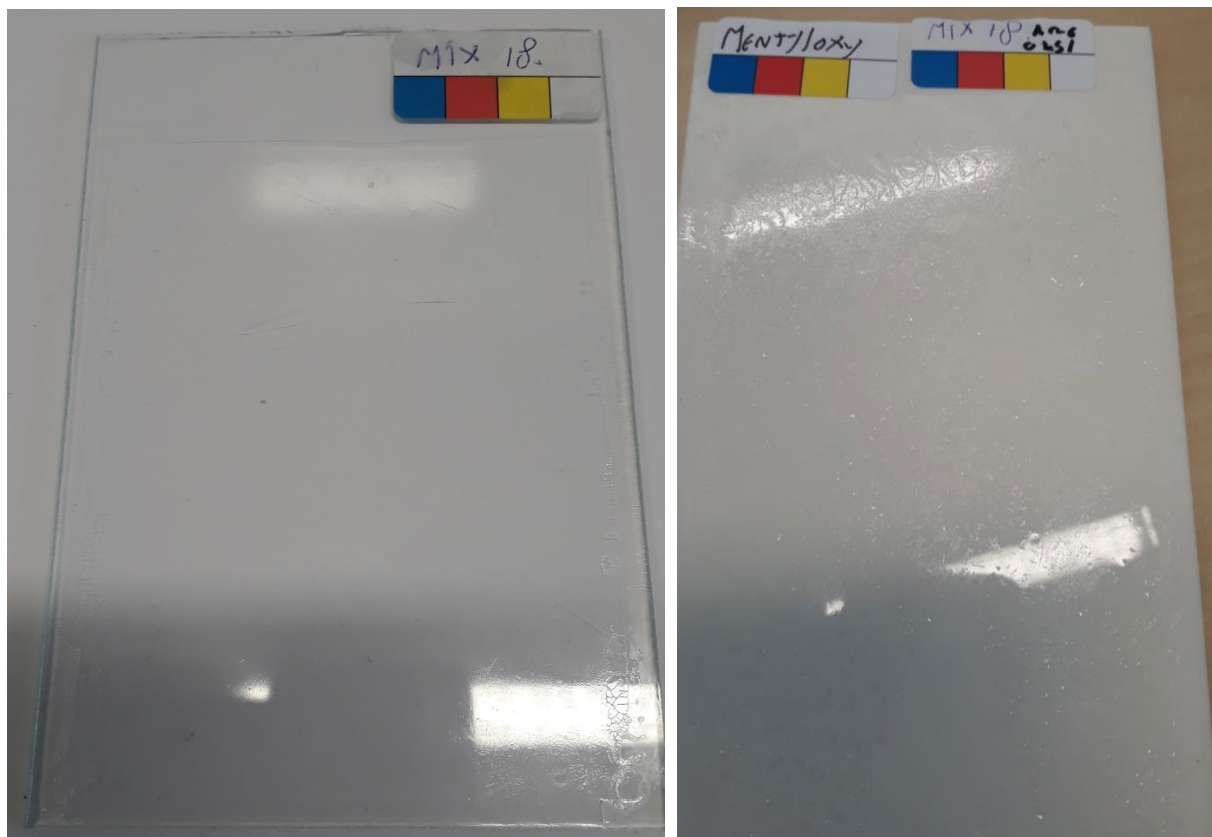




**Fig. S169.** Hexyloxybutenolide coating **HP4** (100 $\mu$ m) on glass surface (left), **HP4** application on polypropylene. Hard uniform coating formation upon UV irradiation (right). Coating formation conditions: alkoxybutenolide – di(ethylene glycol) divinyl ether (1:0.5 ratio), Omnirad 819 (3 mol%), UV irradiation ( $\lambda_{\text{irr}} = 395$  nm), 5 min.



**Fig. S170.** Isopropoxybutenolide coating **IP4** (100  $\mu\text{m}$ ) on glass surface (left), **IP4** application on polypropylene. Droplet formation due to mismatch in hydrophobicity. Immediate breaking and shattering of droplets upon UV irradiation (right). Coating formation conditions: alkoxybutenolide – di(ethylene glycol) divinyl ether (1:0.5 ratio), Omnirad 819 (3 mol%), UV irradiation ( $\lambda_{\text{irr}}=395$  nm), 5 min.



**Fig. S171.** Menthyloxybutenolide coating **MP4** (100  $\mu\text{m}$ ) on glass surface (left), **MP4** application on polypropylene. Immediate breaking and shattering of the film upon UV irradiation (right). Coating formation: alkoxybutenolide – di(ethylene glycol) divinyl ether (1:0.5 ratio), Omnirad 819 (3 mol%), 23 w% of butyl acetate, UV irradiation ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ), 5 min.



**Fig. S172.** Uniform transparent alkoxybutenolide coating on glass surface (example: hexyloxybutenolide coating **HP4**). Coating formation conditions: alkoxybutenolide – di(ethylene glycol) divinyl ether (1:0.5 ratio), Omnirad 819 (3 mol%), UV irradiation ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ), 5 min.

## Coating Properties

Pendulum hardness (Persoz hardness) of the cured coatings were determined according to ISO 1522. The number of pendulum swings for the amplitude of the pendulum to decrease from 12 to 4 degrees was determined and expressed in amount of swings.

The UV-cured coating thus obtained was tested as described below for water resistance and solvent resistance and for hardness, after 4 days of storing at 23 °C and 50 % relative humidity.

The chemical resistance to water and organic solvent (MEK) was determined using the standard spot tests. (43,46)

For the water resistance a droplet of demineralized water was put on the cured coating and covered by a watch glass. After 60 minutes, the water droplet was wiped off and the effect on the coating was determined visually on a scale of 0 to 5, wherein 5 means that the water droplet has no visible impact on the coating, and 0 means that the water droplet has a detrimental impact.

For the solvent resistance a droplet of 2-butanone (methyl ethyl ketone, MEK) was put on the cured coating. After 1 minute, the methyl ethyl ketone droplet was wiped off and the effect on the coating was determined visually on a scale of 0 to 5, wherein 5 means that the solvent droplet has no visible impact on the coating, and 0 means that the solvent droplet has a detrimental impact.

The crosslink density and glass transition temperature ( $T_g$ ) is determined via Dynamic Mechanical Thermal Analysis (DMTA). A 100  $\mu\text{m}$  wet film of coating composition was drawn on a polypropylene panel using a drawing bar. The wet film was cured by irradiating the film with UV light using a UV-A LED irradiation device (ex. SemiLEDs Corporation) with 12 LED lamps emitting UV light with a wavelength of 395 nm and a total irradiance of 4.5  $\text{mW}/\text{cm}^2$  during 5 minutes at a distance of 10 cm. The cured coating was then removed from the panel and subjected to Dynamic Mechanical Thermal Analysis (DMTA) according to ISO 6721-11, using a TA Instruments RSA3 dynamic mechanical analyzer. The oscillation frequency was 10 rad/s, the temperature of the sample was increased from 20 °C to 200 °C with temperature increments of 5.0 °C.

In the case of **BP4**, **IP4** and **MP4** the resulting coatings were too hydrophilic to be applied on the surface panel of polypropylene. To get a value for the crosslink density and glass transition temperature, as these are measured from a polypropylene surface, the wettability of the mixture had to be increased by the addition of VeoVa-10. Furthermore the addition of VeoVa-10 reduces the hardness and the glass transition temperature of the coatings, **Table S40**. The equivalents of DVE were lowered from 1.0 to 0.7 and 0.6 equivalents of VeoVa-10 were added. In this way the total amount of alkenes and butenolide in the reaction mixture remained constant.

The crosslink density ( $M_c$ ) of the coatings **BP4**, **IP4** and **MP4** containing 0.6 equivalents VeoVa-10 was calculated from the measured storage modulus  $E'$  (kPa) at temperature (K) where  $E'$  is at a minimum, according to the following equation (50):

**Equation S6.** Crosslink density.

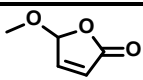
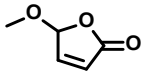
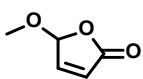
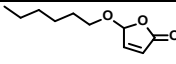
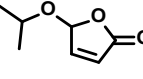
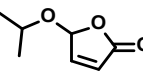
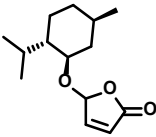
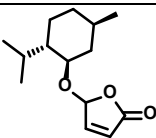
$$M_c = \frac{3RTd}{E'}$$

With the ideal gas constant  $R$  ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and the  $d$  being the polymer density ( $\text{g}/\text{cm}^3$ ) of 1.1, resembling a polyacrylate (polybutyl acrylate = 1.087).

The calculated crosslink densities are summarized in **Table S41**.

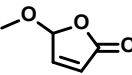
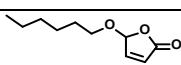
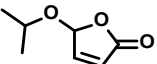
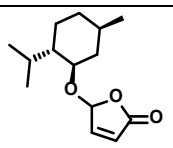
In the case of menthyloxycoating **MP4**, the DMTA measurement showed a broad glass transition range (**Fig. S175**). Therefore the calculation of the crosslink density is inaccurate.

**Table S40.** Summary of properties of alkoxybutenolide coatings. Coating formation: alkoxybutenolide – di(ethylene glycol) divinyl ether (1:0.5 ratio), Omnirad 819 (3 mol%), UV irradiation ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ), 5 min. a) Water/MEK resistance, 0 = damaged coating, 5 = no damage. b) 23 w% (0.9 mL) of butyl acetate was added to dissolve the monomers. c) VeoVa-10 added for increasing hydrophobicity to coat on polypropylene, butenolide/DVE/VeoVa-10 – 2/0.7/0.6 eq. ND = not determined, N/A = not available.

Polymer	Monomer 1	Dry Film thickness ( $\mu\text{m}$ )	Water resistance (0–5) <sup>a</sup>	MEK resistance (0–5) <sup>a</sup>	Hardness (oscillations)	VeoVa-10 added <sup>c</sup> (+/–)	Glass transition temperature (°C)
BP4		120	5	3	249	–	ND
BP4		100	5	4	285	–	N/A
BP4 (+)		100	5	4	218	+	156
HP4		100	5	5	145	–	86
IP4		100	5	4	241	–	N/A
IP4 (+)		100	5	4	220	+	95
MP4 <sup>b</sup>		100	5	4	261	–	N/A
MP4 <sup>b</sup> (+)		100	5	3	149	+	108

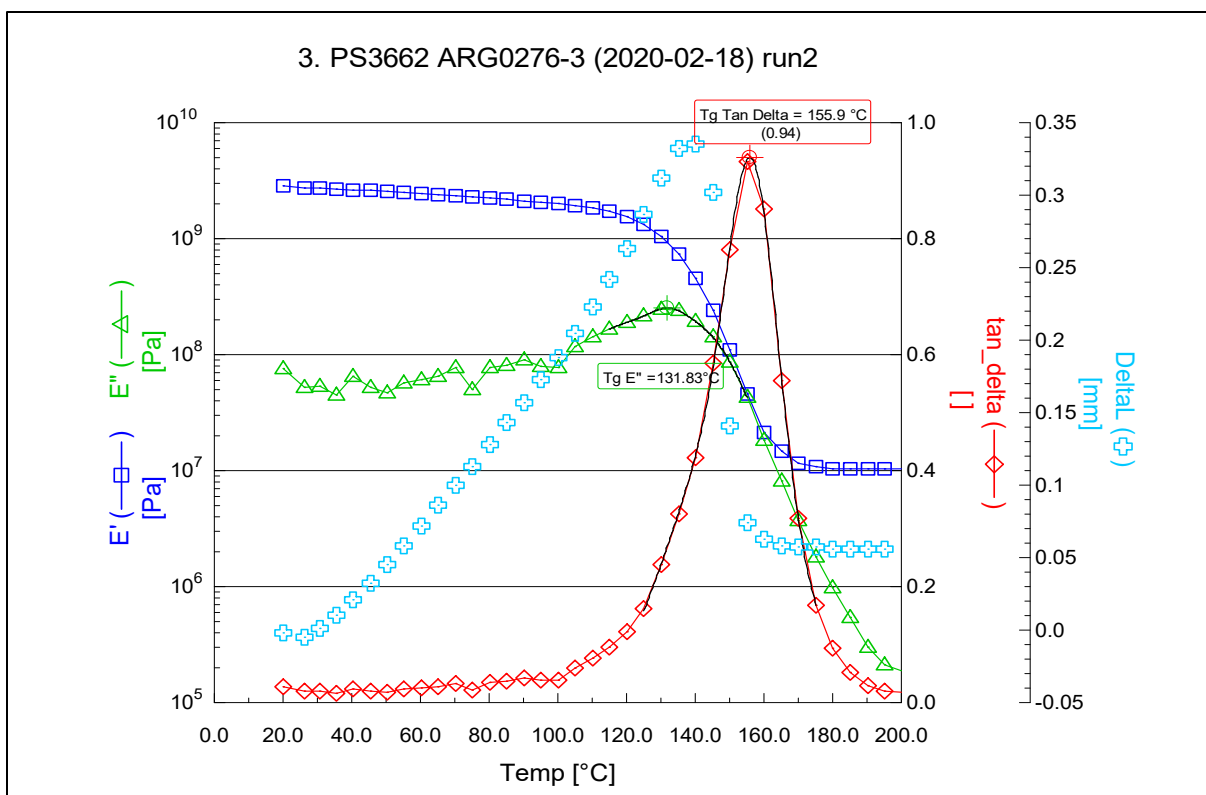


**Table S41.** Summary of crosslink densities of alkoxybutenolide coatings. Coating formation: alkoxybutenolide – di(ethylene glycol) divinyl ether (1:0.5 ratio), Omnirad 819 (3 mol%), UV irradiation ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ), 5 min. a) VeoVa-10 was added for increasing the hydrophobicity to coat on polypropylene, alkoxybutenolide–DVE–VeoVa-10 (2:0.7:0.6 ratio).

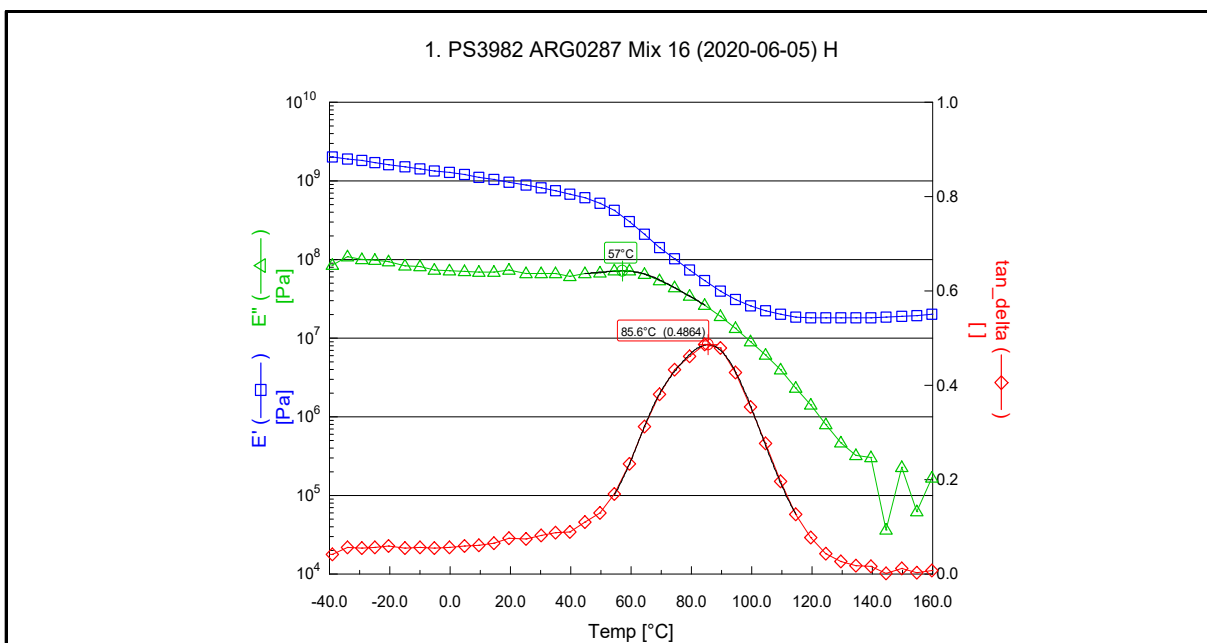
Polymer	Monomer 1	Dry Film thickness ( $\mu\text{m}$ )	Crosslink density (g/mol)
BP4 <sup>a</sup> (+)		100	1251
HP4		100	619
IP4 <sup>a</sup> (+)		100	1402
MP4 <sup>a</sup> (+)		100	11018



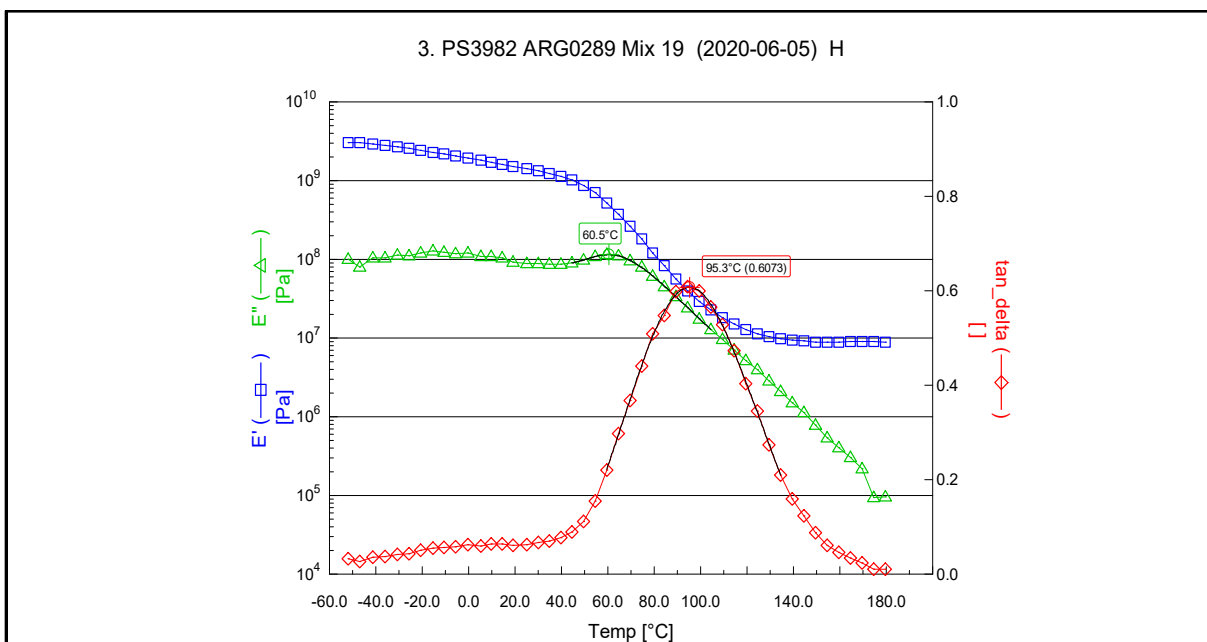
**Fig. S173.** Methoxybutenolide coating **BP4** subjected to standardized spot tests, droplet of water removed after 1 hour, droplet of 2-butanone (MEK) removed after 1 min. Water has no effect on coating resulting in no visible defects. MEK has a minor effect on coating resulting in very slight discoloring. Coating formation conditions: alkoxybutenolide – di(ethylene glycol) divinyl ether (1:0.5 ratio), Omnirad 819 (3 mol%), UV irradiation ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ), 5 min.



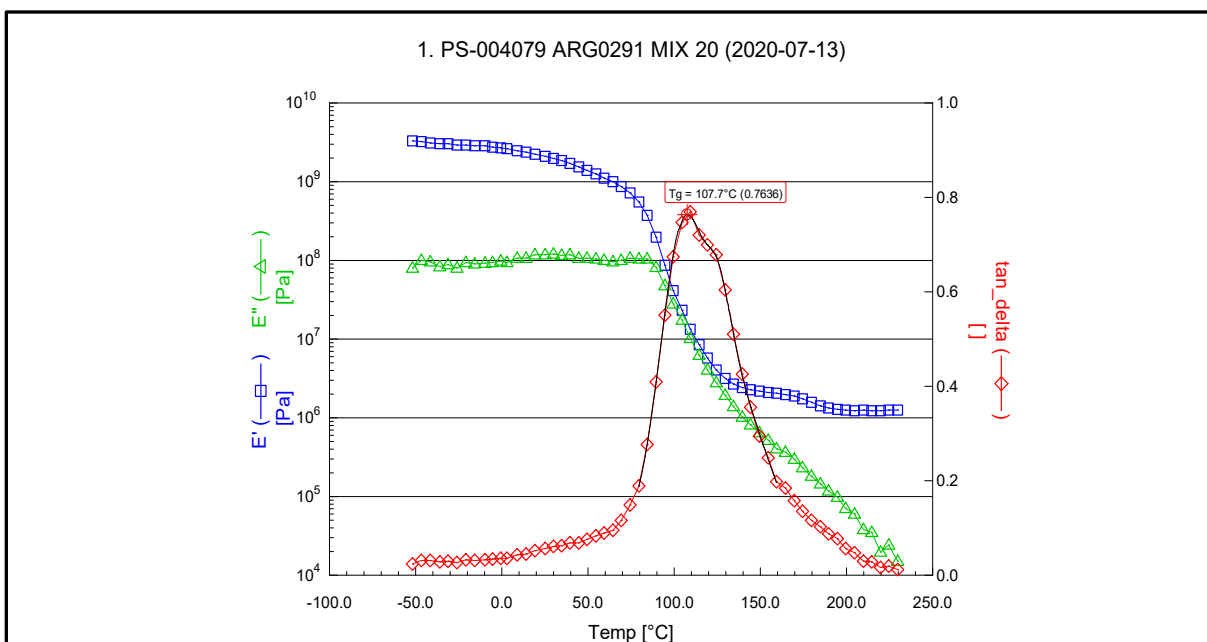
**Fig. S174.** DMTA analysis for determination of crosslink density and glass transition temperature of methoxybutenolide coating **BP4**, VeoVa-10 added for lower hardness, alkoxybutenolide–DVE–VeoVa-10 (2:0.7:0.6 ratio). Coating formation: Omnirad 819 (3 mol%), ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ), 5 min.



**Fig. S175.** DMTA analysis for determination of crosslink density and glass transition temperature of hexyloxybutenolide coating **HP4**. Coating formation: alkoxybutenolide–DVE (1:0.5 ratio), Omnirad 819 (3 mol%), ( $\lambda_{irr} = 395$  nm), 5 min.



**Fig. S176.** DMTA analysis for determination of crosslink density and glass transition temperature of isopropoxybutenolide coating **IP4**, VeoVa-10 added for lower hardness, alkoxybutenolide–DVE–VeoVa-10 (2:0.7:0.6 ratio). Coating formation: Omnirad 819 (3 mol%), ( $\lambda_{\text{irr}} = 395 \text{ nm}$ ), 5 min.



**Fig. S177.** DMTA analysis for determination of crosslink density and glass transition temperature of menthyloxybutenolide coating **MP4**, VeoVa-10 added for lower hardness, alkoxybutenolide–DVE–VeoVa-10 (2:0.7:0.6 ratio). Coating formation: 23 w% butyl acetate, Omnirad 819 (3 mol%), ( $\lambda_{\text{irr}} = 395$  nm), 5 min



## NMR spectra compounds

### 5-hydroxy-2(5H)-furanone (hydroxybutenolide) B1

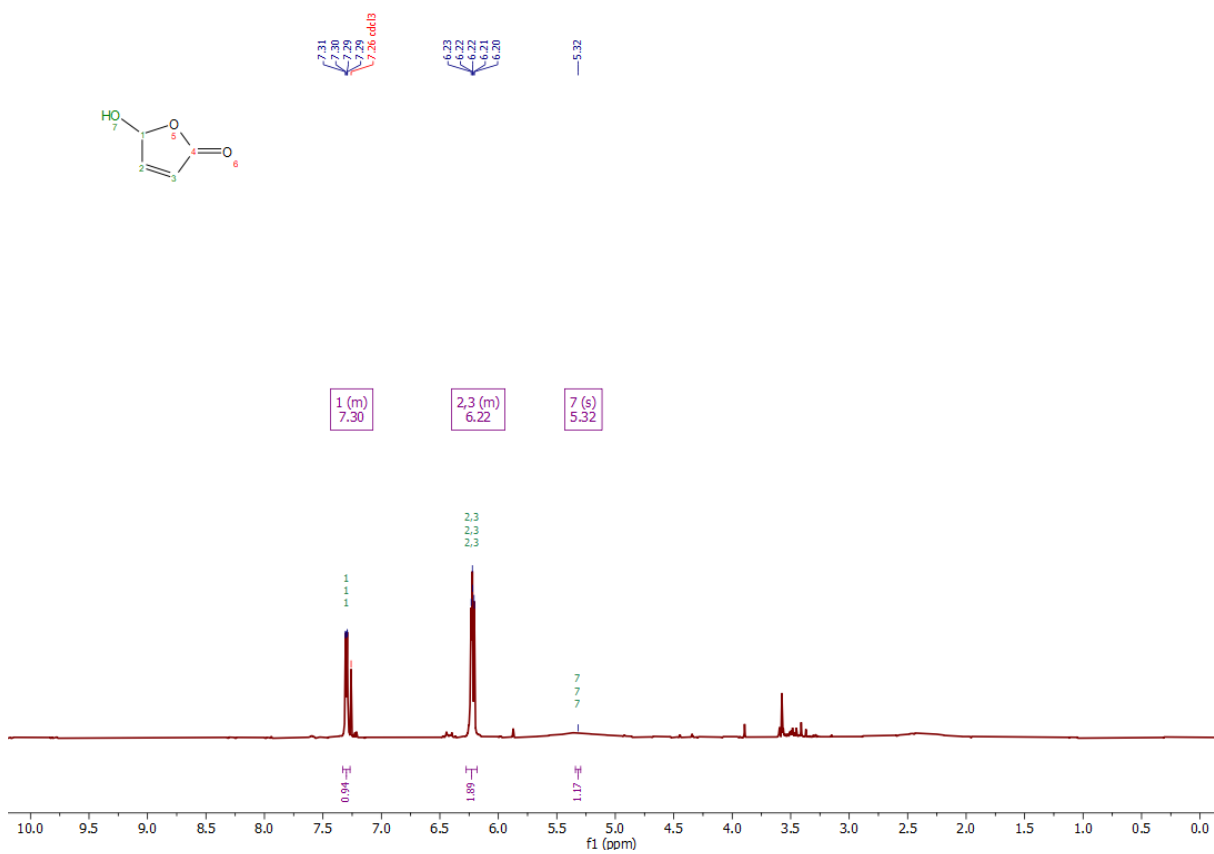
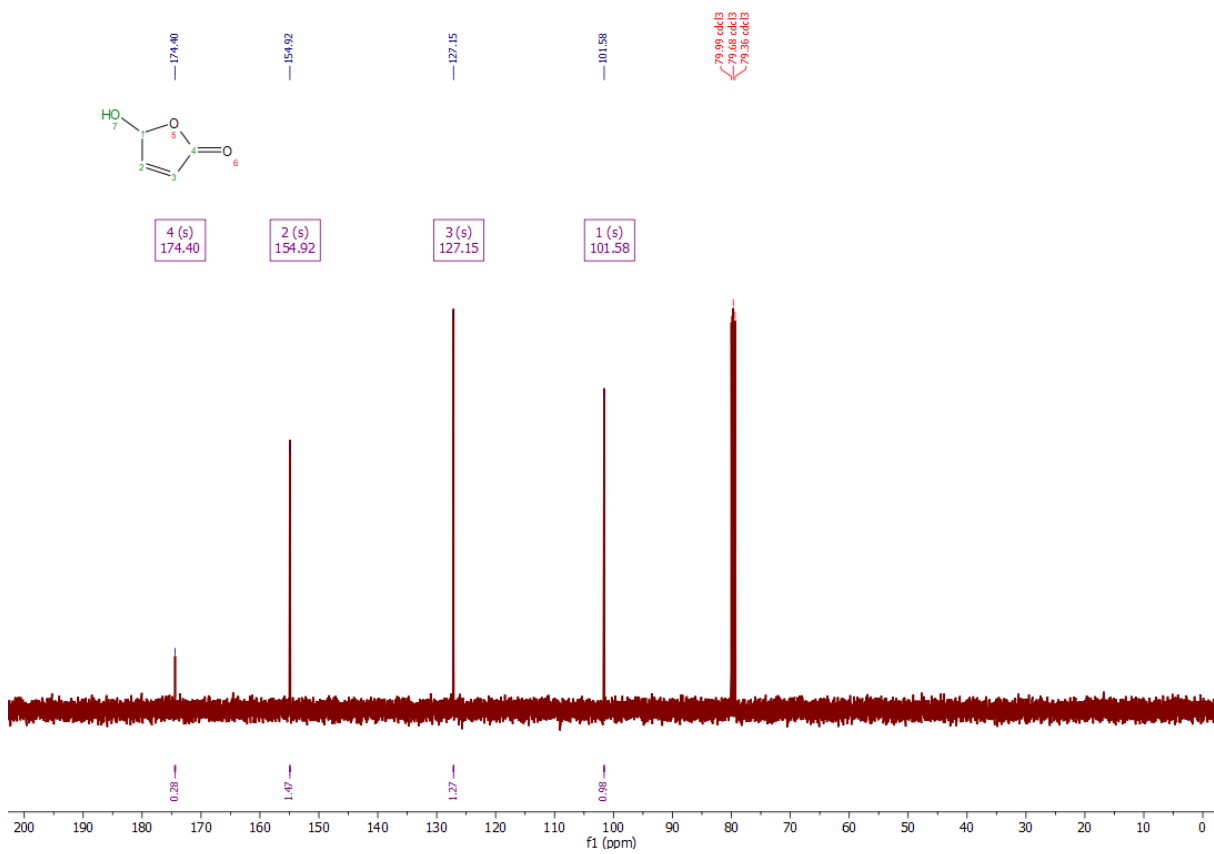
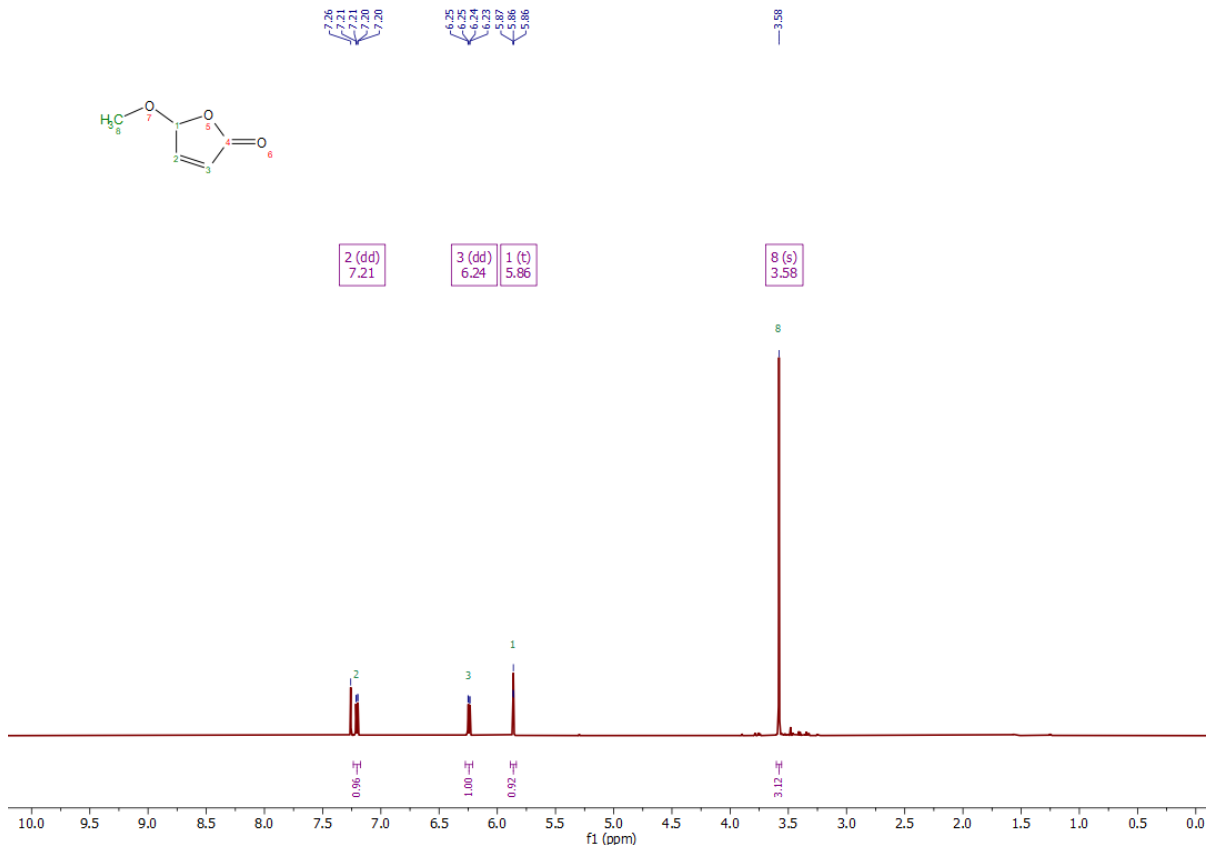


Fig. S178.  $^1\text{H-NMR}$  spectrum of B1 measured at 298 K in  $\text{CDCl}_3$ .

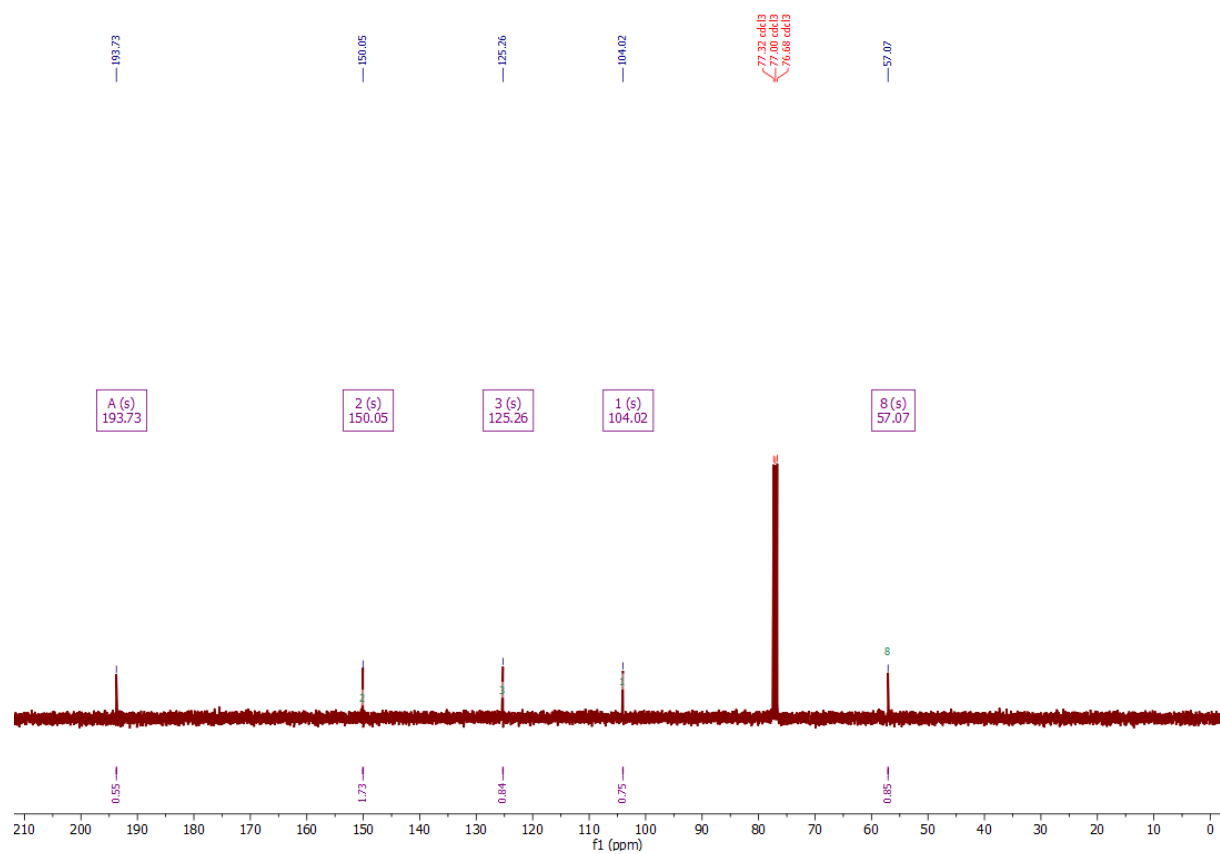


**Fig. S179.**  $^{13}\text{C}$ -NMR spectrum of **B1** measured at 298 K in  $\text{CDCl}_3$ .

**5-methoxy-2(5H)-furanone (methoxybutenolide) B2**

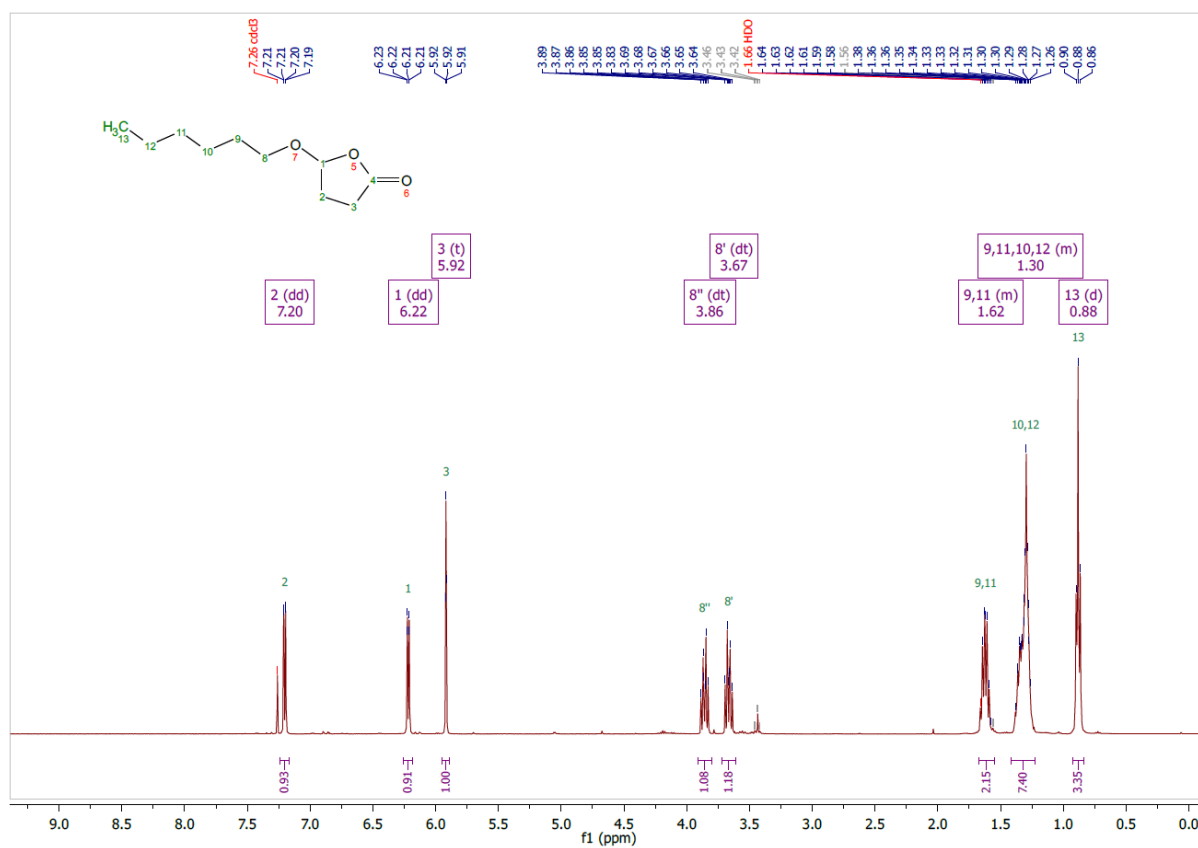


**Fig. S180.** <sup>1</sup>H-NMR spectrum of **B2** measured at 298 K in CDCl<sub>3</sub>.

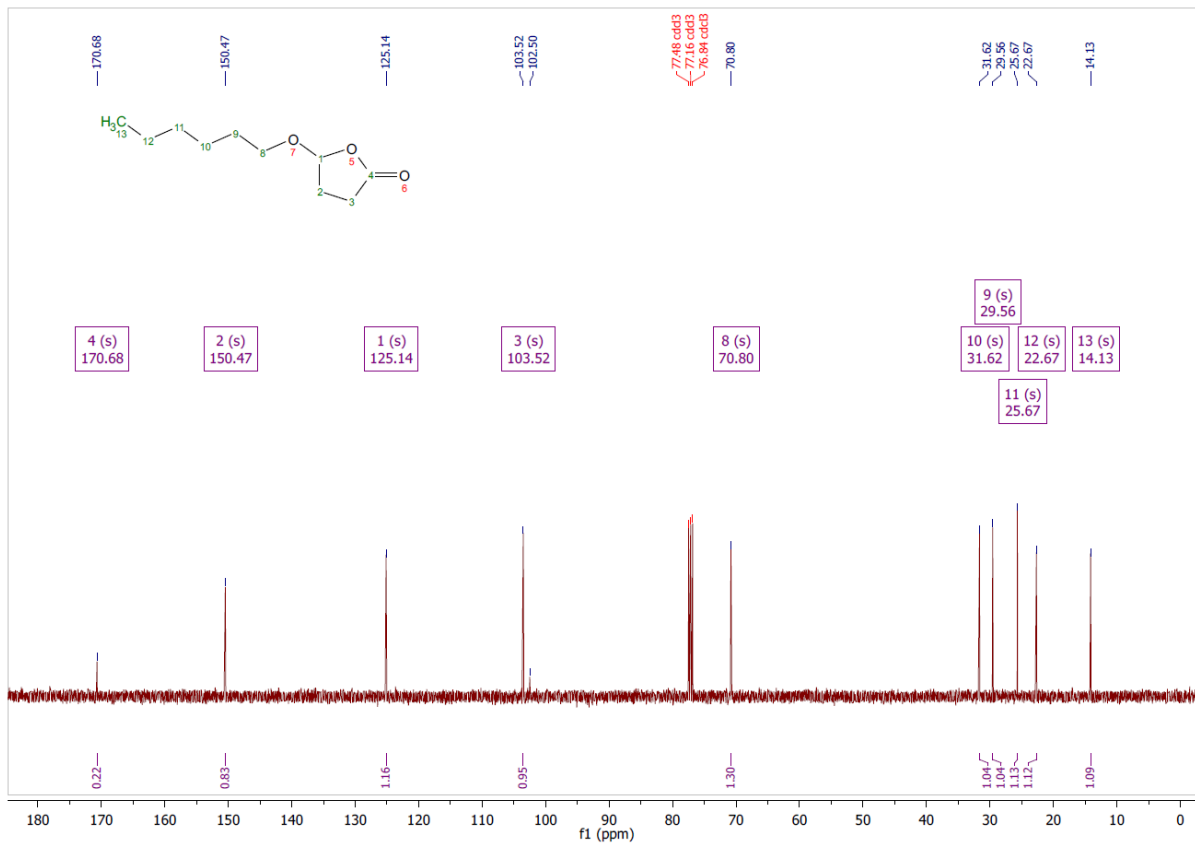


**Fig. S181.**  $^{13}\text{C}$ -NMR spectrum of **B2** measured at 298 K in  $\text{CDCl}_3$ .

**5-hexyloxy-2(5H)-furanone (hexyloxybutenolide) B3**



**Fig. S182.** <sup>1</sup>H-NMR spectrum of **B3** measured at 298 K in CDCl<sub>3</sub>.



**Fig. S183.** <sup>13</sup>C-NMR spectrum of **B3** measured at 298 K in CDCl<sub>3</sub>.



### 5-isopropoxy-2(5H)-furanone (isopropoxybutenolide) B4

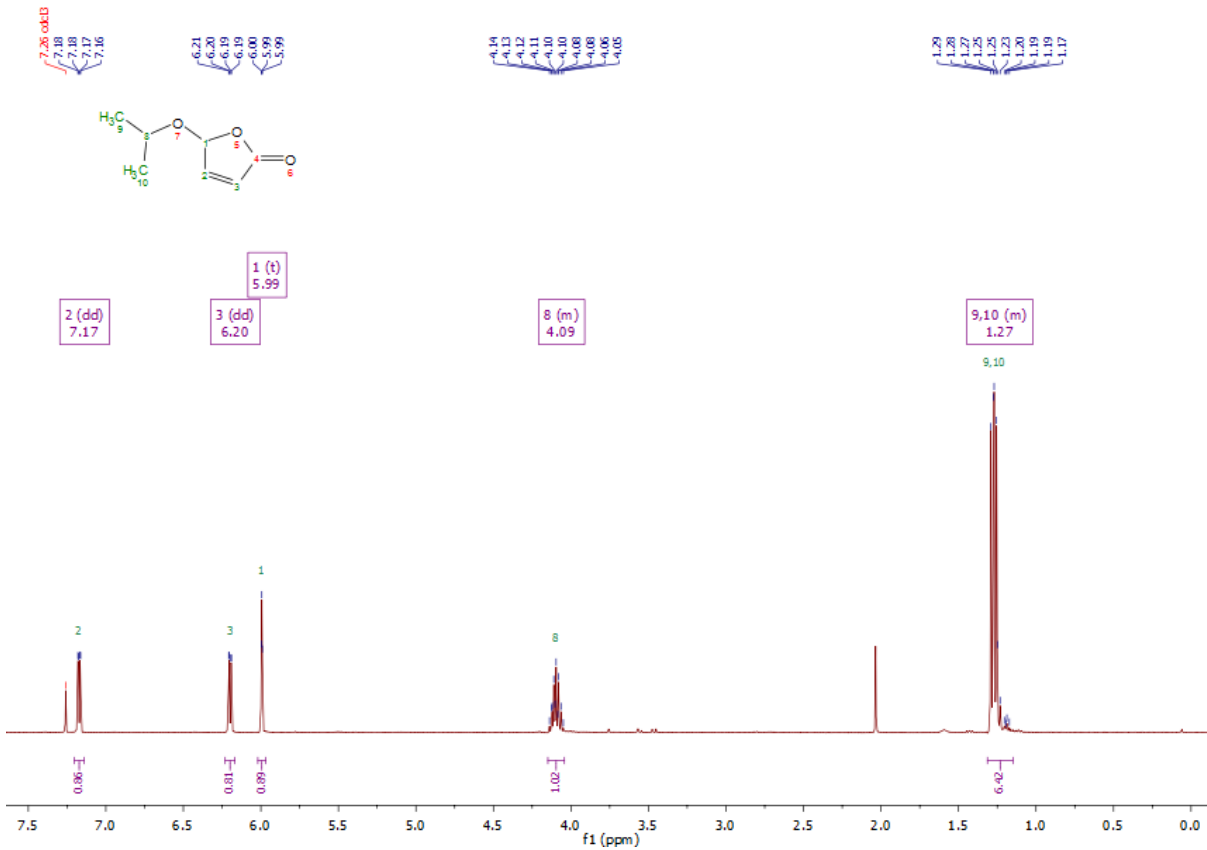
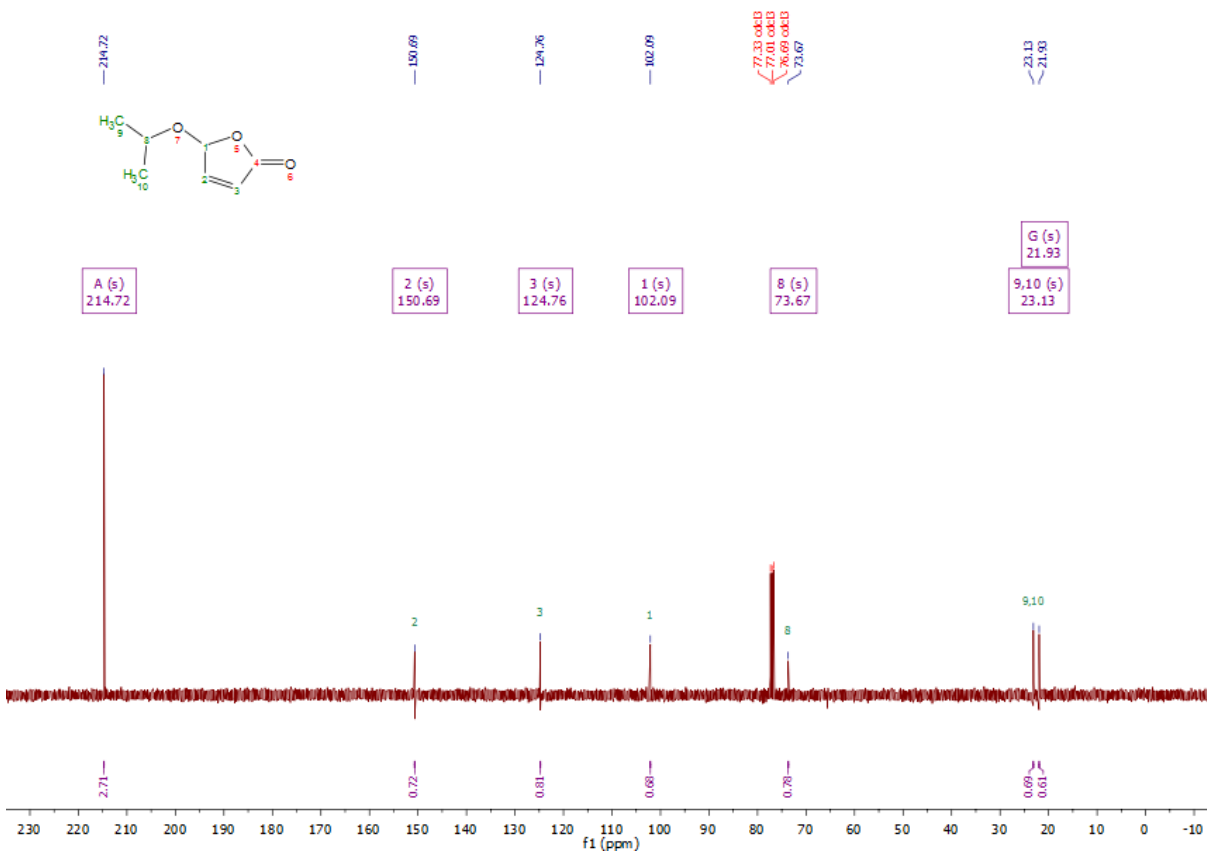
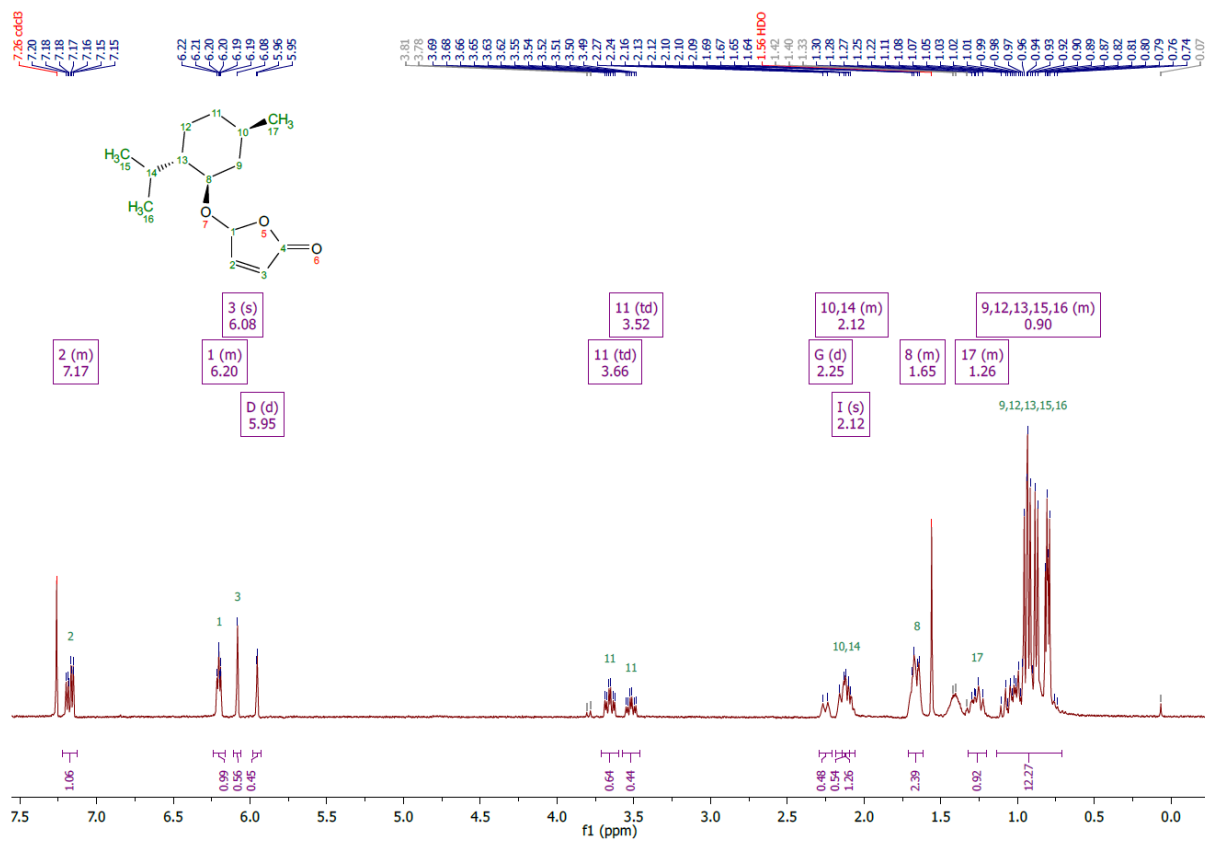


Fig. S184. <sup>1</sup>H-NMR spectrum of B4 measured at 298 K in CDCl<sub>3</sub>.

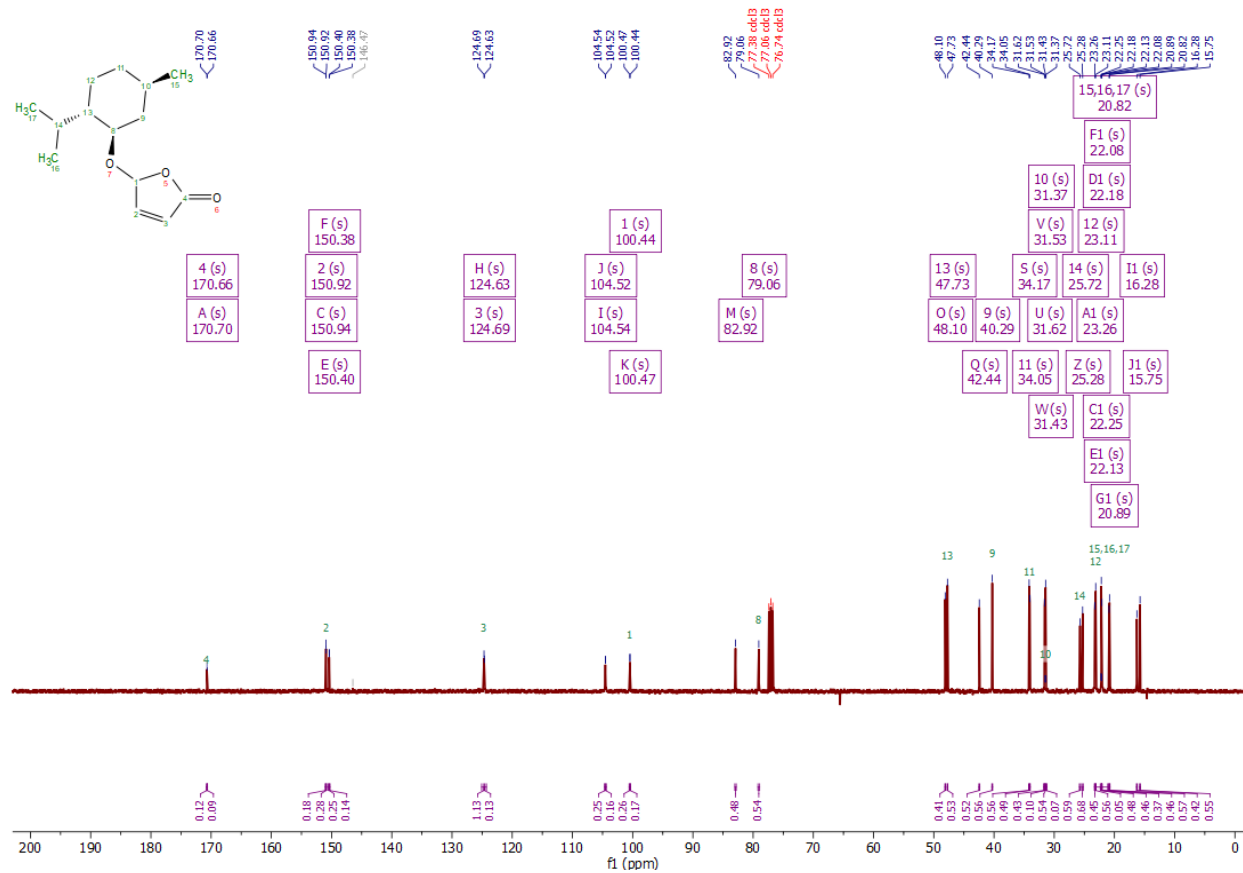


**Fig. S185.**  $^{13}\text{C}$ -NMR spectrum of **B4** measured at 298 K in  $\text{CDCl}_3$ .

**5-menthyloxy-2(5H)-furanone (menthyloxybutenolide) B5  
(mixture of diastereomers)**

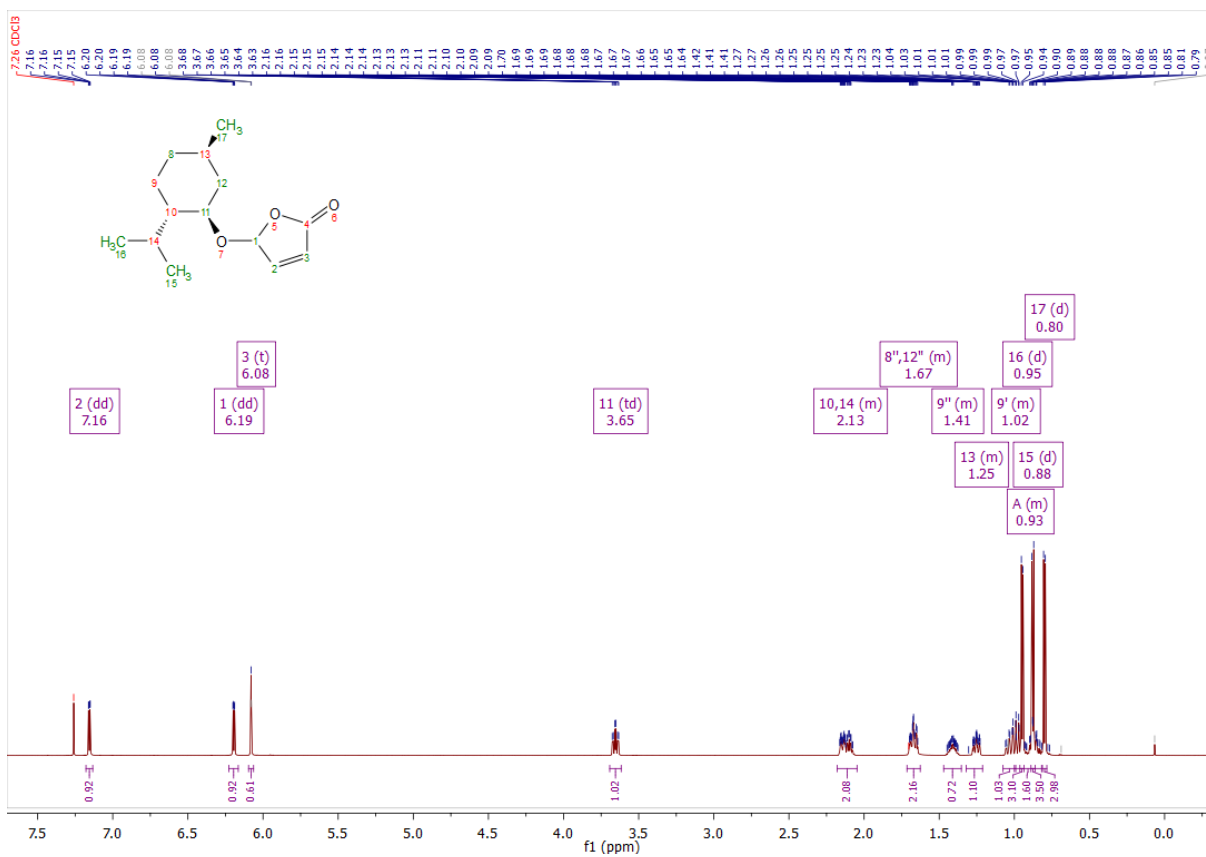


**Fig. S186.** <sup>1</sup>H-NMR spectrum of mixture of diastereomers **B5** measured at 298 K in CDCl<sub>3</sub>.

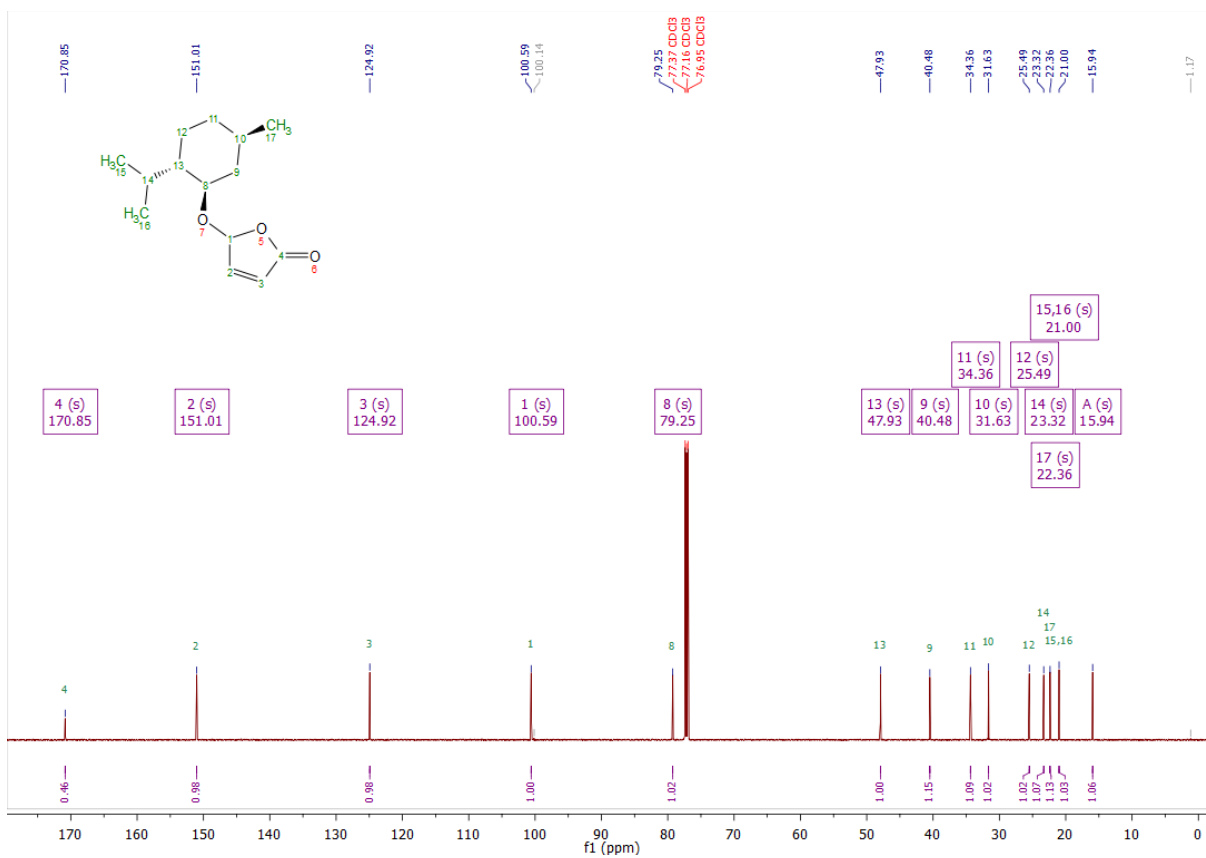


**Fig. S187.**  $^{13}\text{C}$ -NMR spectrum of mixture of diastereomers **B5** measured at 298 K in  $\text{CDCl}_3$ .

**5-menthyloxy-2(5H)-furanone (menthyloxybutenolide) B5**  
**(diastereomerically pure)**



**Fig. S188.** <sup>1</sup>H-NMR spectrum of diastereomerically pure **B5** measured at 298 K in CDCl<sub>3</sub>.



**Fig. S189.** <sup>13</sup>C-NMR spectrum of diastereomerically pure **B5** measured at 298 K in CDCl<sub>3</sub>.

5-methyl-5-methoxy-2(5H)-furanone (methylethoxybutenolide) B6

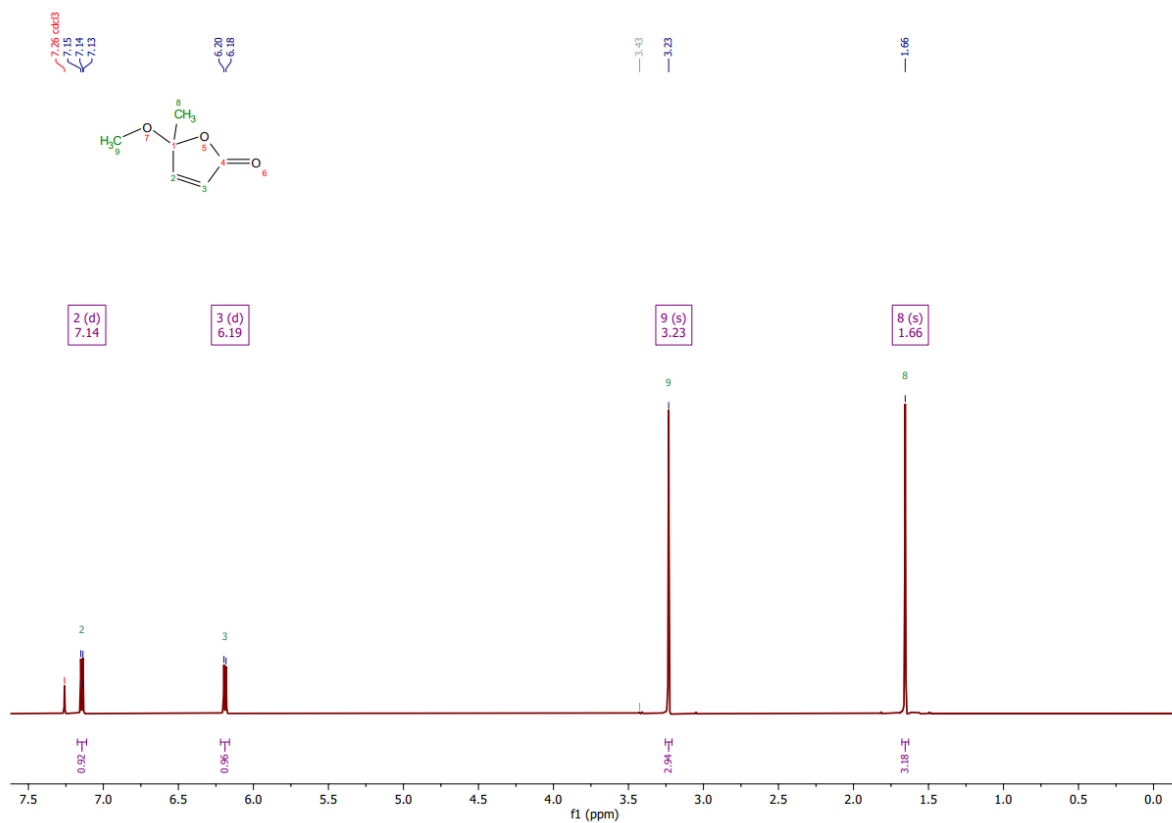
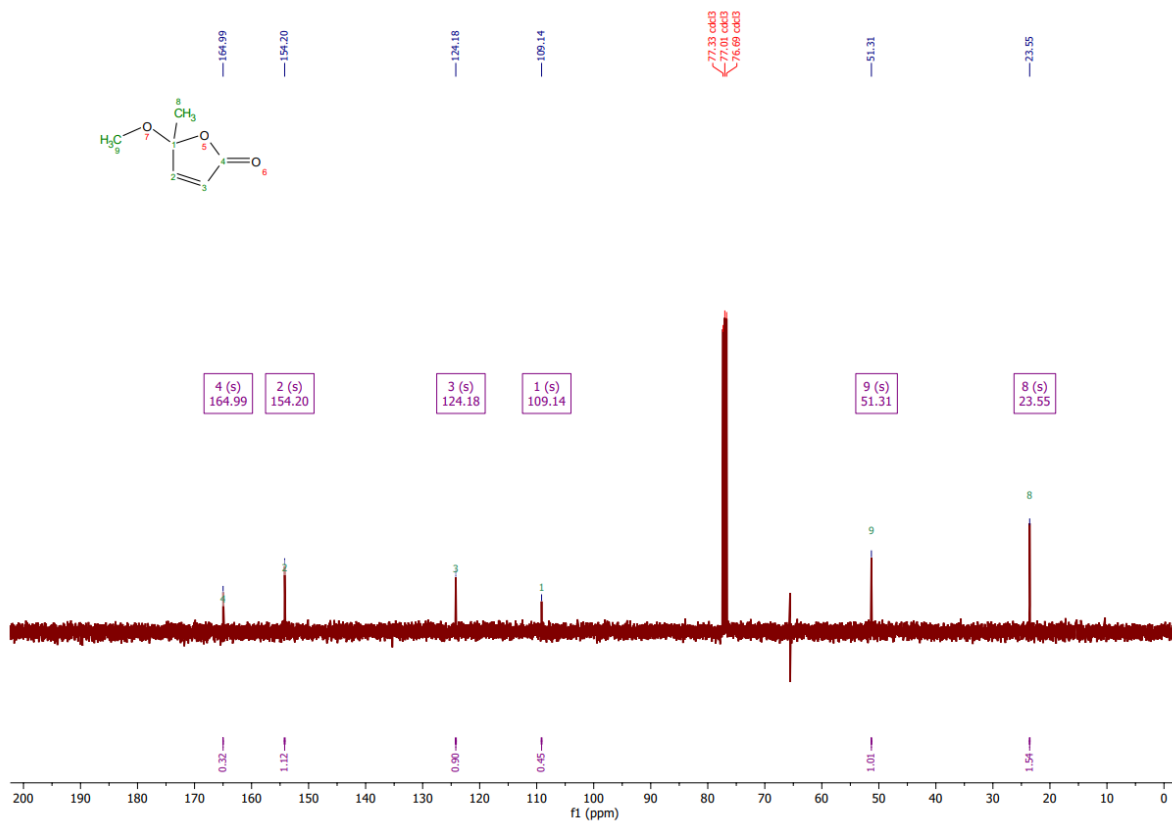


Fig. S190. <sup>1</sup>H-NMR spectrum of B6 measured at 298 K in CDCl<sub>3</sub>.





**Fig. S191.** <sup>13</sup>C-NMR spectrum of **B6** measured at 298 K in CDCl<sub>3</sub>.

# HRMS Spectra

## 5-hydroxy-2(5H)-furanone (hydroxybutenolide) B1

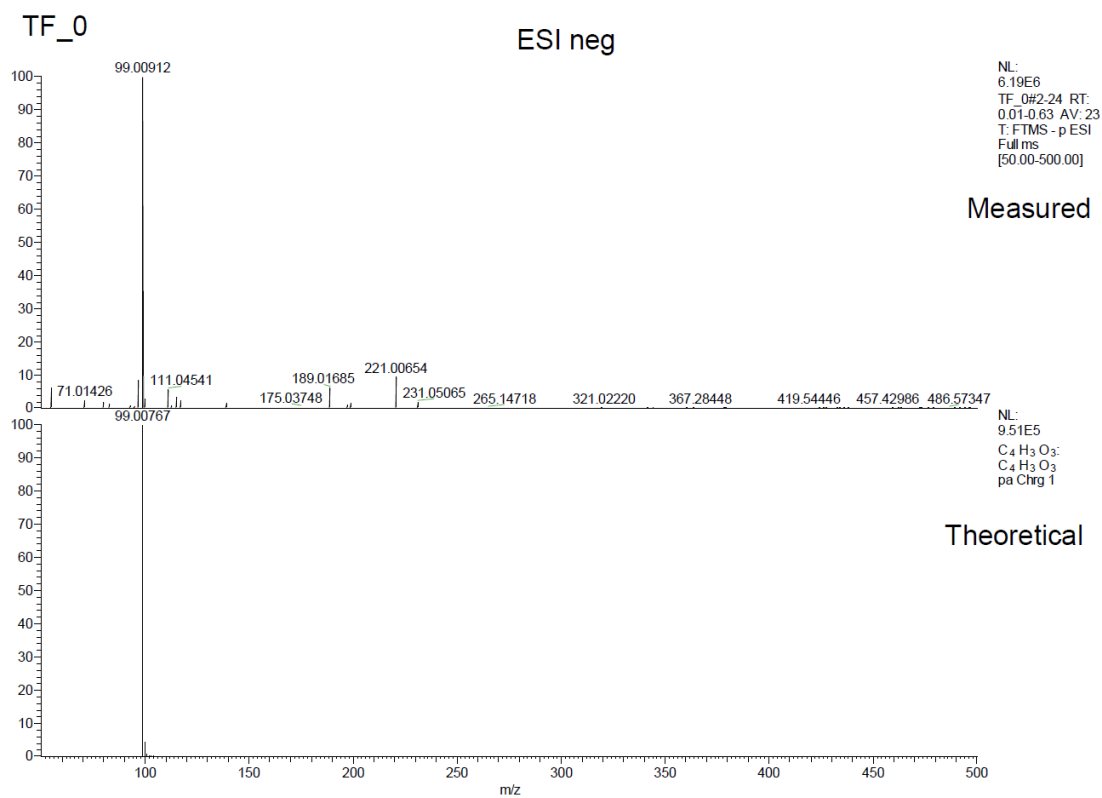
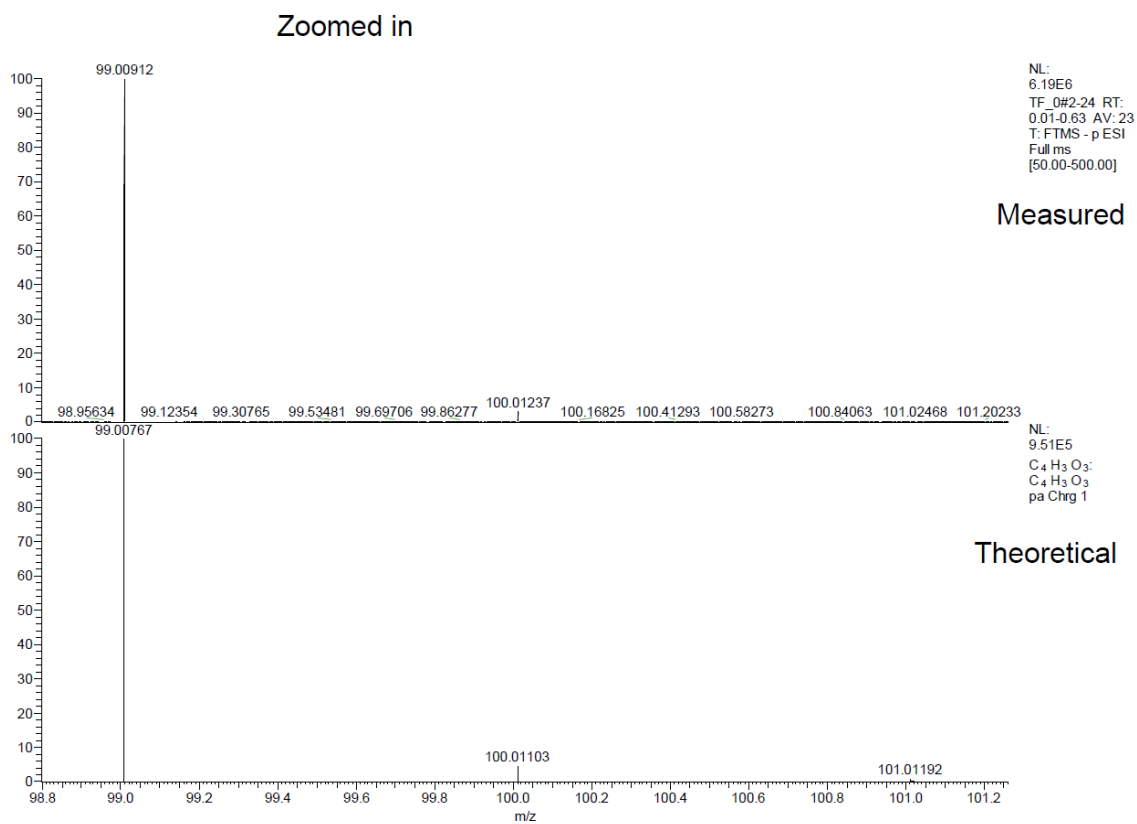


Fig. S192. HRMS of B1 (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).



**Fig. S193.** HRMS (zoomed in) of **B1** (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).

# 5-methoxy-2(5H)-furanone (methoxybutenolide) B2

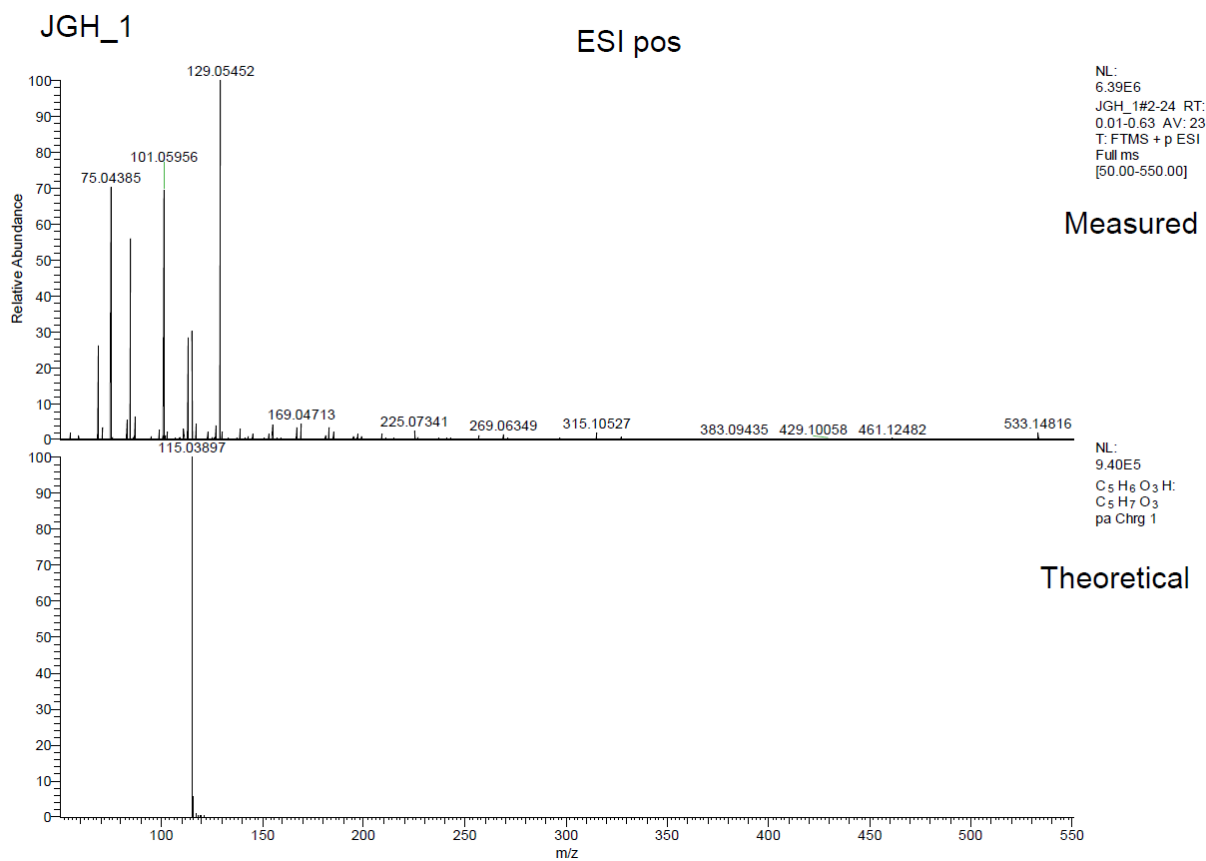
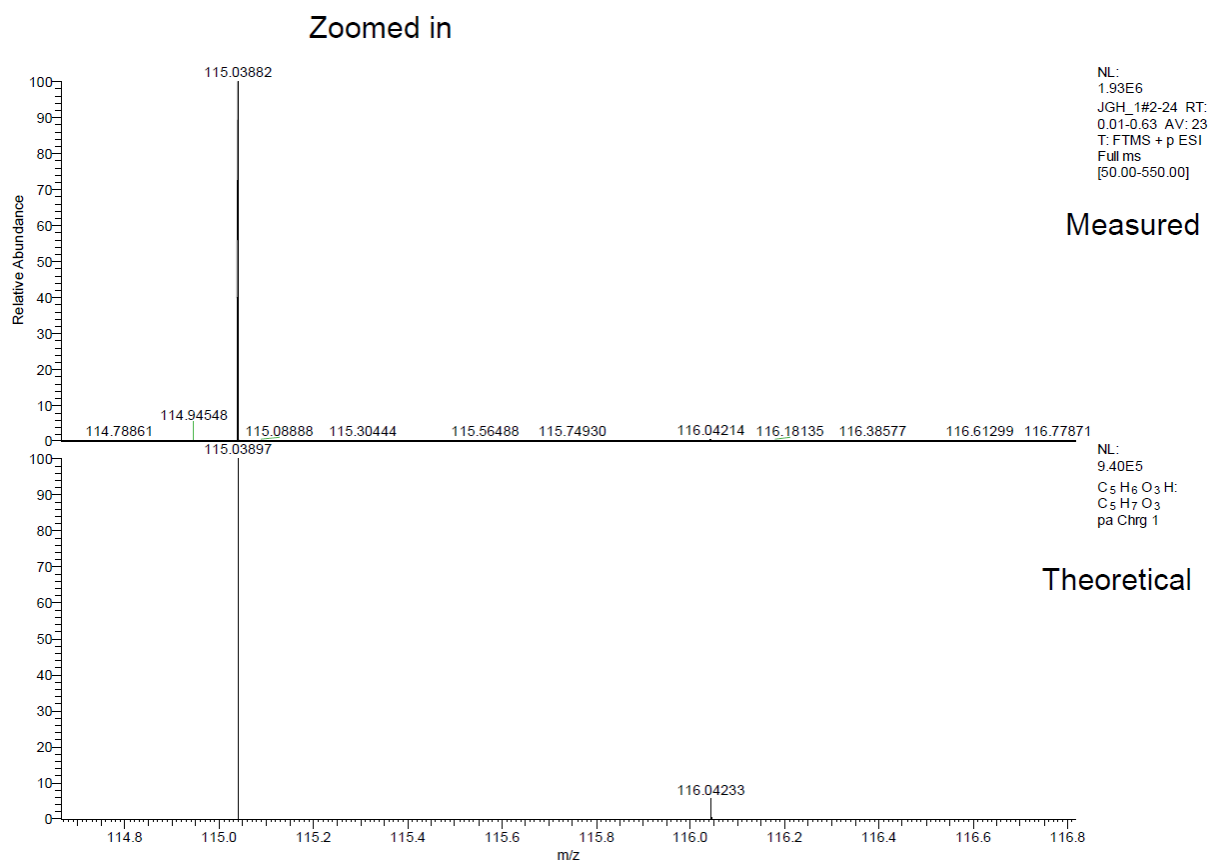


Fig. S194. HRMS of B2 (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).



**Fig. S195.** HRMS (zoomed in) of **B2** (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).

5-hexyloxy-2(5H)-furanone (hexyloxybutenolide) B3

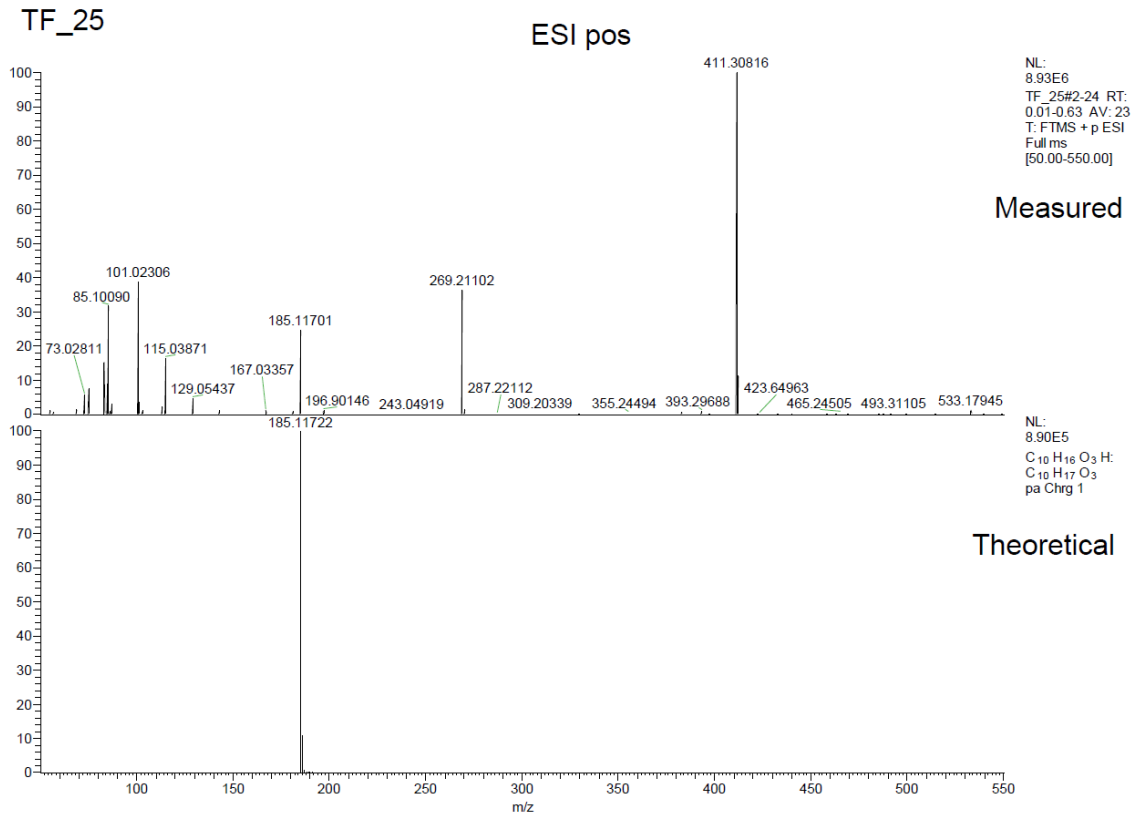
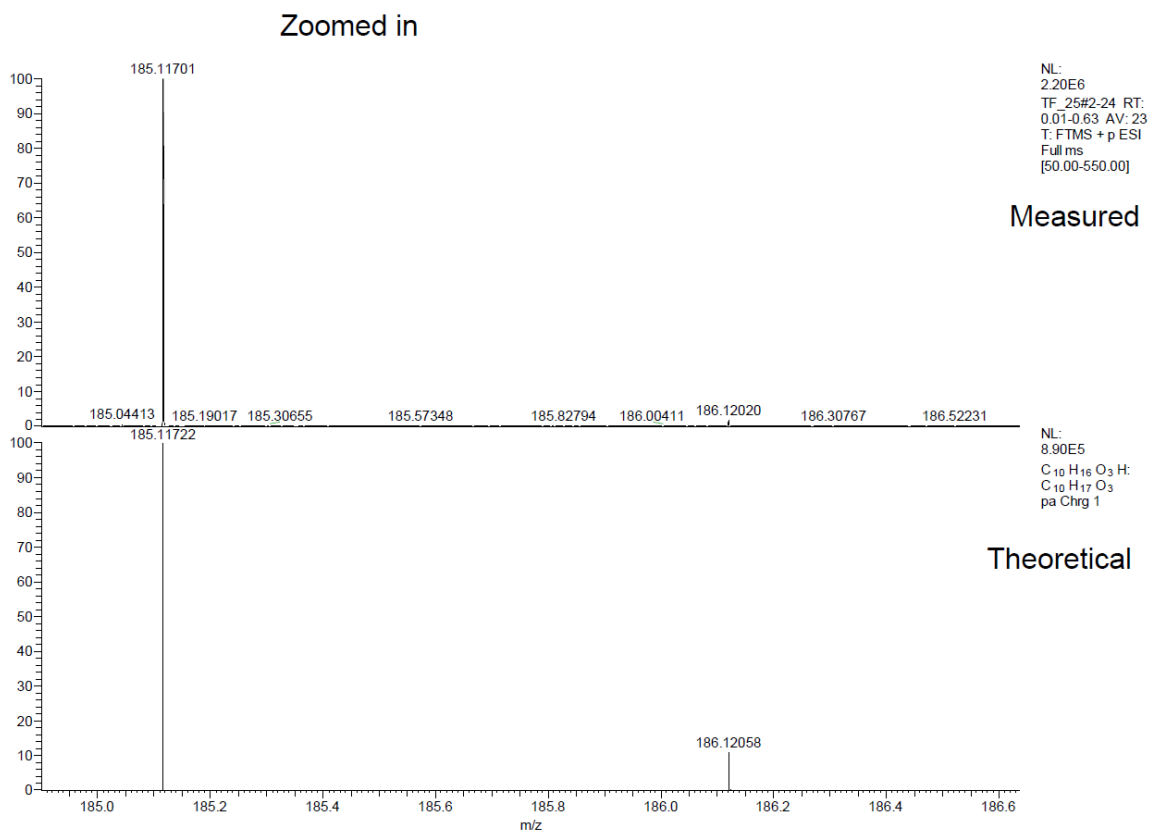


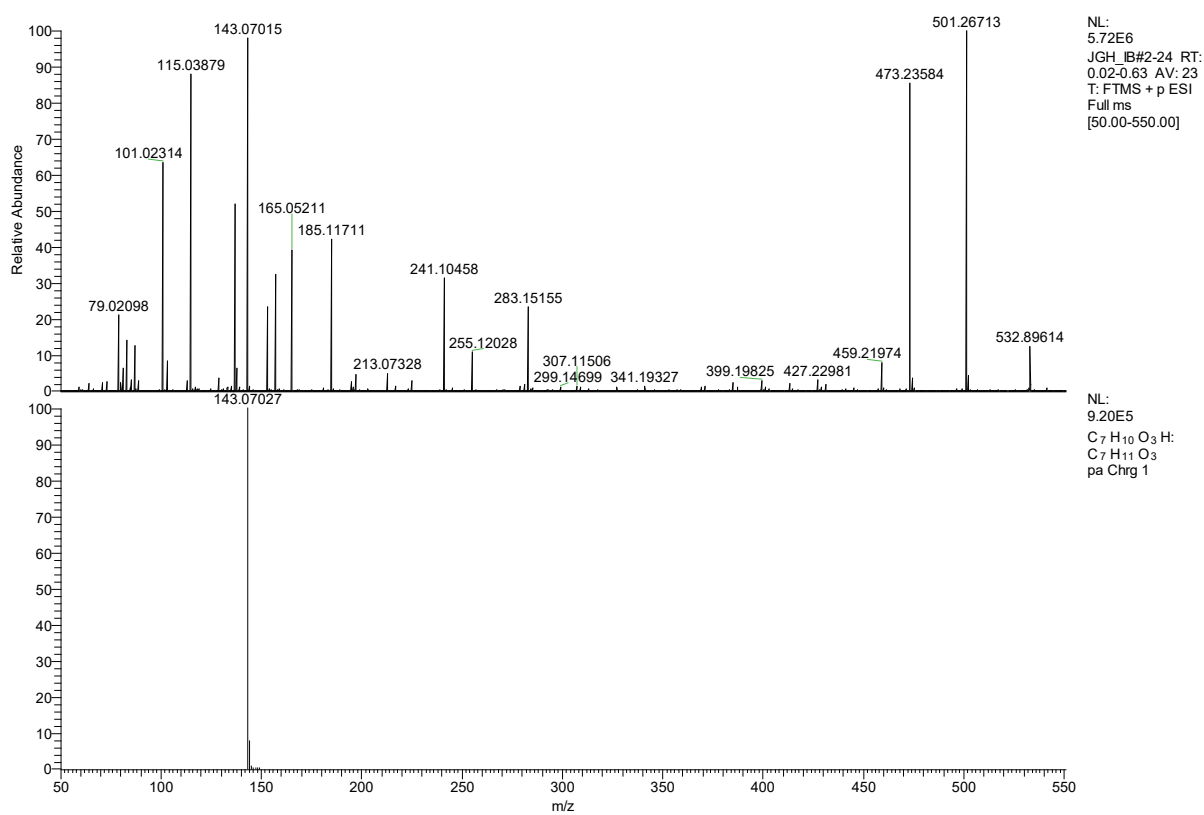
Fig. S196. HRMS of B3 (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).



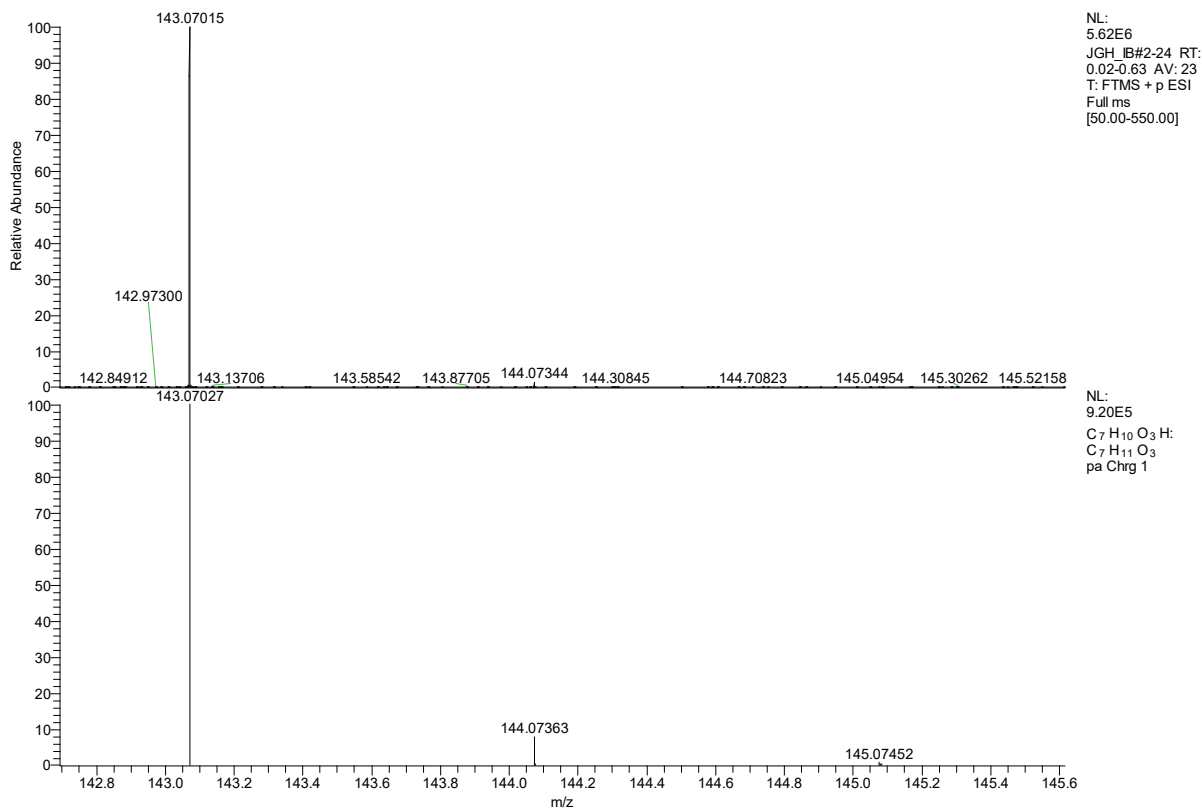
**Fig. S197.** HRMS (zoomed in) of **B3** (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).



### 5-isopropoxy-2(5H)-furanone (isopropoxybutenolide) B4



**Fig. S198.** HRMS of **B4** (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).



**Fig. S199.** HRMS (zoomed in) of **B4** (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).

# 5-menthyloxy-2(5H)-furanone (menthyloxybutenolide) B5

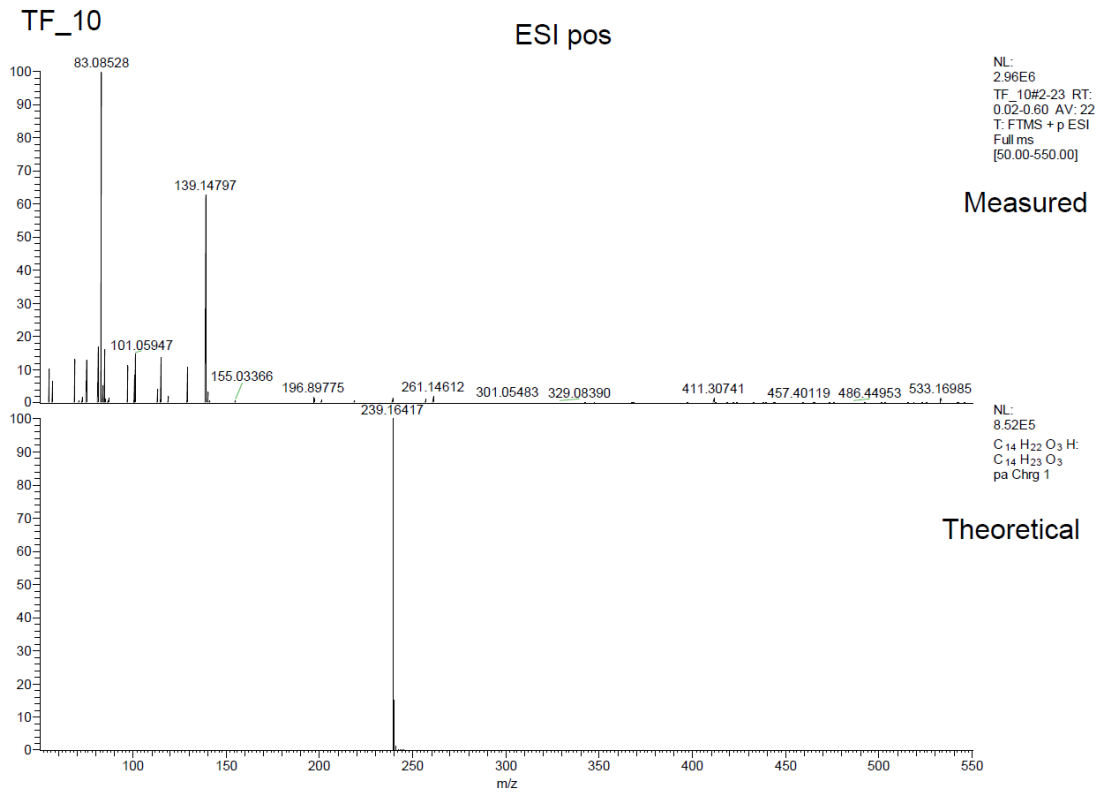
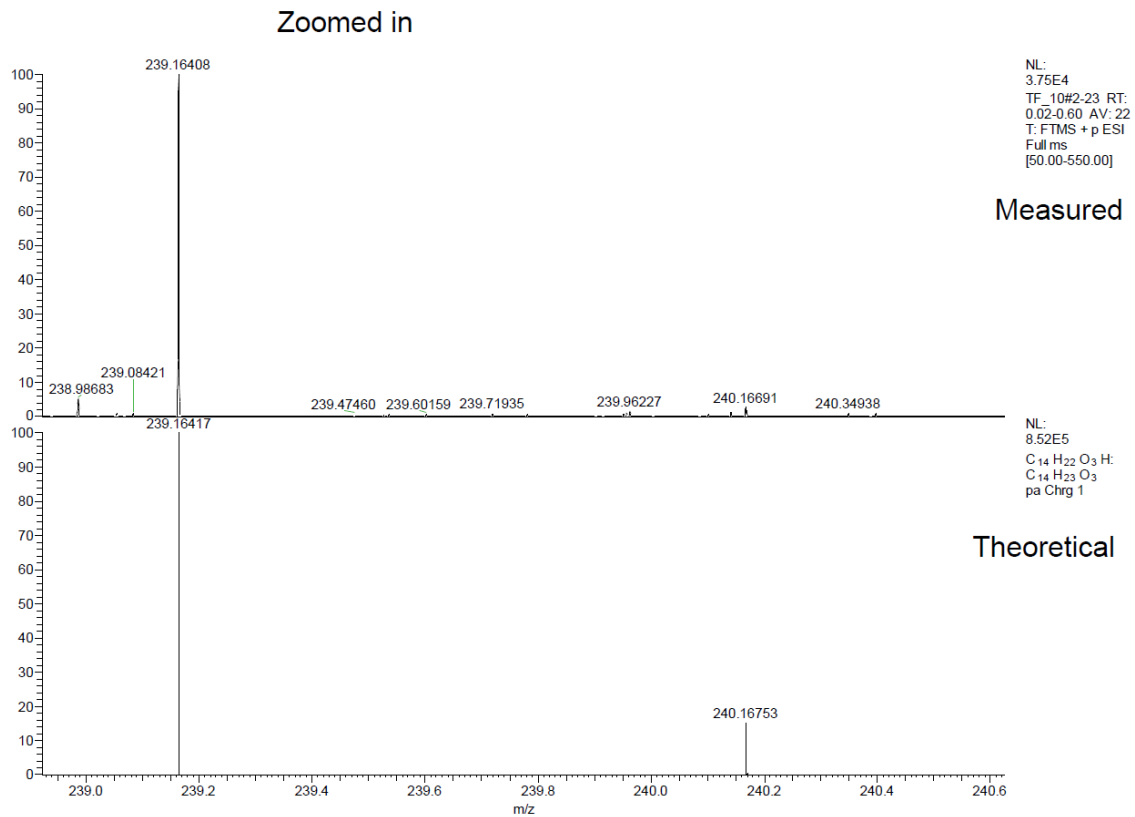


Fig. S200. HRMS of B5 (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).



**Fig. S201.** HRMS (zoomed in) of **B5** (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).

### 5-methyl-5-methoxy-2(5H)-furanone (methyl-methoxybutenolide) B6

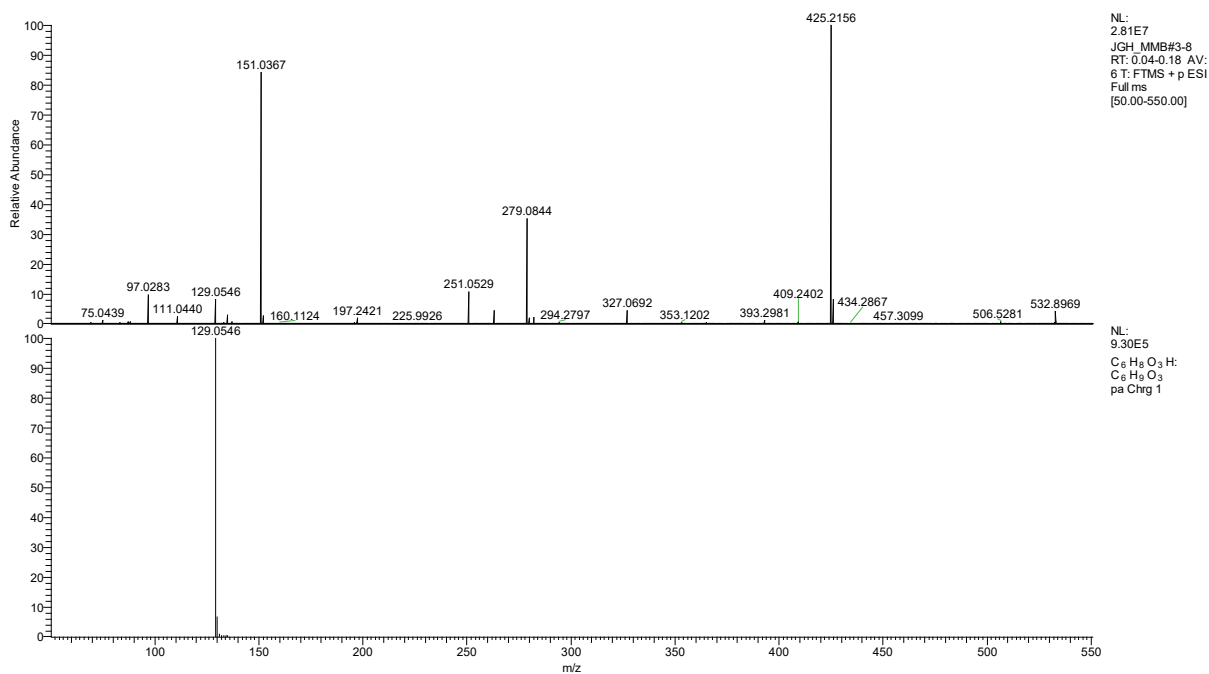
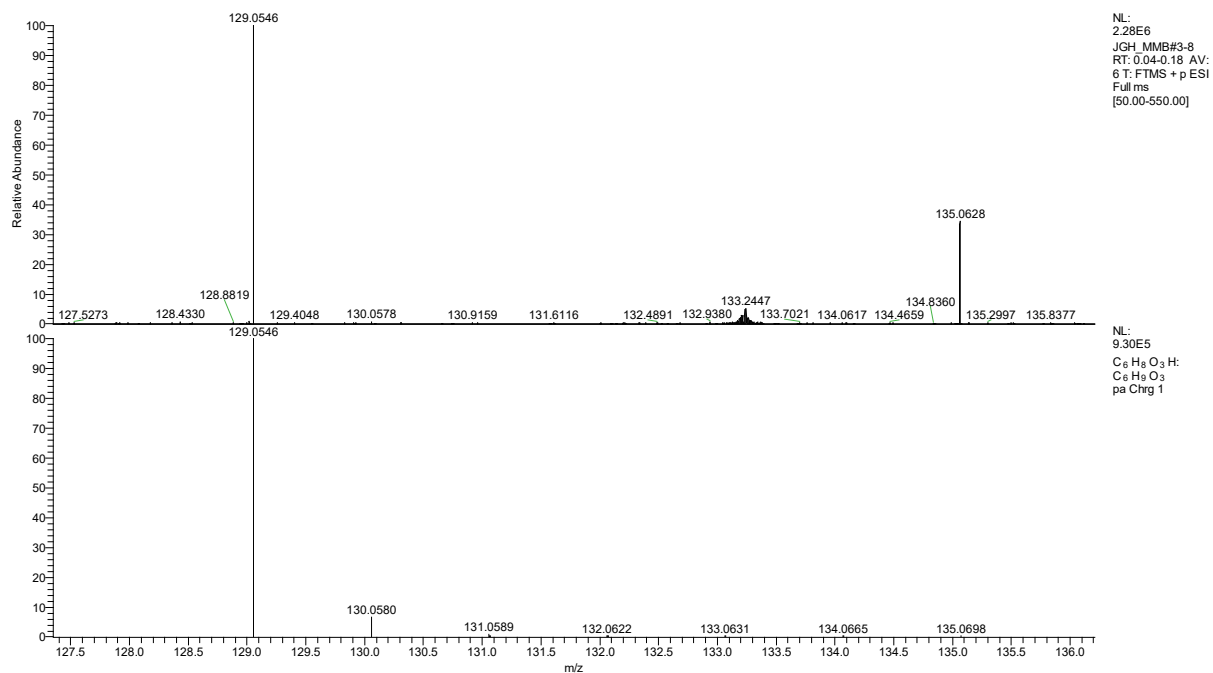


Fig. S202. HRMS of B6 (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).



**Fig. S203.** HRMS (zoomed in) of **B6** (top: measured, bottom: calculated), LTQ Orbitrap XL (ESI+).

## REFERENCES AND NOTES

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