

## Supplementary Information

### Low volume shrinkage polymers by photo Polymerization of 1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropanes

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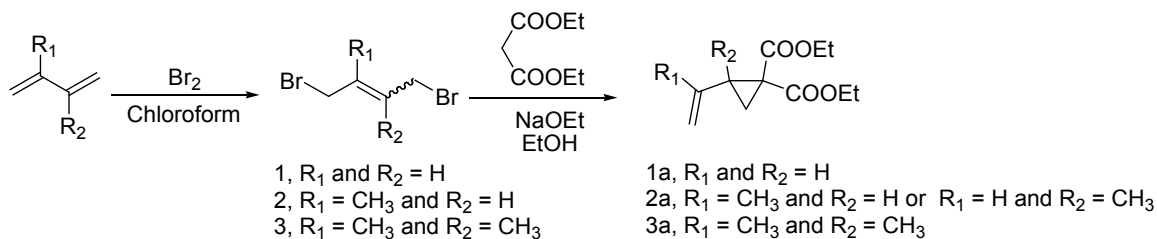
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#### Monomer Synthesis

Scheme 1



#### Synthesis of (*E*)-1,4-dibromo-2-methylbut-2-ene (2)

The reaction was carried out in a flame dried 250 mL round bottom flask, 35 mL (23.8 g, 349.3 mmol) of isoprene was added along with 150 mL of chloroform (CHCl<sub>3</sub>). To this solution 17.9 mL (55.84g, 349.3 mmol) bromine dissolved in CHCl<sub>3</sub> was added drop wise through a dropping funnel at a temperature of -10 °C. After complete addition of bromine, reaction mixture was stirred overnight. After the reaction, the solvent was evaporated by rotary evaporator and the crude product was recovered in a vacuum fractionating column which was distilled at a pressure of 0.04 mbar and 60 °C. The synthesized *cis-trans* isomer was represented by a 30:70 distribution, confirmed by <sup>1</sup>H-NMR and GC-FID.

Yield 39 g (49%):  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 5.90 (t,  $^3J = 8.4$  Hz, *trans*- $\text{CH}_{\text{sp}^2}$ , 1H (70 %)), 5.71 (t,  $^3J = 8.4$  Hz, *cis*- $\text{CH}_{\text{sp}^2}$ , 1H (30 %)), 4.10-3.95 (m,  $\text{CH}_2$ , 4H), 1.92 (s, *cis*- $\text{CH}_3$ , 3H (30 %)), 1.87 (s, *trans*- $\text{CH}_3$ , 3H (70 %)).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 138.30 ( $\text{C}_{\text{sp}^2}$ , *cis*-C), 138.25 ( $\text{C}_{\text{sp}^2}$ , *trans*-C), 125.97 ( $\text{C}_{\text{sp}^2}$ , *cis*-C), 125.71 ( $\text{C}_{\text{sp}^2}$ , *trans*-C), 39.18 ( $\text{CH}_2$ , *trans*-C), 29.30 ( $\text{CH}_2$ , *cis*-C), 27.50 ( $\text{CH}_2$ , *trans*-C), 26.53 ( $\text{CH}_2$ , *cis*-C), 22.07 ( $\text{CH}_3$ , *cis*-C), 14.65 ( $\text{CH}_3$ , *trans*-C).

### Synthesis of *trans*-1,4-dibrom-2,3-dimethyl-but-2-en (3)

18.88 g (0.23 mol) of 2,3-dimethylbutadiene was dissolved in 100 mL  $\text{CHCl}_3$  and the mixture was cooled to  $-20$  °C using ice-salt mixture. 11.77 mL of bromine (36.73 g, 0.23 mol) was dissolved in 50 mL  $\text{CHCl}_3$  and dropped into the flask over a period of 2 hour with vigorous stirring in a counter current of argon. After complete addition of the bromine, the solution was stirred for an additional 1 hr. at  $-10$  °C and 0.5h at  $0$  °C. The solvent was removed by vacuum. Residual liquid was kept in the refrigerator overnight. Lower temperature induced crystallization of the product and the crystals were filtered and washed with cold hexane. Residual filtrate was again concentrated and kept in the refrigerator. The step was repeated till no further crystals were observed on cooling. Yield 28g (50%):  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 3.99 (s, 4H,  $\text{CH}_2$ ), 1.88 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 131.92 ( $\text{C}_{\text{sp}^2}$ ), 35.01 ( $\text{CH}_2$ ), 17.19 ( $\text{CH}_3$ ).

### Diethyl 2-vinylcyclopropane-1,1-dicarboxylate (1a)

A sodium ethoxide solution was prepared by dissolving sodium in dry ethanol. The sodium was purified prior by melting it up in kerosene. 2.2 eq. of the sodium ethoxide solution were added drop wise at  $0$  °C to a solution of 1.0 eq. of 1,4-dibromo-2-butene and 1.0 eq. of diethyl malonate in a counter current of argon. After the addition, the reaction mixture was stirred overnight and then heated for 1 h at  $65$  °C. The resulting mass was filtered and the filtrate was charged to a rotary evaporator to remove the solvent. The residue was extracted with diethyl ether and water. The organic layer was washed with brine and dried over magnesium sulphate. The raw product was distilled under reduced pressure. bp  $60$ - $64$  °C/ $0.04$  bar; yield (82%):

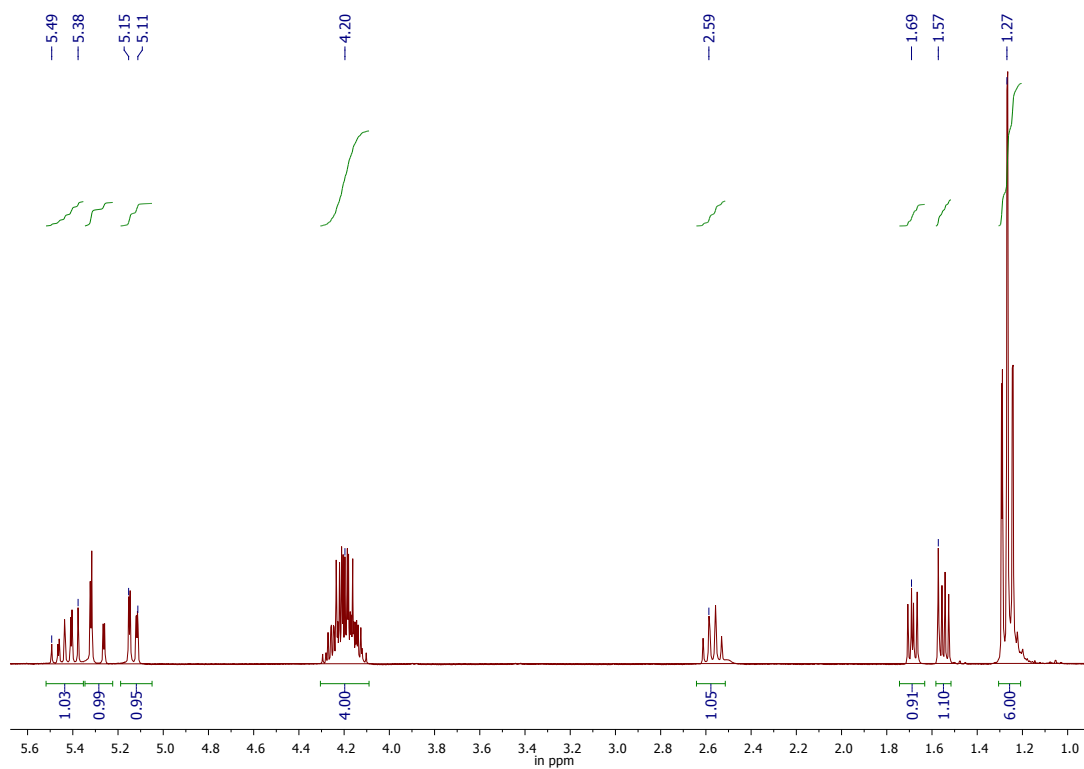


Figure S1:  $^1\text{H}$  NMR of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (1a) ( $\text{CDCl}_3$ , 300 MHz).

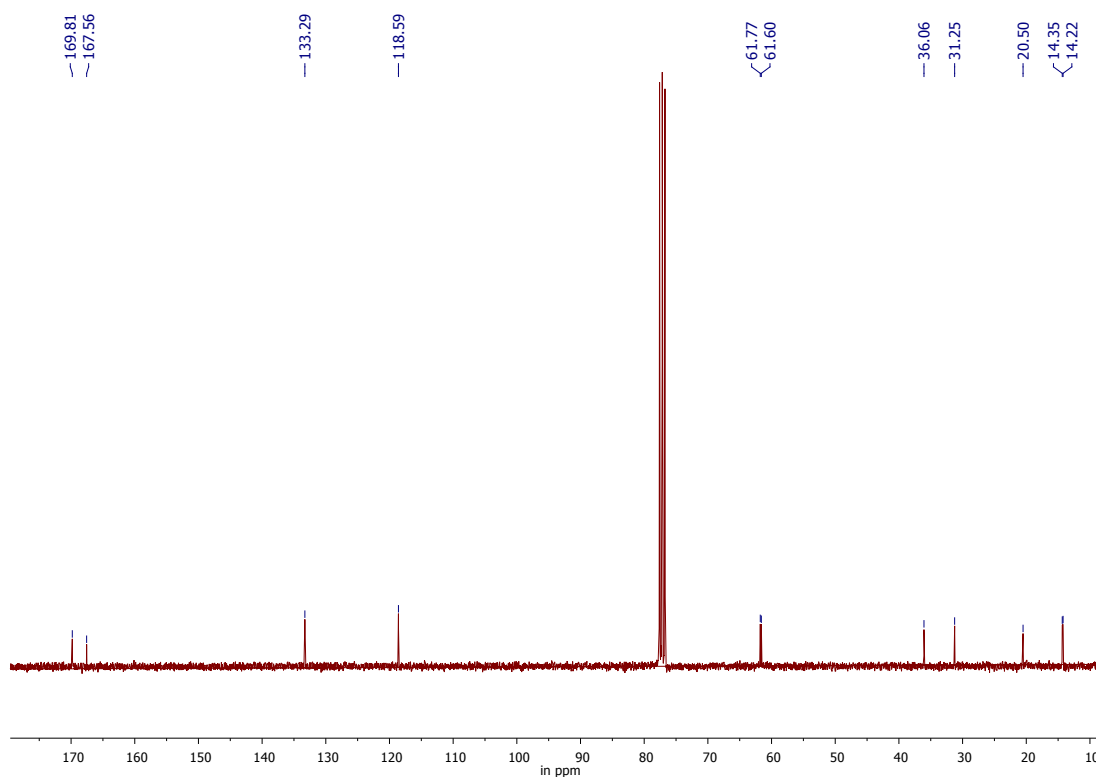
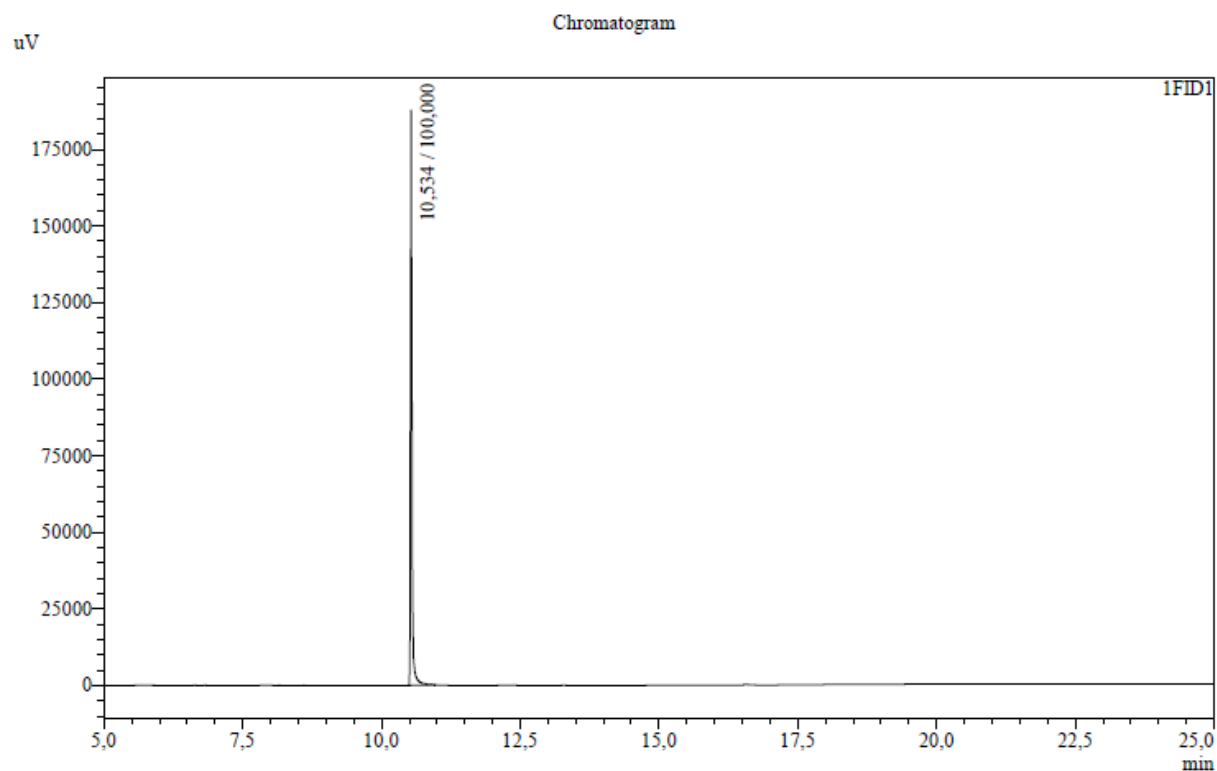


Figure S2:  $^{13}\text{C}$  NMR of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (1a) ( $\text{CDCl}_3$ , 75 MHz).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ): 5.43-5.23 (m, 1 H), 5.29-5.23 (dd, *J* = 9.45 Hz, 1.95 Hz, 1H), 5.09-5.03 (dd, *J* = 5.85 Hz, 2.1 Hz, 1H), 4.29-4.08 (m, 4H), 2.59-2.51 (q, *J* = 8.7 Hz, 1H), 1.68-1.64 (dd, *J* = 6.3 Hz, 5.1 Hz, 1H), 1.53-1.48 (dd, *J* = 6.9 Hz, 4.8 Hz, 1 H), 1.28-1.21 (m, 6 H, CH<sub>3</sub>, H1). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, δ): 169.52 (C=O), 167.27 (C=O), 133.08 (C<sub>sp2</sub>), 118.27 (C<sub>sp2</sub>), 61.47 (OCH<sub>2</sub>), 61.30 (OCH<sub>2</sub>), 35.83 (C<sub>quart.</sub>) 30.94 (CH<sub>2</sub>), 20.20 (CH<sub>2</sub>), 14.08 (CH<sub>3</sub>), 13.96 (CH<sub>3</sub>).



Peak Table

FID1

Peak#	Ret. Time	Area%	Area	Height
1	10.534	100.000	362940	187874
Total		100.000	362940	187874

Figure S3: GC-FID chromatogram of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (1a) (0.5 µg/mL in acetone, injection volume 1.0 µl, N<sub>2</sub> as carrier gas, split ratio 50, initial temperature 50 °C (hold for 2min) and temperature gradient of 15 C/min up to 300 °C).

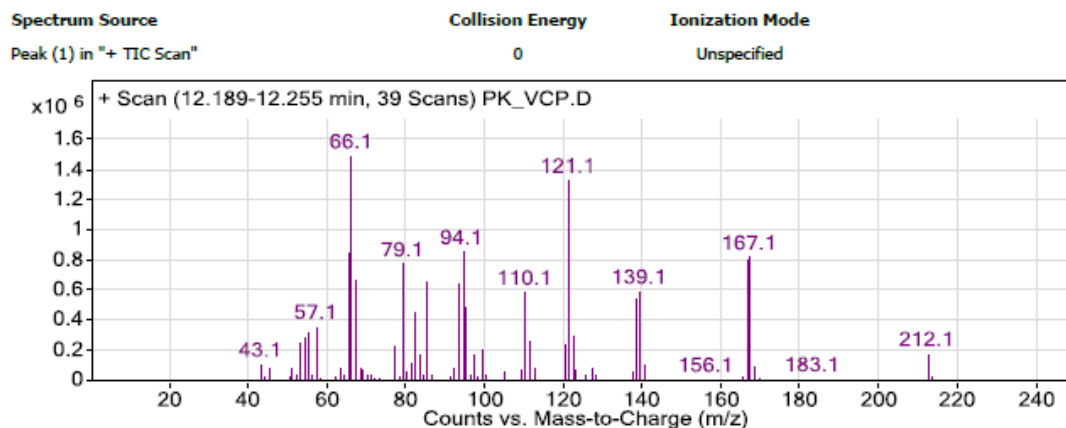


Figure S4: Mass spectrum (Quadropol MS Agilent 5977A MSD: EI with 1000 eV) of GC-MS detected diethyl 2-vinylcyclopropane-1,1-dicarboxylate (1a).

### Diethyl 2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate and diethyl 2-methyl-2-vinylcyclopropane-1,1-dicarboxylate (2a)

The procedure is analog to monomer (1a) with the difference of using 1,4-dibromo-2-methylbut-2-ene (2) instead of 1,4-dibromo-2-butene. bp 75 °C/0.04 bar; yield (42%).

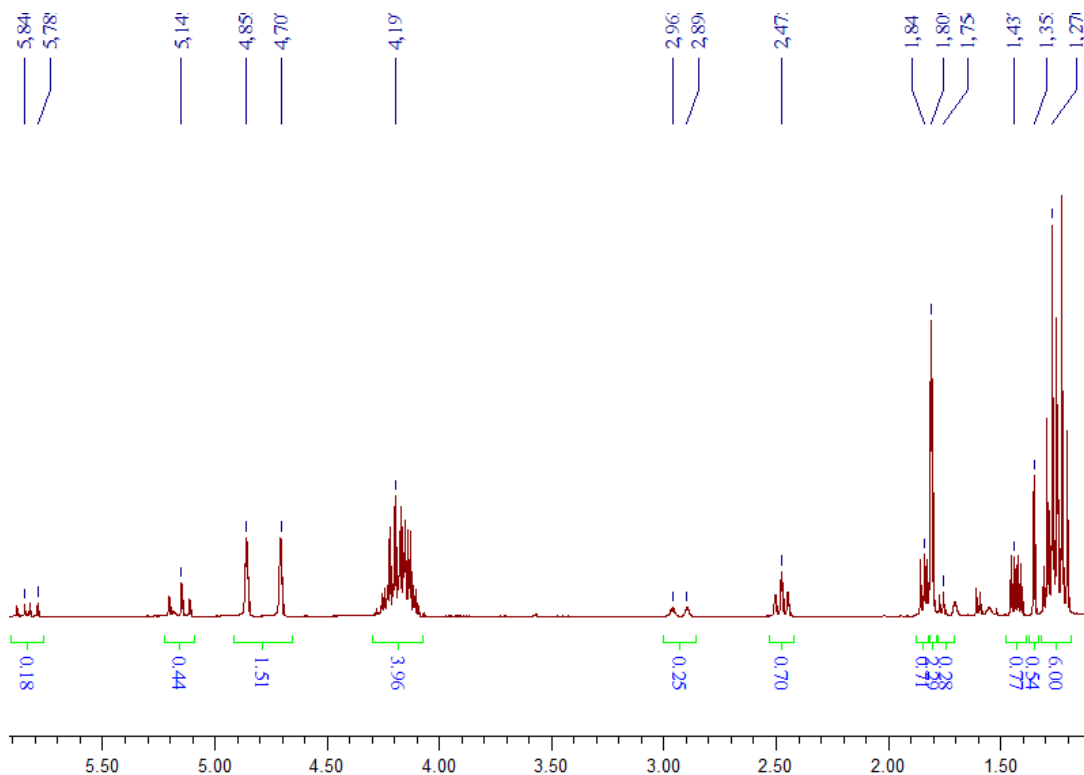


Figure S5: <sup>1</sup>H NMR of diethyl 2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate and diethyl 2-methyl-2-vinylcyclopropane-1,1-dicarboxylate (2a) (CDCl<sub>3</sub>, 300 MHz).

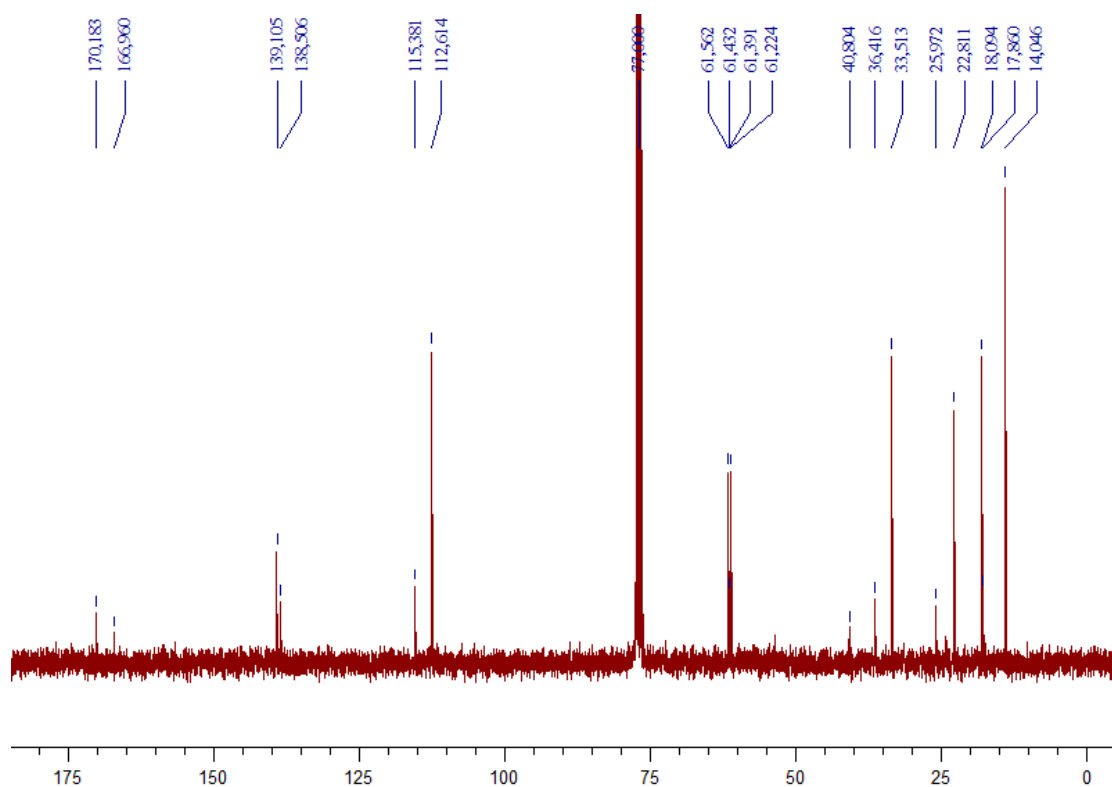
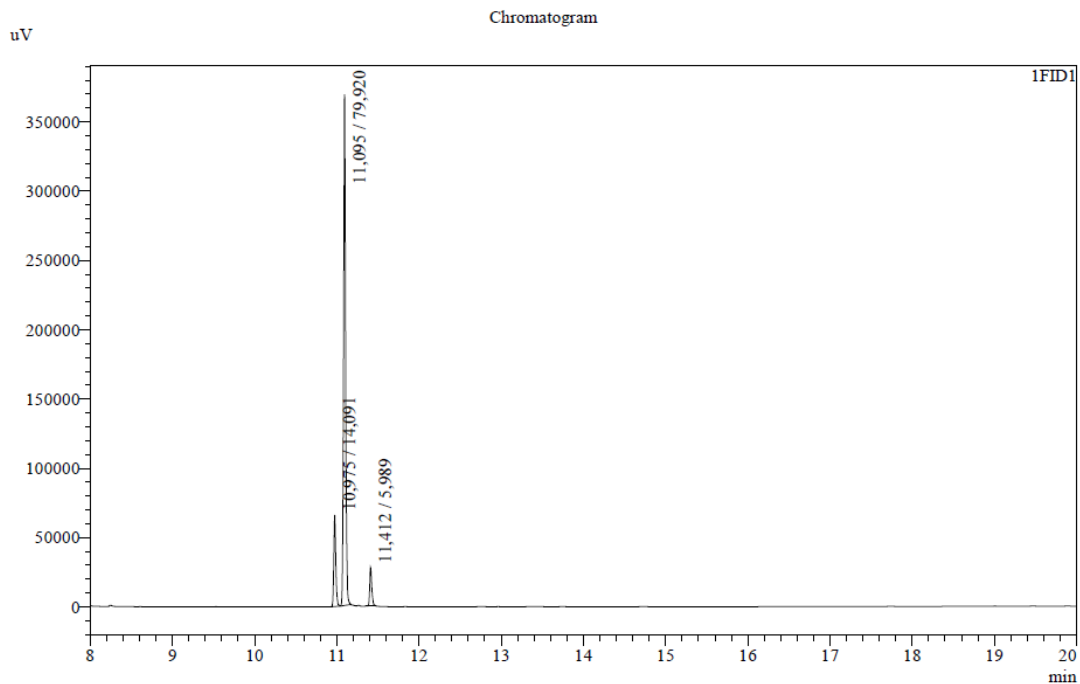


Figure S6:  $^{13}\text{C}$ -NMR of diethyl 2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate and diethyl 2-methyl-2-vinylcyclopropane-1,1-dicarboxylate (2a) ( $\text{CDCl}_3$ , 75 MHz).

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 5.85-5.77 (dd,  $J = 13.8$  Hz, 10.8 Hz, 1H (25 %)), 5.116 (m, 2H (25 %)), 4.7-4.83 (d, 2H (75 %)), 4.06-4.25 (m, 4H), 2.86-2.94 (m, 1H), 2.42-2.47 (t,  $J = 8.4$  Hz, 1H), 1.83-1.80 (m, 1H (75 %)), 1.78 (s, 3H (75 %)), 1.75 (m, 1 H (25 %)), 1.34-1.42 (dd,  $J = 7.05$  Hz, 5.01 Hz, 1 H (75 %)), 1.32 (s, 3H (25 %)), 1.17-1.27 (m, 6H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 170.18 (C=O, (75 %)), 16.96 (C=O, (25 %)), 139.11 ( $\text{C}_{\text{sp}2}$ ), 138.51 ( $\text{C}_{\text{sp}2}$ ), 115.38 ( $\text{C}_{\text{sp}2}$ ), 112.61 ( $\text{C}_{\text{sp}2}$ ), 61.56 ( $\text{OCH}_2$ , (75 %)), 61.43 ( $\text{OCH}_2$ , (25 %)), 61.39 ( $\text{OCH}_2$ , (25 %)), 61.22 ( $\text{OCH}_2$ , (75 %)), 40.81 ( $\text{C}_{\text{quart.}}$ , (25 %)), 36.42 ( $\text{C}_{\text{quart.}}$ , (75 %)), 33.51 (CH), 25.97 (CHH), 22.81 ( $\text{CH}_3$ ), 18.09 (CHH), 17.86 ( $\text{CH}_3$ ), 14.05 ( $\text{CH}_3$ ).



Peak Table

Peak#	Ret. Time	Area%	Area	Height
1	10.975	14.091	113551	65967
2	11.095	79.920	644005	368496
3	11.412	5.989	48257	27379
Total		100.000	805813	461841

Figure S7: GC-FID chromatogram of diethyl 2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate and diethyl 2-methyl-2-vinylcyclopropane-1,1-dicarboxylate (2a) (0.5 µg/mL in acetone, injection volume 1.0 µl, N<sub>2</sub> as carrier gas, split ratio 50, initial temperature 50 °C (hold for 2min) and temperature gradient of 15 C/min up to 300 °C). The appearance of three chromatogram peaks relies on the stereo isomeric separation of the diethyl 2-methyl-2-vinylcyclopropane-1,1-dicarboxylate.

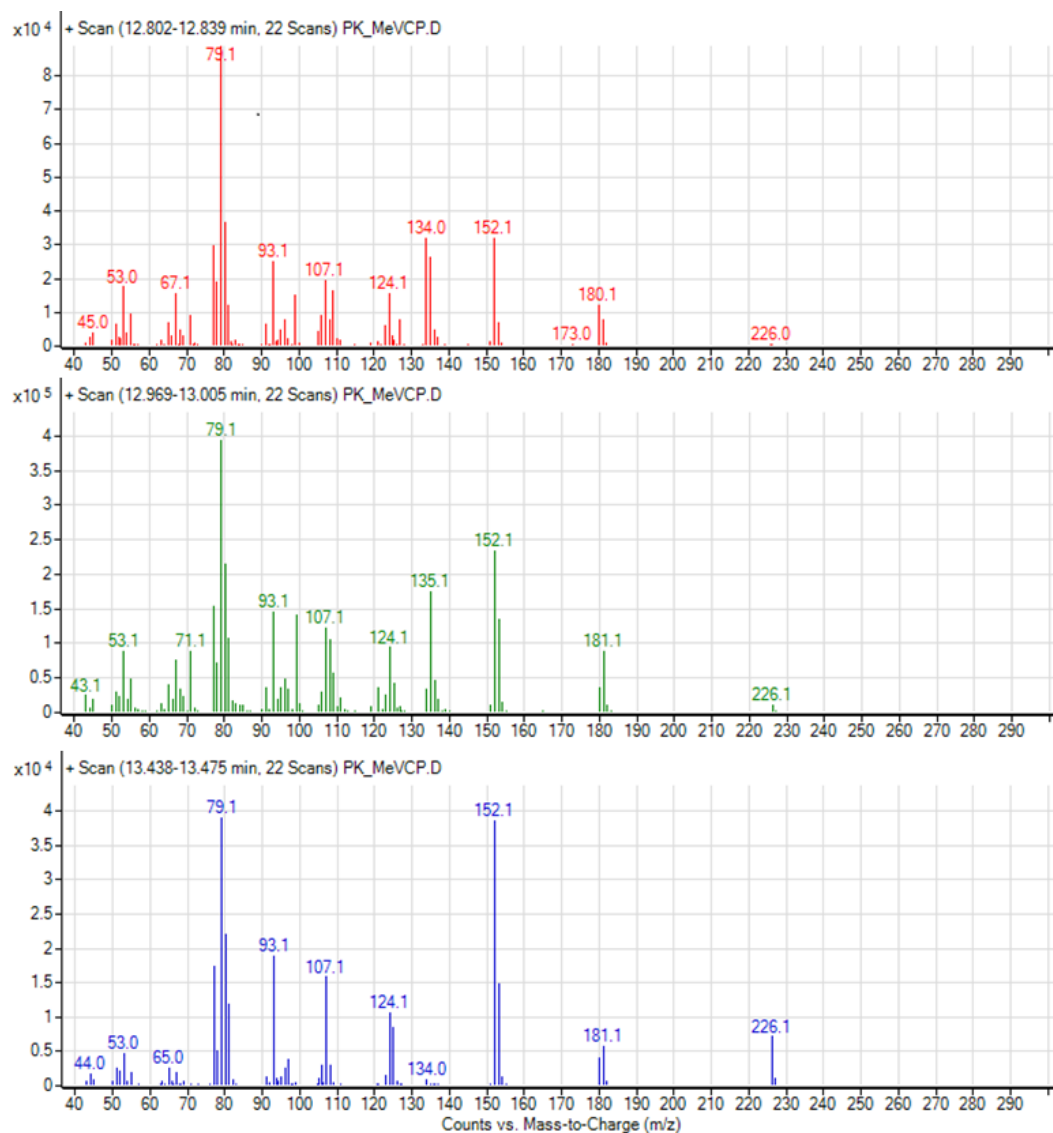


Figure S8: Mass spectra (Quadrupole MS Agilent 5977A MSD: EI with 1000 eV) of GC-MS detected diethyl 2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate and diethyl 2-methyl-2-vinylcyclopropane-1,1-dicarboxylate (2a). The appearance of the three chromatogram peaks within the GC-FID and GC-MS relies on the stereo isomeric separation of the diethyl 2-methyl-2-vinylcyclopropane-1,1-dicarboxylate, as all three mass spectra are almost identical. .

### Diethyl 2-methyl-2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (3a)

The procedure is analog to monomer (1a) with the difference of using *trans*-1,4-dibrom-2,3-dimethyl-but-2-en (3) instead of 1,4-dibromo-2-butene. bp 75 °C/0.04 bar; yield (41%)



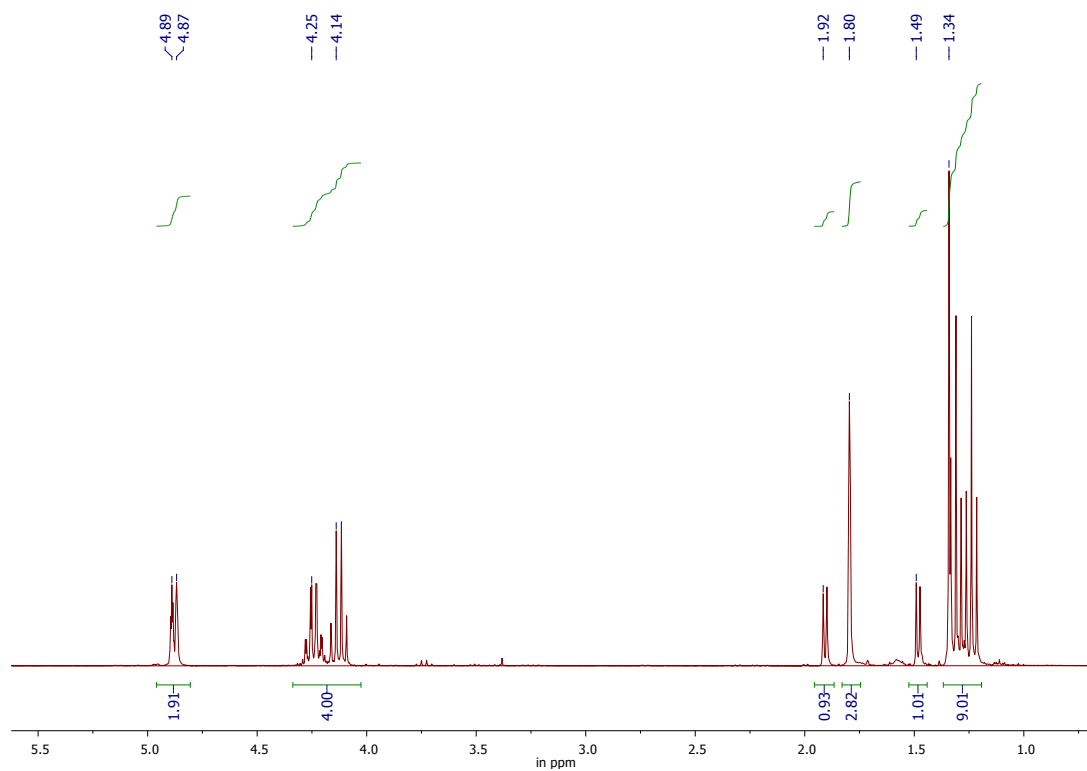


Figure S9:  $^1\text{H}$  NMR of diethyl 2-methyl-2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (3a) ( $\text{CDCl}_3$ , 300 MHz).

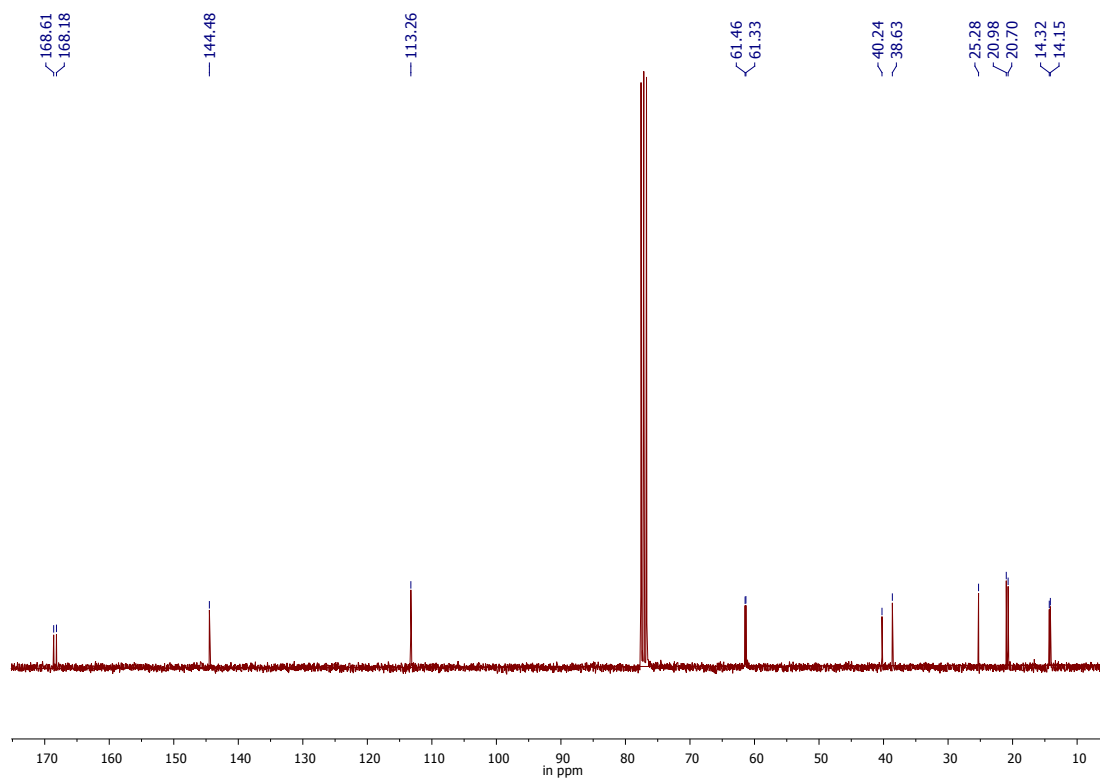
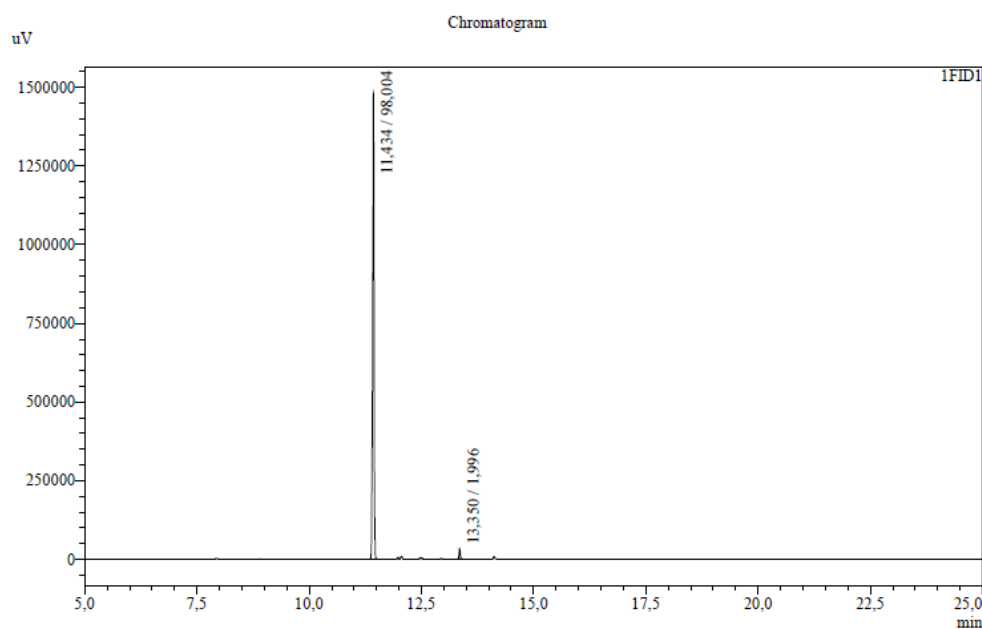


Figure S10:  $^{13}\text{C}$ -NMR of diethyl 2-methyl-2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (3a) ( $\text{CDCl}_3$ , 75 MHz).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, δ): 4.87 (d, 2J = 5.4 Hz, 2H), 4.25-4.05 (m, 4H), 1.88 (d, 2J = 5.0 Hz, 1H), 1.77 (s, 3 H), 1.45 (d, 2J = 5.0 Hz, 1H), 1.32 (s, 3H), 1.31-1.20 (m, 6H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, δ): 168.45 (C=O), 168.01 (C=O), 144.38 (C<sub>sp2</sub>), 113.10 (C<sub>sp2</sub>), 61.72 (OCH<sub>2</sub>), 61.15 (OCH<sub>2</sub>), 40.15 (C<sub>quart.</sub>), 38.46 (C<sub>quart.</sub>), 25.10 (CHH), 20.86 (CH<sub>3</sub>), 20.51 (CH<sub>3</sub>), 14.15 (CH<sub>3</sub>), 13.98 (CH<sub>3</sub>).



Peak Table

Peak#	Ret. Time	Area%	Area	Height
1	11.434	98.004	3300365	1480692
2	13.350	1.996	67210	34840
Total		100.000	3367576	1515532

Figure S11: GC-FID chromatogram of diethyl 2-methyl-2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (3a) (0.5 μg/mL in acetone, injection volume 1.0 μL, N<sub>2</sub> as carrier gas, split ratio 50, initial temperature 50 °C (hold for 2min) and temperature gradient of 15 C/min up to 300 °C).

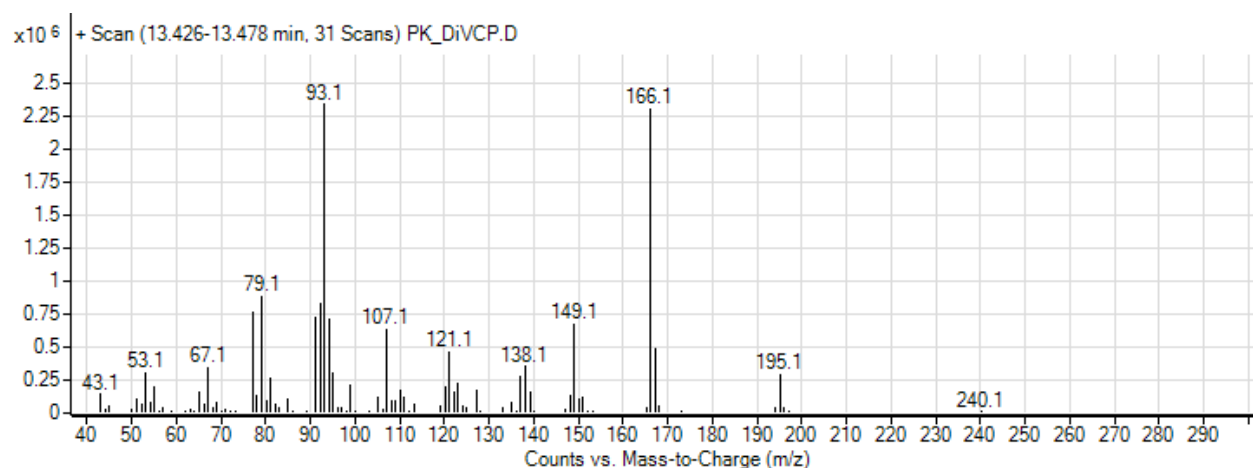


Figure S12: Mass spectrum (Quadropol MS Agilent 5977A MSD: EI with 1000 eV) of GC-MS detected diethyl 2-methyl-2-(prop-1-en-2-yl)cyclopropane-1,1-dicarboxylate (3a).

## Structure of Polymer 1a

It has been described by Sanda that a 1,5-type ring-opened polymer unit is primarily formed in the polymerization of 1,1-disubstituted 2-vinylcyclopropanes (1).<sup>[3;29]</sup> The structure of the polymers (poly(1a) and poly(2a)) was examined by <sup>1</sup>H-NMR. In the <sup>1</sup>H-NMR spectrum of poly(1a) (Figure S7), there was a smooth signal at 1.5-2.5 ppm. According to the reported literature that signal is caused by the formation of a cyclobutane containing unit (1a<sub>II</sub>) which has no olefinic protons. According to this the ratio of olefinic proton is smaller than that for polymers which consists only of a 1,5-type ring-opened unit(1a<sub>I</sub>).

Scheme 2

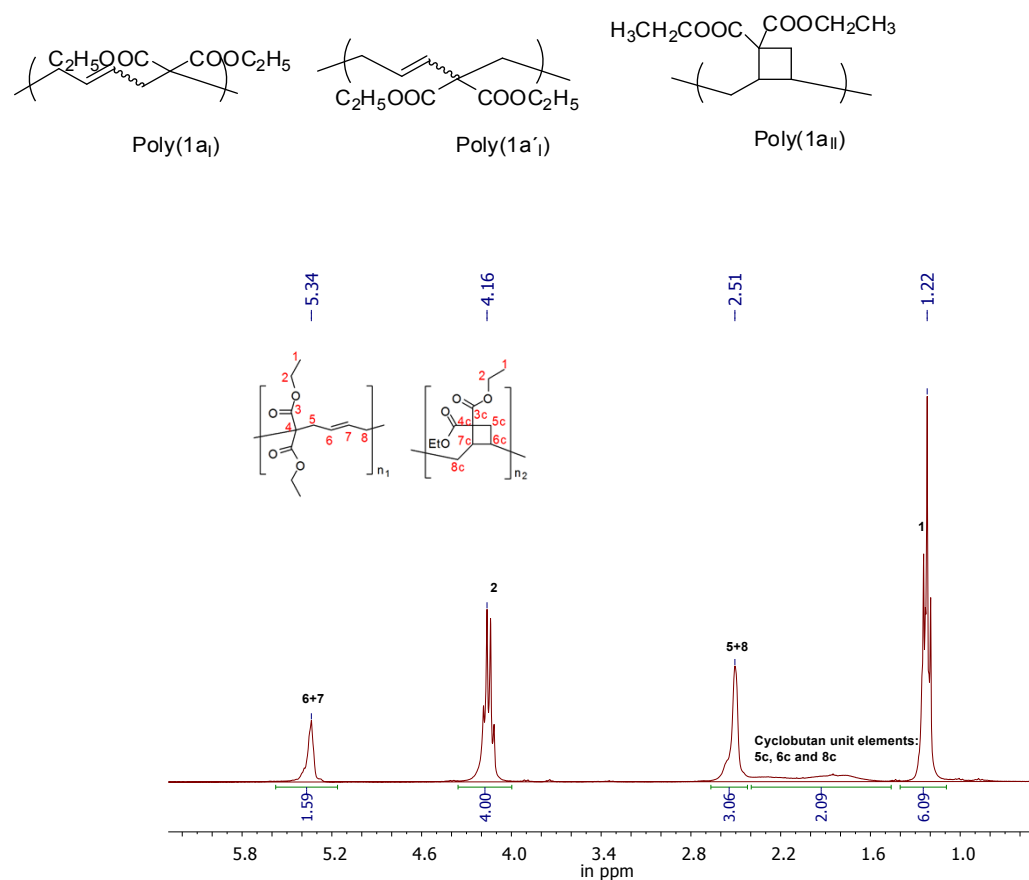
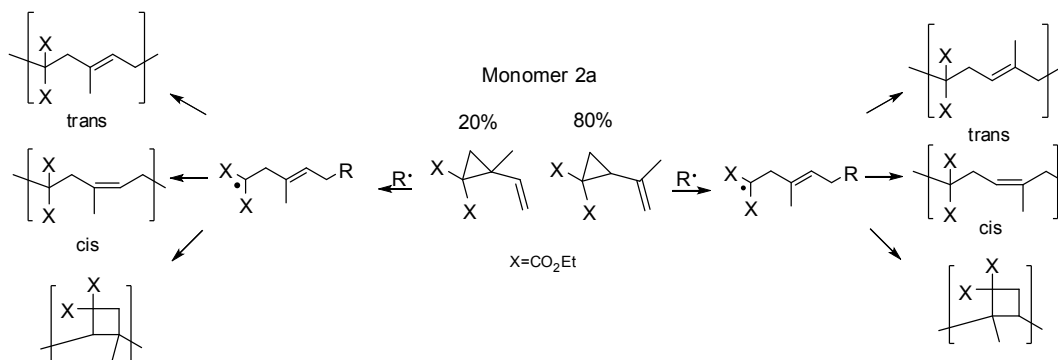


Figure S13: <sup>1</sup>H NMR of Poly(1a) (solvent CDCl<sub>3</sub>, 300 MHz), (Polymerization conditions: 1 mol % CQ; 2 mol % EDMAB, 2 mol % DPIHFP).

## Structure of Polymer 2a

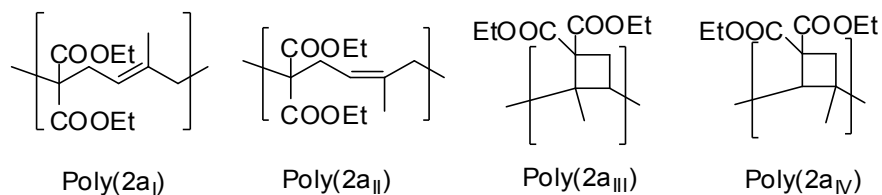
As mentioned in the experimental part the synthesized monomer 2a consists of a constitution isomer of around 80:20 (Figure S5-S8). Nevertheless the existence of the constitution isomer did not influence the polymer structure overall, as head and tail conjunctions results in nearly the same polymer structure (Scheme S3).

**Scheme S3:** Schematic description of the expected polymer structures for monomer (2a).



Within the polymer structure of poly(2a) a cis and trans unit appears, which could be confirmed within the two-dimensional NOESY measurement, as only cross peaks for 9a-5 (trans isomer) could be detected, whereas the cis configuration was proved by the absence of an NOE correlation (Figure S17).

**Scheme S4:** Proved polymer structures for monomer(2a).



Furthermore the polymer structure was verified by a unique interpretation of the polymer signals by <sup>1</sup>H-, <sup>13</sup>C-, HSQC-, NOESY, HMBC-NMR measurements (Figures S14-S17).

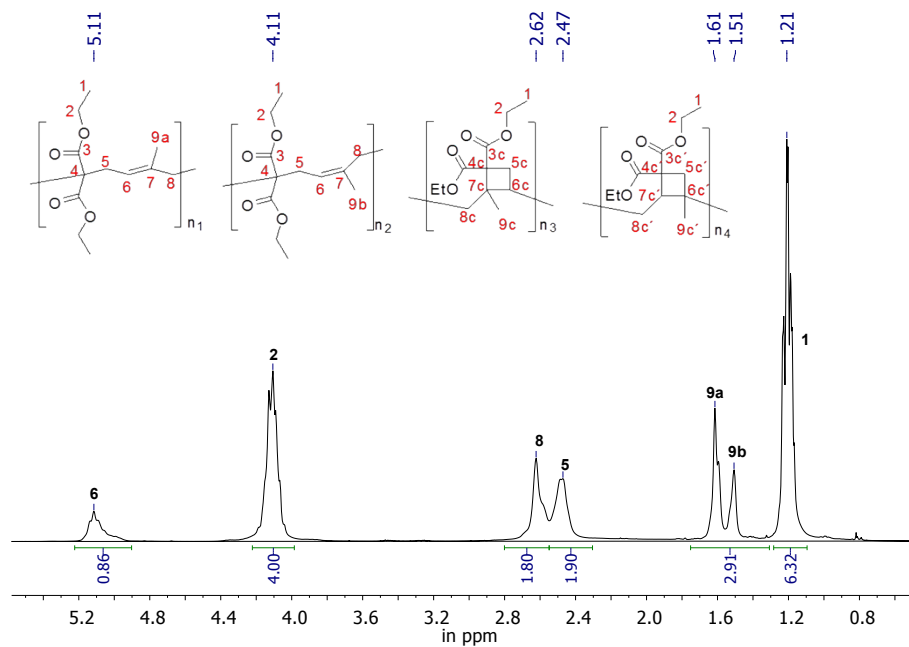


Figure S14:  $^1\text{H}$  NMR of Poly(2a) (solvent  $\text{CDCl}_3$ , 300 MHz), (polymerization conditions: 1 mol % CQ; 2 mol % EDMAB, 2 mol % DPIHFP).

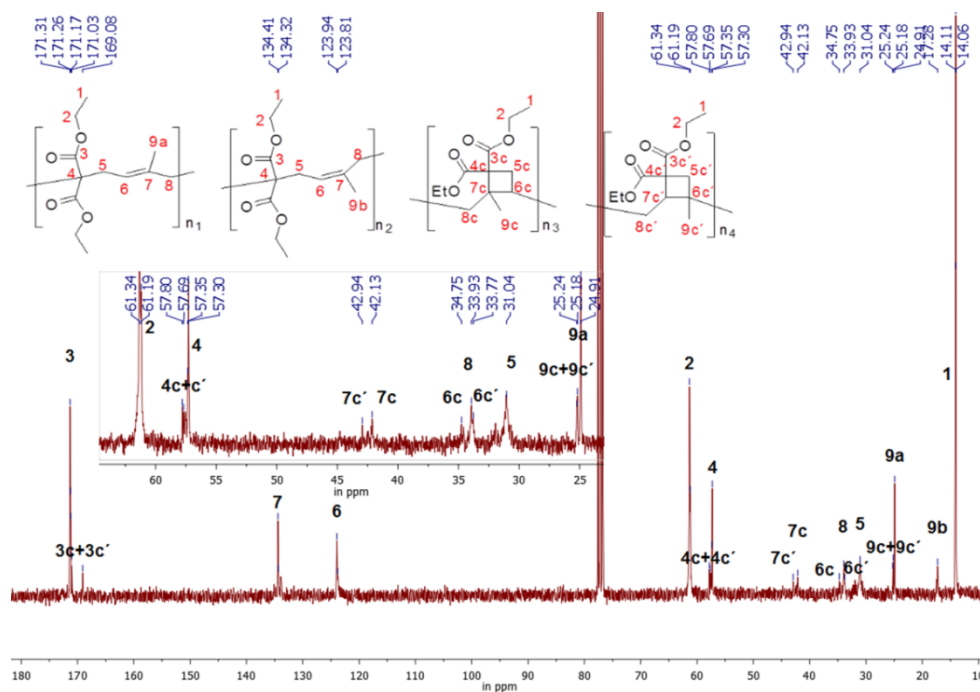


Figure S15:  $^{13}\text{C}$  NMR of Poly(2a) (solvent  $\text{CDCl}_3$ , 300 MHz), (polymerization conditions: 1 mol % CQ; 2 mol % EDMAB, 2 mol % DPIHFP), inclusive an expansion from  $^{13}\text{C}$  NMR between 70-20 ppm.

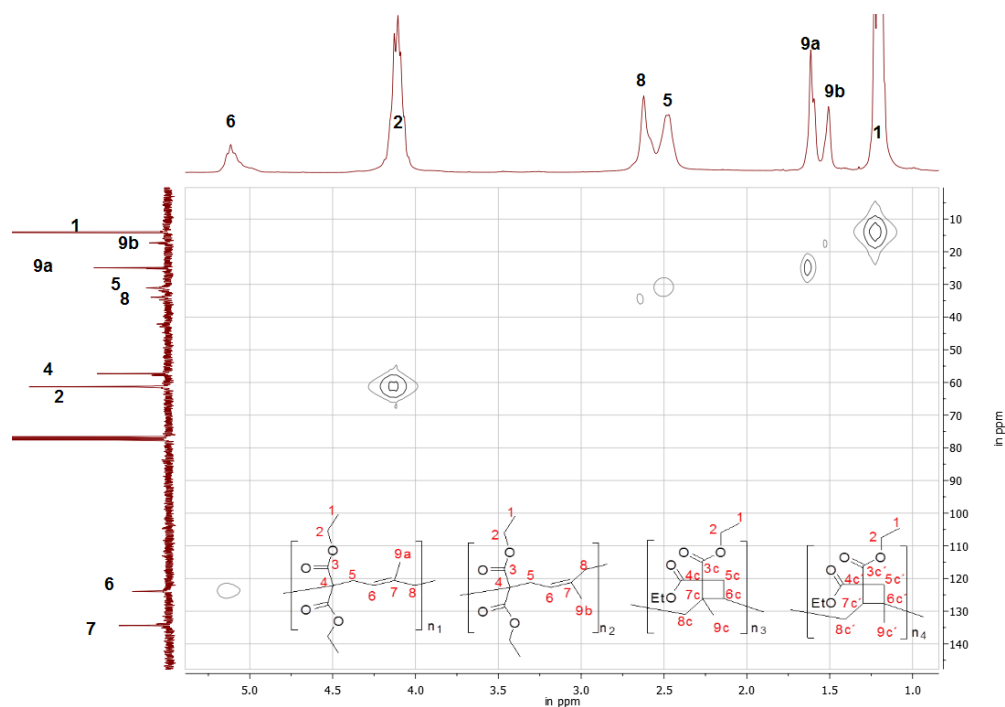


Figure S16: 2D-HSQC NMR of Poly(2a) (solvent  $\text{CDCl}_3$ , 300 MHz), (polymerization conditions: 1 mol % CQ; 2 mol % EDMAB, 2 mol % DPIHFP).

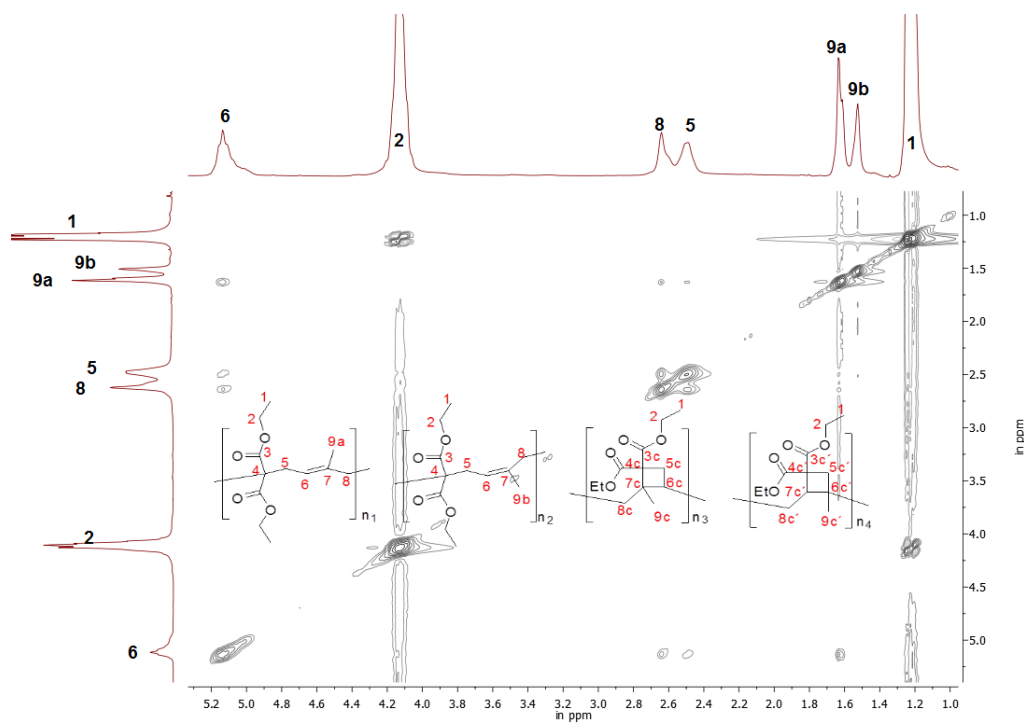


Figure S17: 2D-NOESY NMR of Poly(2a) (solvent  $\text{CDCl}_3$ , 300 MHz), (polymerization conditions: 1 mol % CQ; 2 mol % EDMAB, 2 mol % DPIHFP).

## Adjustments of the volume shrinkage values

The polymerization shrinkage was calculated from the difference in density of the monomer to the formed polymers. The densities of the monomers were measured by a 1mL pycnometer, the densities of the polymers by water displacement of 400mg cured samples. The volume shrinkage of the light cured samples was adjusted to a complete monomer conversion by determination the polymerization yield by  $^1\text{H-NMR}$ . To determine the conversion the  $^1\text{H-NMR}$  integral values of the ethyl ester protons of the monomer and polymer (H2 Figure S18) have been normalized to a value of four, as these exhibit for the monomer and polymer in an analog chemical shift. The content of monomer was calculated by the ratio of the monomer signals H5, H5' and H8 (Figure S18) to their theoretical once. The measured volume shrinkage was then divided by the yield of polymerization, to obtain the adjusted value.

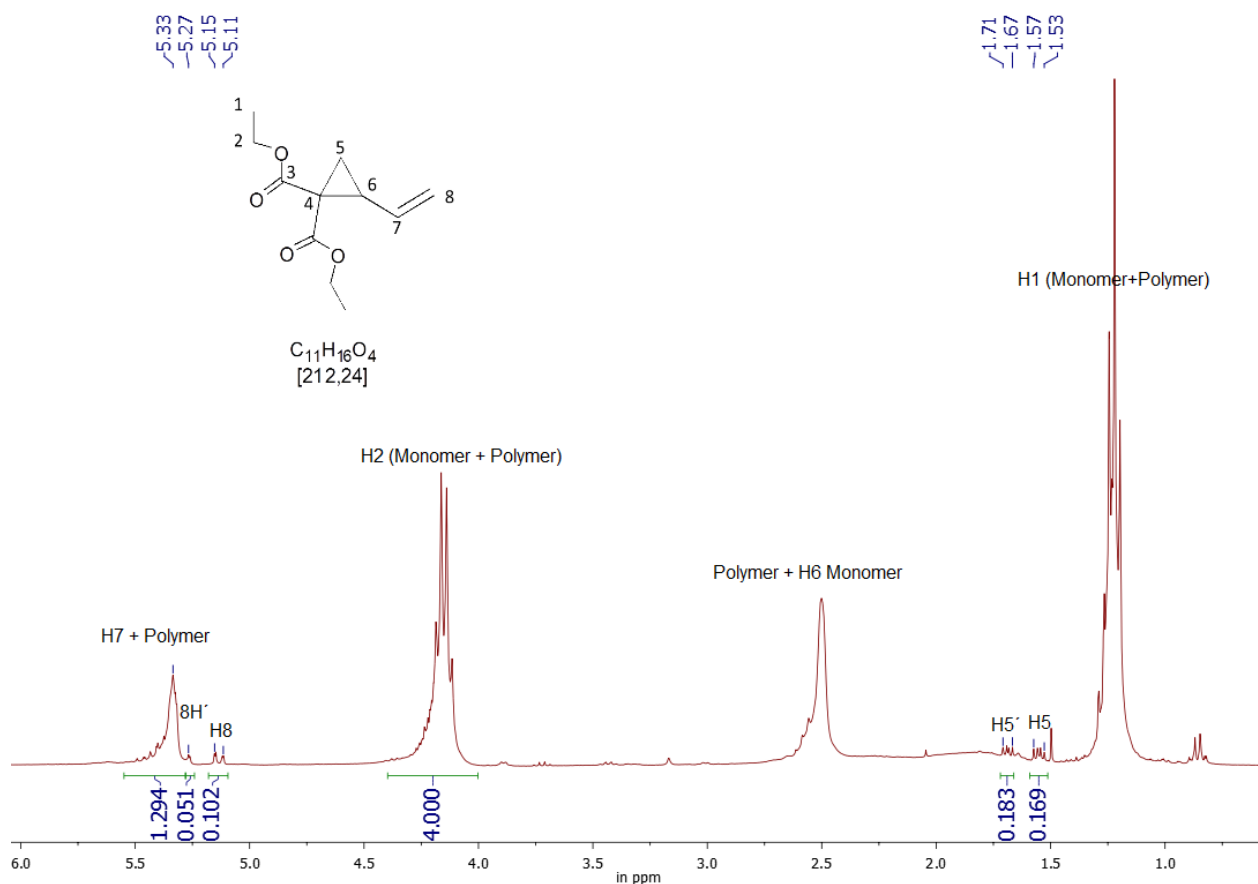


Figure S18: Example of a  $^1\text{H-NMR}$  spectrum of a poly(1a) specimen after 48h photo polymerization (solvent  $\text{CDCl}_3$ , 300 MHz), without precipitating the polymer to calculate the monomer conversion for adjustment of the volume shrinkage value.