Hybrid Photo-Induced Copolymerization of Ring-Strained and Vinyl Monomers Utilizing Metal-Free ROMP Conditions

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Content

1 Materials

Ethyl-1-propenyl ether (928-55-2, Sigma Aldrich) and bicyclo[2.2.1]hept-2-en / norbornene (498-66-8, Sigma Aldrich) were used as received. The (meth)acrylates were filtered over basic aluminum oxide (brockmann type I) prior to use. The dry dichloromethane was obtained from a solvent purification system. The photoredox mediator 2.4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate (**MeOTPP⁺BF₄⁻**) and the initiator (2-methoxyvinyl)cyclohexane were synthesized according to literature procedures.[1,2]

2 General procedures

MF-ROMP (Co)-Polymerization

Catalyst **MeOTPP⁺BF₄⁻** (0.03 eq), norbornene (50 eq) and the respective comonomer (50 eq) were dissolved in dry dichloromethane (monomer concentration ~ 2 mol·L^{-1}). Subsequently, the respective initiator (1 eq) was added, the reaction vial closed and deoxygenated for 5 min by purging the solution with nitrogen gas. Finally, the stirred reaction mixture was irradiated for 1 hour with a blue LED (λ_{max} = 445 nm, 10 W) through the bottom of the vial with a 2 cm distance between LED and vial bottom. During the reaction time the set up was cooled with a fan to ensure ambient temperature. For purification, the solution was precipitated in cold methanol, centrifuged and the solid residue dried *in vacuo*.

3 Synthesis

Tris(4-methoxyphenyl)pyrylium tetrafluoroborate (MeOTPP⁺BF₄⁻)
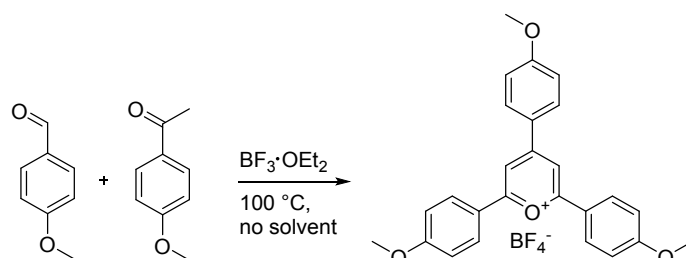
Synthesis adapted from reference[1]

7.6 mL (60 mmol, 2.4 eq) of BF3•Et2O was added slowly to a mixture of 3 mL (25 mmol, 1 eq) of 4-methoxybenzaldehyde and 7.5 g (50 mmol, 2 eq) of 4-methoxyacetophenone. The mixture was heated for 100 min at 100 °C and the oily product was dissolved in acetone and subsequently precipitated in diethyl ether. The residue was purified by three re-crystallizations from acetone to yield MeOTPP⁺BF₄⁻ as an orange powder.

¹H NMR (600 MHz, DMSO-d⁶) δ 8.73 (m, 2H), 8.60 (m, 2H), 8.48 (m, 4H), 7.28 (m, 6H), 3.97 (d, *J* = 10.6 Hz, 9H).
¹³C NMR (150 MHz, DMSO-d⁶) δ 56.04, 56.15, 111.09, 115.37, 115.40, 121.61, 124.68, 130.76, 132.43, 162.04, 164.50, 165.23, 168.07.

ESI-MS: [M]⁺ = 399.1589 (*m/z*^{exp}); 399.1591 *(m/z*^{theo})

(2-Methoxyvinyl)cyclohexane
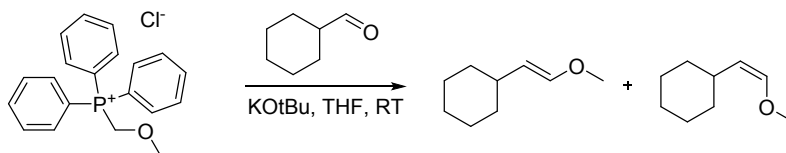
Synthesis adapted from reference[2]

2.93 g (26 mmol, 1.5 eq) of potassium *tert*-butoxide, 8.97 g (methoxymethyl)triphenylposphonium chloride (26 mmol, 1.5 eq) and 2.1 mL of cyclohexanecarboxaldehyde (17 mmol, 1 eq) were dissolved in 80 mL of dry THF. The reaction mixture was continuously stirred at ambient temperature for 4 hours. After completion of the reaction THF was evaporated at 40 °C. Subsequently, the residue was diluted with *n*-hexane and filtered. The filtration product was washed three times with water. Next, any residual solvent was evaporated. The crude product was purified *via* column chromatography (SiO$_2$, ethylacetate:cyclohexane = 4:1 *v/v*).
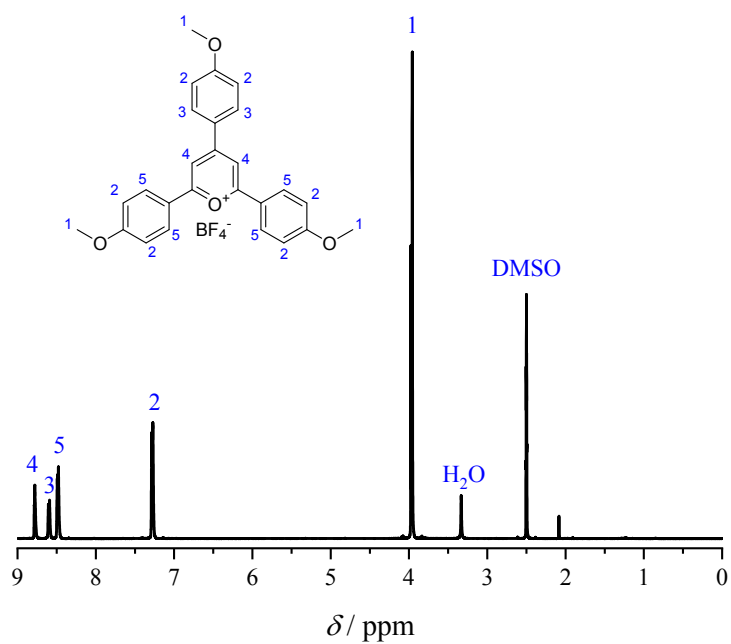
^{1}H NMR (600 MHz, CDCl$_3$) δ 6.28 (d, *J* = 12.6 Hz, 1H), 5.78 (dd, *J* = 5.88 Hz, *J* = 1.0 Hz, 0.5H), 4.69 (dd, *J* = 12.6 Hz, *J* = 7.8 Hz, 1H), 4.22 (dd, *J* = 9.1 Hz, *J* = 6.3 Hz, 0.5H), 3.57 (s, 1.5H), 3.49 (s, 3H), 2.41 (m, 0.5H), 1.87 (m, 1H), 1.74-0.78 (m, cyclohexane$_{cis/trans}$).

^{13}C NMR (150 MHz, CDCl$_3$) δ 26.03, 26.12, 26.20, 33.43, 33.57, 34.47, 36.96, 55.83, 59.55, 109.79, 113.41, 144.55, 145.73.
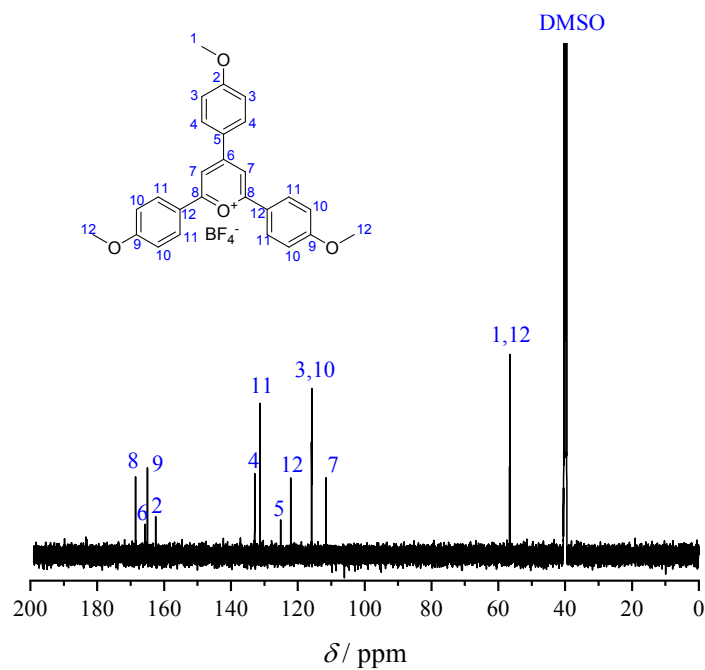
ESI-MS: [M+H]$^+$ = 141.1272 *(m/z^{exp})*; 141.1274 *(m/z^{theo})*
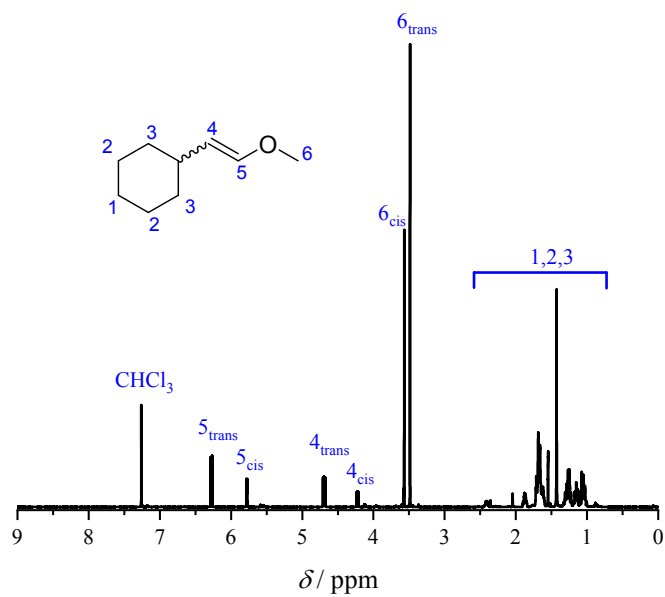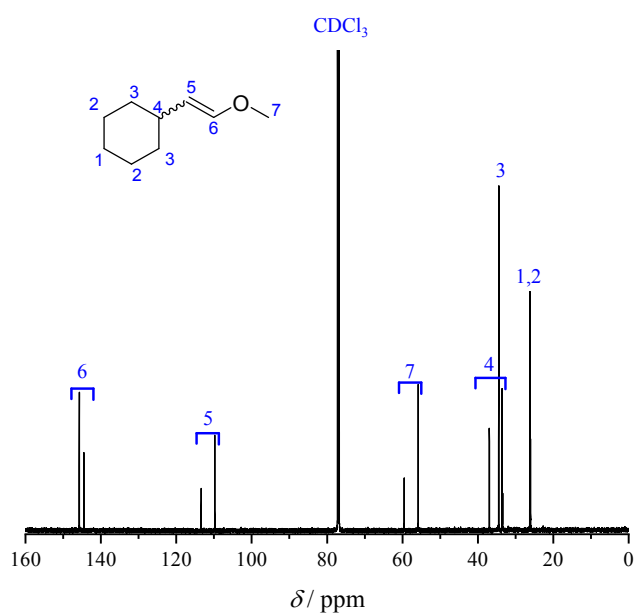
4   Analysis

NMR spectra

Fig. S1: ^{1}H-NMR spectrum of the photocatalyst MeOTPP$^+$BF$_4^-$ in DMSO-*d6*.

Fig. S2: ^{13}C-NMR spectrum of the photocatalyst MeOTPP$^+$BF$_4^-$ in DMSO-*d6*.

Fig. S3: ^{1}H-NMR spectrum of the initiator (2-methoxyvinyl)cyclohexane in CDCl$_3$.


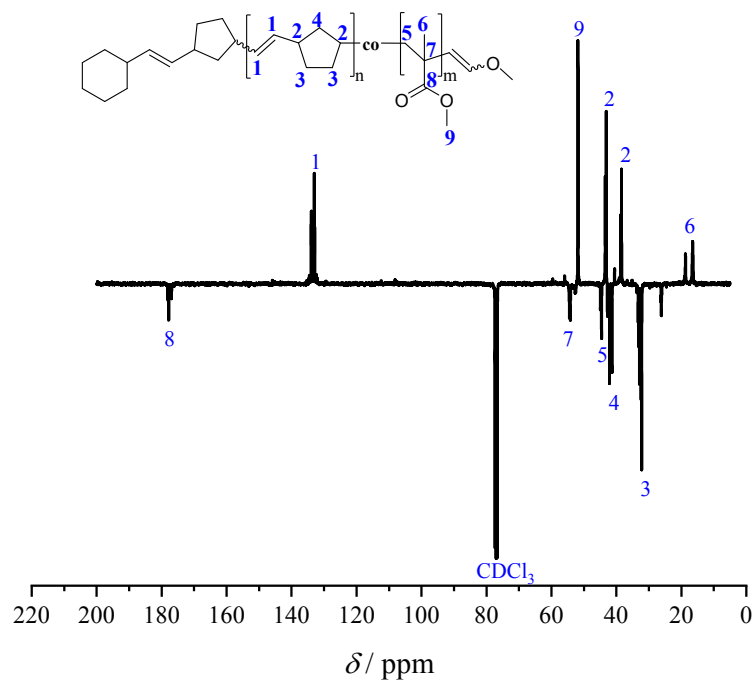**Fig. S4:** ^{13}C-NMR spectrum of the initiator (2-methoxyvinyl)cyclohexane in CDCl$_3$.
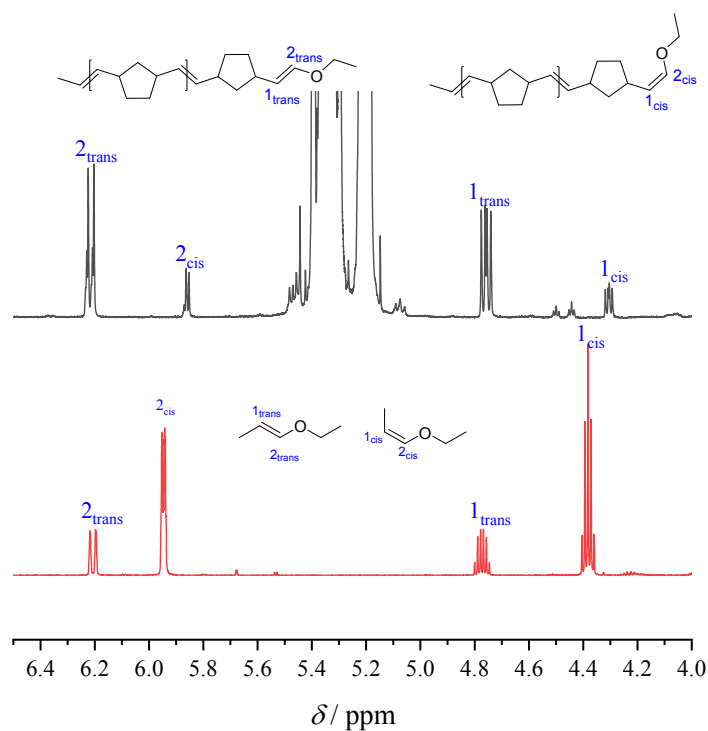
Fig. S5: ^{1}H-NMR spectrum of the initiator ethyl-1-propenyl ether (top) and norbornene homopolymer (bottom) obtained *via* MF-ROMP with ethyl-1-propenyl ether as initiator. The multiplicity of the *cis* and *trans* end group double bond resonances at 4.3 and 4.75 ppm changed from a higher order structure in ethyl-1-propenyl ether into a doublet of doublets in the polymer, evidencing the new connection of the initiator double bond to a norbornene unit at the ω-chain end.
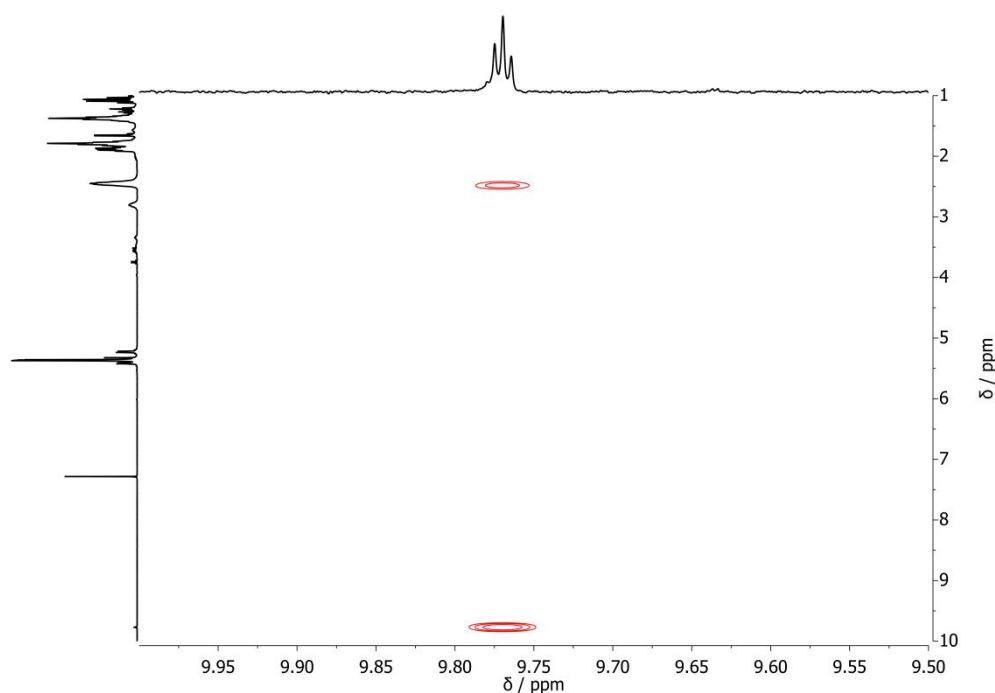
Fig. S6: Zoomed region of the ^{1}H/^{1}H COSY of a norbornene homopolymer obtained *via* MF-ROMP with ethyl-1-propenyl ether as initiator. The feed ratio of norbornene : initiator : photocatalyst was 5 : 1 : 0.03. The sample was deoxygenated and irradiated at 445 nm in dry dichloromethane for 75 min. The aldehyde multiplicity is a triplet that couples to the alkyl region.
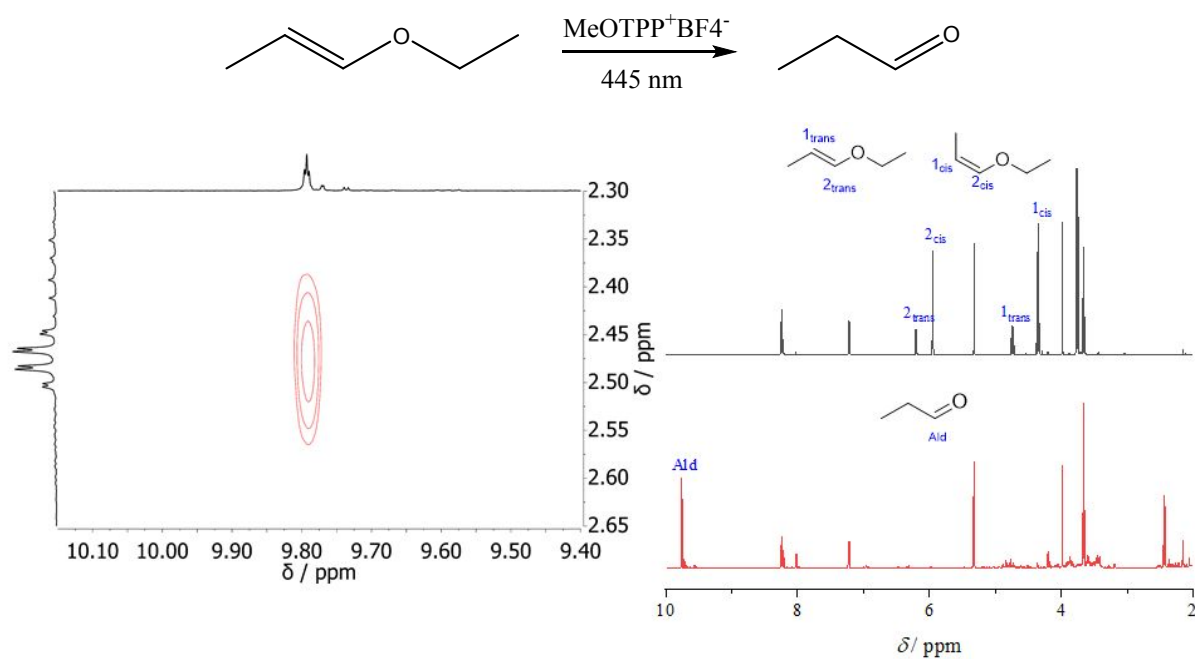
Fig. S7: 'Cocktail experiment': ^{1}H-NMR spectra of the reaction mixture before and after irradiation at 445 nm for 60 min. Reaction mixture consisting of 1 eq ethyl-1-propenyl ether and 0.03 eq MeOTPP$^+$BF$_4^-$ in deuterated dichloromethane without deoxygenation. Inset: Corresponding ^{1}H/^{1}H-COSY spectrum. The reaction leads to aldehyde formation after cleavage of ethanol.

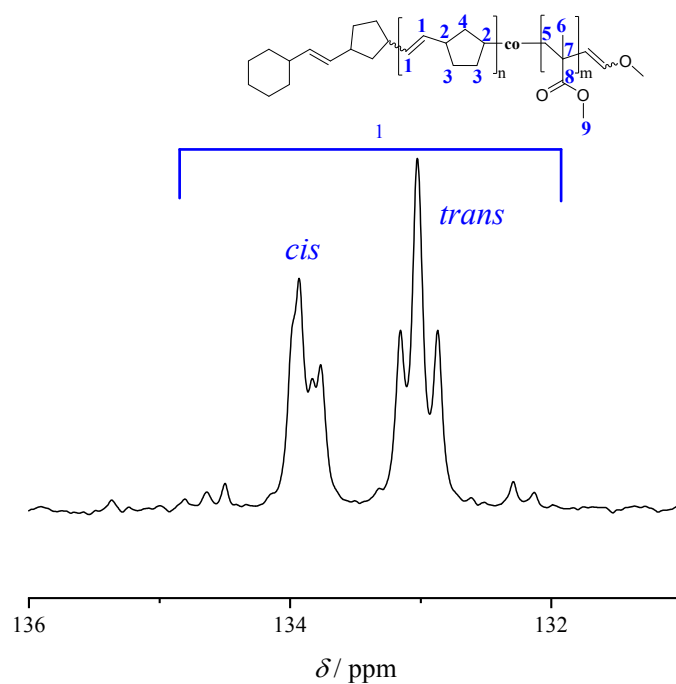**Fig. S8:** ^{13}C-NMR spectrum of poly(norbornene-*co*-MMA) in CDCl$_3$.The copolymer was synthesized with (2-methoxyvinyl)cyclohexane as initiator and a 50/50 mixture of norbornene and MMA under constant irradiation at 445 nm for 180 min. The polymer was purified *via* precipitation in cold methanol.
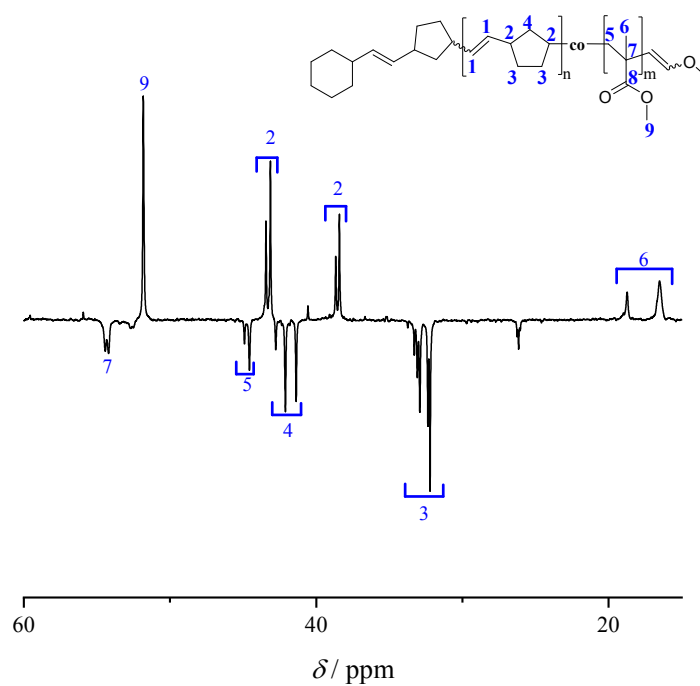
Fig. S9: Zoomed part of the spectrum shown in Figure S5.

Fig. S10: Zoomed part of the spectrum shown in Figure S5.

Fig. S11: ^{1}H-NMR spectra of the block chain extension of poly(norbornene-*co*-MMA) with norbornene affording poly(norbornene-*co*-MMA)-*block*-poly(norbornene). The precursor copolymer was synthesized with (2-methoxyvinyl)cyclohexane as initiator and a 50/50 mixture of norbornene and MMA under constant irradiation at 445 nm for 60 min. The precursor polymer was purified *via* precipitation in cold methanol. The chain extension was performed with freshly added norbornene, MeOTPP^{+}BF$_{4}^{-}$ and dry dichloromethane under constant irradiation for 60 min.
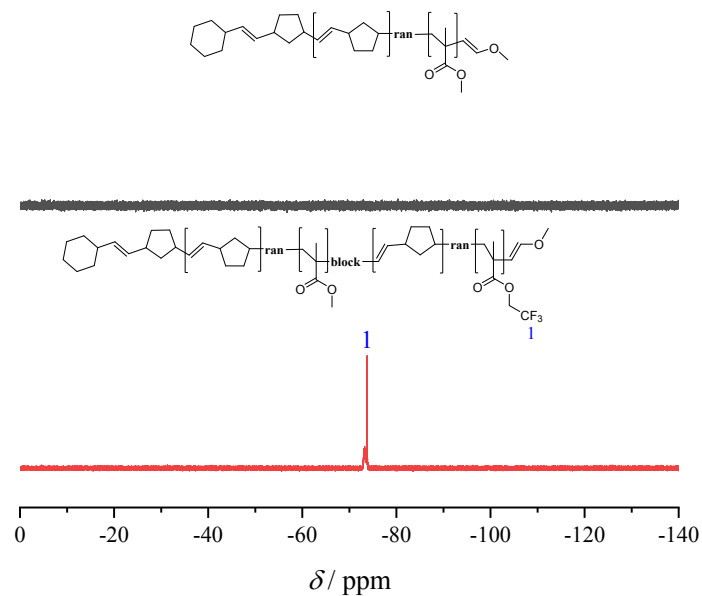
Fig. S12: ^{19}F-NMR spectra of the block chain extension of poly(norbornene-*co*-MMA) with norbornene and 2,2,2-trifluoroethyl methacrylate (TFEMA) yield poly(norbornene-*co*-MMA)-*block*-poly(norbornene-*co*-TFEMA). The precursor copolymer was synthesized with (2-methoxyvinyl)cyclohexane as initiator and a 50/50 mixture of norbornene and MMA under constant irradiation at 445 nm for 60 min. The precu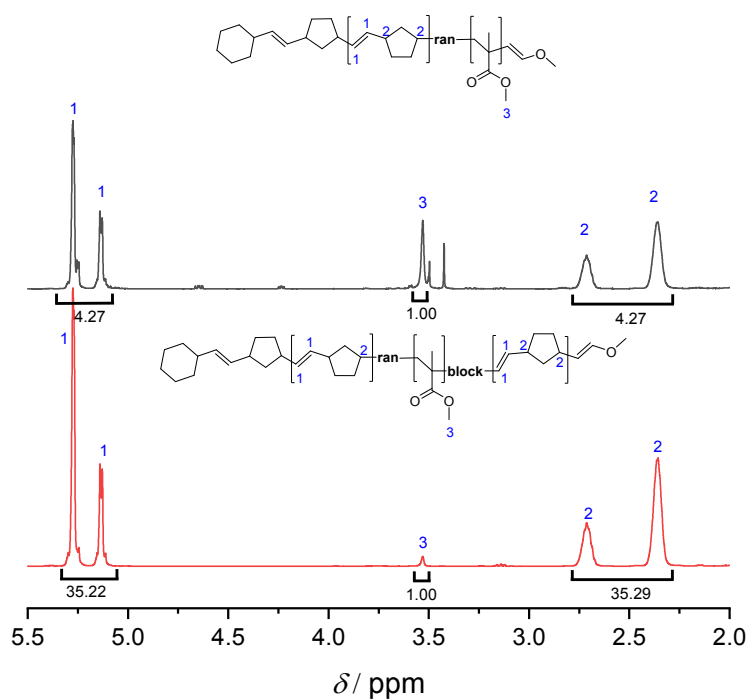rsor polymer was purified *via* precipitation in cold methanol. The chain extension was performed with a 50/50 mixture of norbornene and 2,2,2-trifluoroethyl methacrylate and fresh addition of MeOTPP$^+$BF$_4^-$ and dry dichloromethane under constant irradiation for 60 min.

Emission spectrum of the blue LED
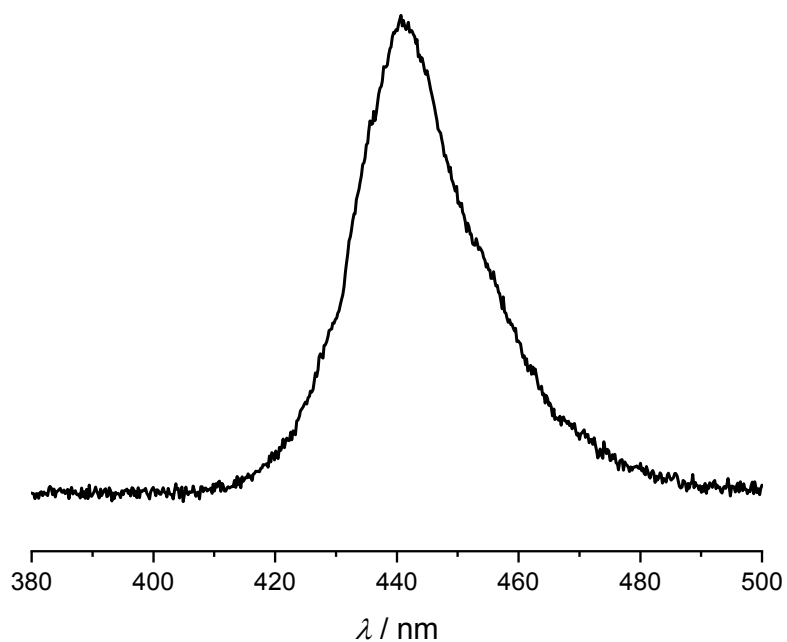
Fig. S13: Emission spectrum of the blue LED used for the polymerization (λ_{max} = 445 nm, 10 W), for a standard experiment 8.85 V forward voltage (0.75 A) was used and the vial containing the reaction mixture was irradiated through the bottom at a distance of 2 cm from the LED. In addition to the heat sink of the LED we utilized a fan to assure ambient temperatures for the reaction.

Size Exclusion Chromatography (SEC)
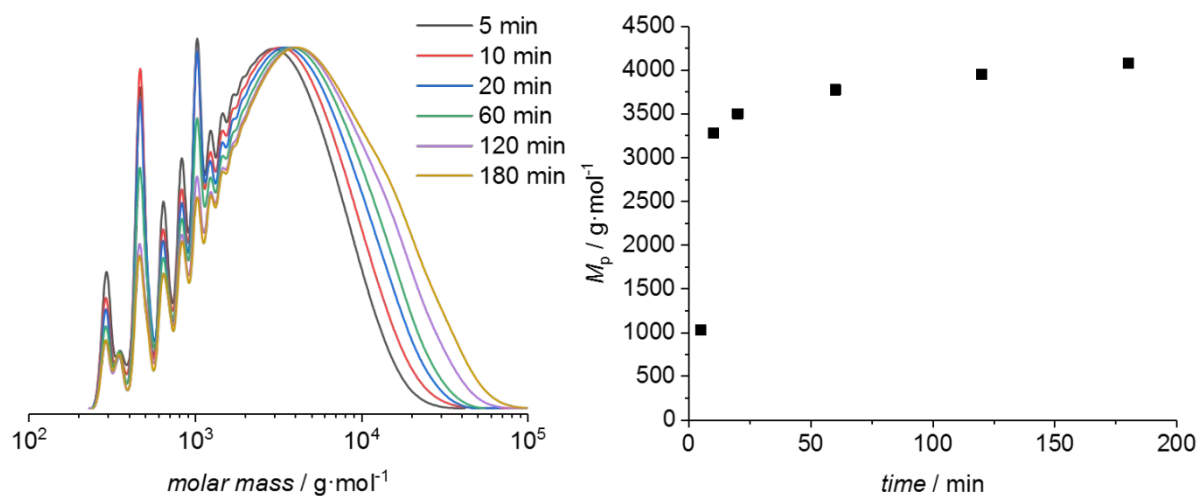

Fig. S14: Molar mass distribution (left) and increase of M_p (right) at several time intervals of a 50 % norbornene and 50% methyl acrylate copolymer utilizing (2-methoxyvinyl)cyclohexane as initiator. The typical copolymerization conditions of feed ratios of 100 eq monomer, 1 eq initiator and 0.03 eq catalyst were used. The reaction was performed for the stated times in dry dichloromethane using 445 nm LED light as an irradiation source.
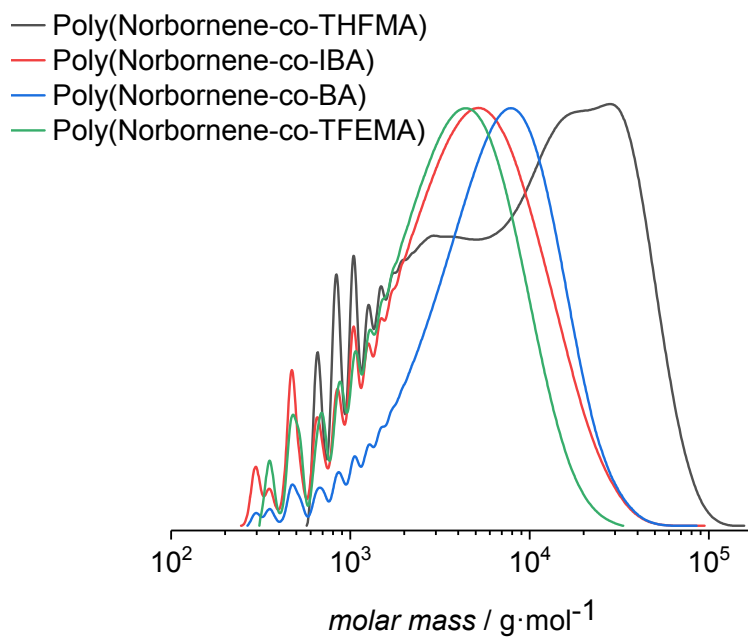
Fig. S15: Molecular weight distribution of poly(norbornene-*co*-tetrahydrofurfuryl methacrylate) (black trace), poly(norbornene-*co*-isobutyl acrylate) (red trace), poly(norbornene-*co*-butyl acrylate) (blue trace) and poly(norbornene-*co*-trifluoroethyl methacyrlat) (green trace). Each copolymer was synthesized according to the standard procedure within 60 min with (2-methoxyvinyl)cyclohexane as initiator at 445 nm constant irradiation in dry dichloromethane.

SEC/HRESI – Mass Spectrometry
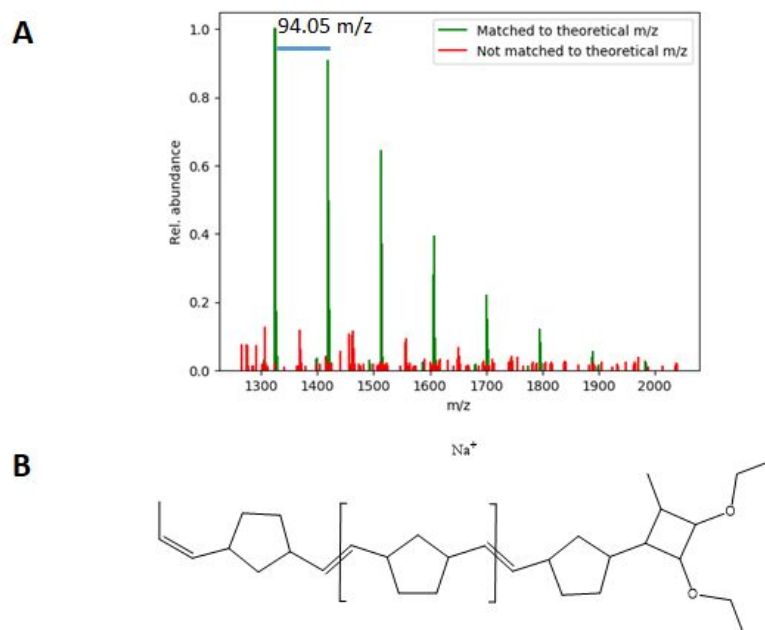
Figure S16: ESI-MS spectrum of a norbornene homopolymer synthesized with ethyl-1-propenyl ether as initiator. The sample was first fractionated *via* online SEC with THF as eluent and subsequently analyzed by ESI-MS using sodium iodide as doping agent. (A) Depiction of matching results (green peaks) and mismatched results (red peaks) between experimentally obtained pattern and simulated isotopic pattern of the proposed structure. (B) The proposed structure of the norbornene homopolymer with sodium as a positive counter ion was identified in the mass spectrum.
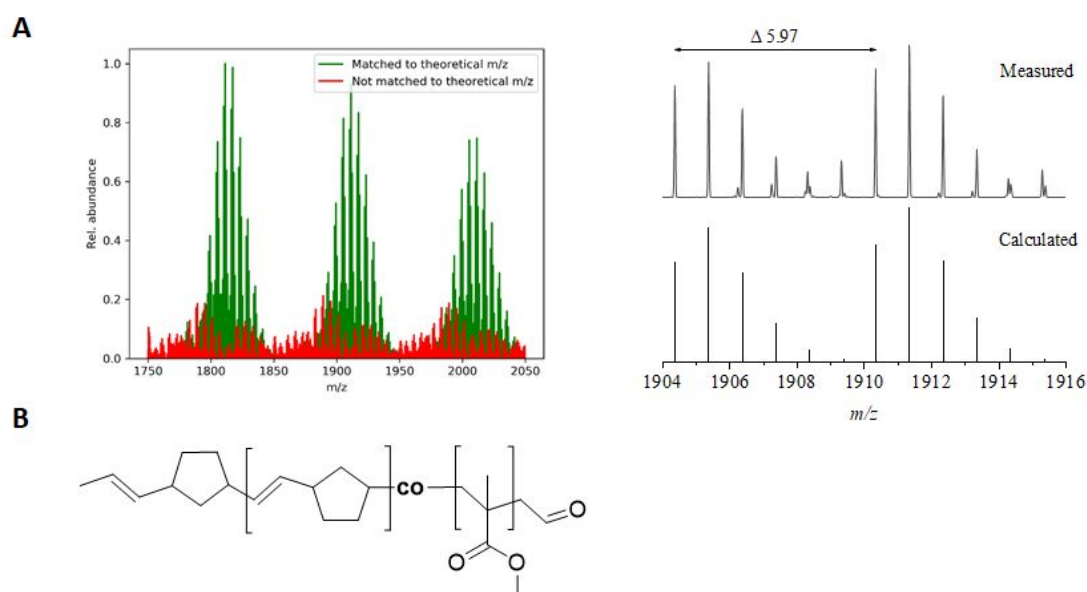
Figure S17: ESI-MS spectrum of a norbornene / methyl methacrylate copolymer (50:50) synthesized with ethyl-1-propenyl ether as initiator. The sample was first fractionated *via* online SEC with THF as eluent and subsequently analyzed by ESI-MS using sodium iodide as doping agent. (A) Depiction of matching results (green peaks) and mismatched results (red peaks) between experimentally obtained pattern and simulated isotopic pattern of the proposed structure. (B) The proposed structure of the norbornene/MMA copolymer with sodium as a positive counter ion was identified in the mass spectrum. A zoomed region of the spectrum shows the match of the experimental spectrum with the calculated one in greater detail.

Figure S18: ESI-MS spectrum of a norbornene / methyl methacrylate copolymer (50:50) synthesized with (2-methoxyvinyl)cyclohexane as initiator. The sample was first fractionated *via* online SEC with THF as eluent and subsequently analyzed by ESI-MS using sodium iodide as doping agent. (A) Depiction of matching results (green peaks) and mismatched results (red peaks) between experimentally obtained pattern and simulated isotopic pattern of the proposed structure. (B) The proposed structure of the norbornene/MMA copolymer with sodium as a positive counter ion was identified in the mass spectrum. A zoomed region of the spectrum shows the match of the experimental spectrum with the calculated one in greater detail.

Figure S19: ESI-MS spectrum of a norbornene / methyl acrylate copolymer (50:50) synthesized with (2-methoxyvinyl)cyclohexane as initiator. The sample was first fractionated *via* online SEC with THF as eluent and

subsequently analyzed by ESI-MS using sodium iodide as doping agent. (A) Depiction of matching results (green peaks) and mismatched results (red peaks) between experimentally obtained pattern and simulated isotopic pattern of the proposed structure. (B) The proposed structure of the norbornene/MA copolymer with sodium as a positive counter ion was identified in the mass spectrum. A zoomed region of the spectrum shows the match of the experimental spectrum with the calculated one in greater detail.
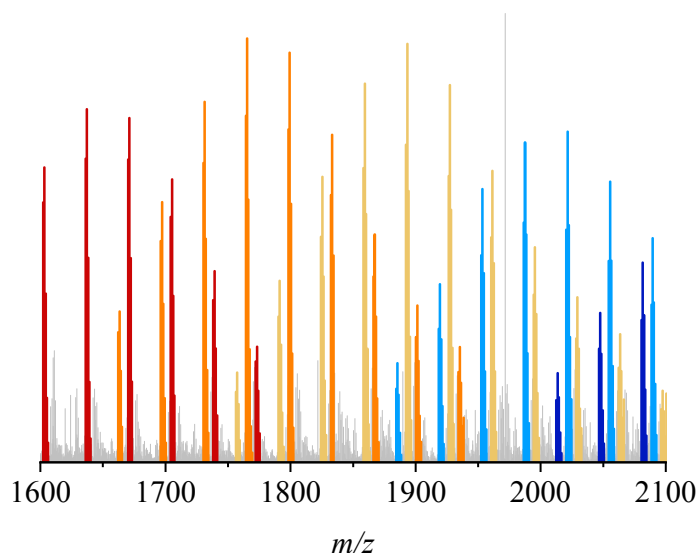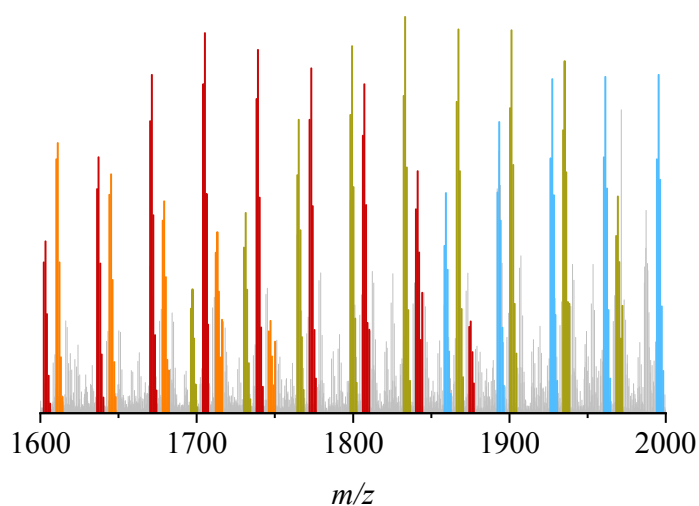

Figure S20: ESI-MS spectrum of a norbornene / butyl acrylate copolymer (50:50) synthesized with (2-methoxyvinyl)cyclohexane as initiator. The sample was first fractionated *via* online SEC with THF as eluent and subsequently analyzed by ESI-MS using sodium iodide as doping agent. The patterns of polymer chains with different degrees of polymerization (DP) overlap with each other and were color coded to guide the eye. The spacing between patterns of the same color is $\Delta 34.01$ *m/z*, corresponding to the difference of the repeating units 128.0837 Da (butyl acrylate) and 94.0783 Da (norbornene).

Figure S21: ESI-MS spectrum of a norbornene / isobutyl acrylate copolymer (50:50) synthesized with (2-methoxyvinyl)cyclohexane as initiator. The sample was first fractionated *via* online SEC with THF as eluent and subsequently analyzed by ESI-MS using sodium iodide as doping agent. The patterns of polymer chains with different degrees of polymerization (DP) overlap with each other and were color coded to guide the eye. The spacing between

patterns of the same color is Δ34.01 *m/z*, corresponding to the difference of the repeating units 128.0837 Da (isobutyl acrylate) and 94.0783 Da (norbornene).
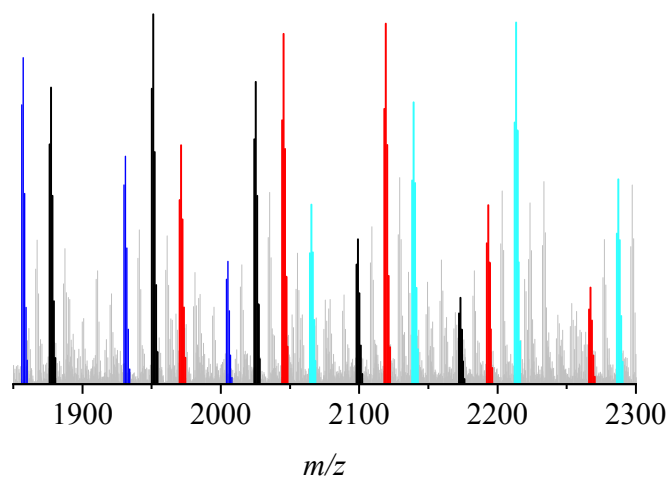

**Figure S22:** ESI-MS spectrum of a norbornene / 2,2,2-trifluoroethyl methacrylate copolymer (50:50) synthesized with (2-methoxyvinyl)cyclohexane as initiator. The sample was first fractionated *via* online SEC with THF as eluent and subsequently analyzed by ESI-MS using sodium iodide as doping agent. The patterns of polymer chains with different degrees of polymerization (DP) overlap with each other and were color coded to guide the eye. The spacing between patterns of the same color is Δ73.96 *m/z*, corresponding to the difference of the repeating units 168.0398 Da (2,2,2-trifluoroethyl methacrylate) and 94.0783 Da (norbornene).

In-situ UV/VIS absorbance measurements
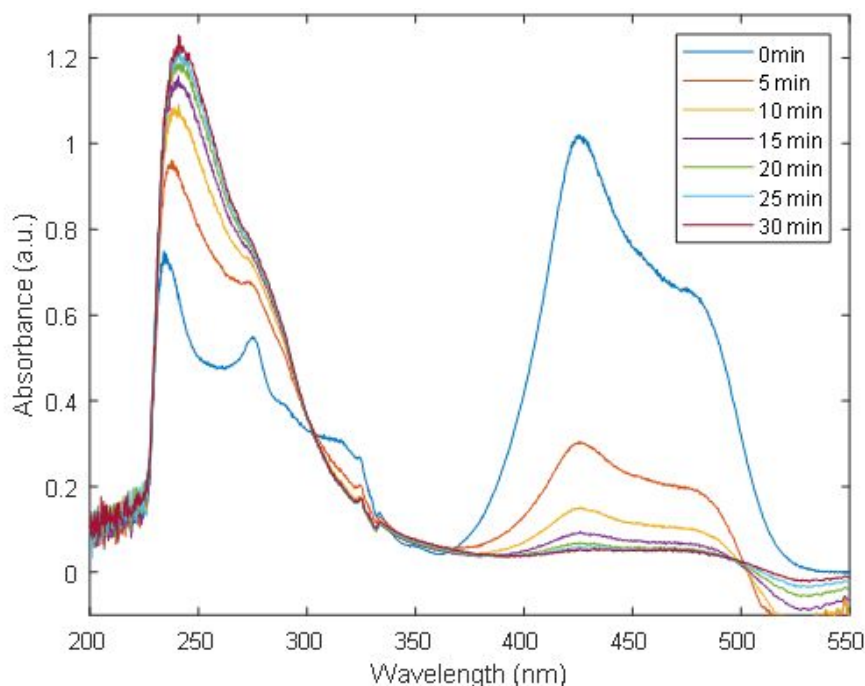
Figure S23. In-situ UV/Vis measurement of a norbornene homopolymerization mixture with 100 eq norbornene, 1 eq 2-cyclohexyl-1-methoxyethylene and 0.03 eq MeOTPP$^+$BF$_4^-$ in dichloromethane under constant irradiation with 445 nm blue light at ambient temperature. The dip in the absorbance above 500 nm can be explained by fluorescence of the catalyst.

Table S1. Higher conversions in the hybrid copolymerization of norbornene and MMA (50/50 feed ratio; 100 eq) utilizing MF-ROMP conditions with ethyl-1-propenyl ether (1 eq) as initiator and MeOTPP$^+$BF$_4^-$ (0.03 eq) in dichloromethane (2 mol·L^{-1}). After 60 min an aliquot was taken for ^{1}H NMR analaysis. Afterwards, 1 mg of the pyrylium salt was dissolved in 2 mL dichloromethane and the solution degassed and subsequently added to the polymerization mixture. The same procedure was repeated after 180 min and the sample was irradiated for in total 420 min reaching higher conversions compared to experiments without sequential addition of pyrylium salt. The molecular weight distribution remained monomodal and leads towards higher molecular weights compared to the other molecular weights reported in table 1 of the main manuscript.

Total Reaction Time (min)	Conversion norbornene (%)	Conversion MMA (%)	M_p (g·mol^{-1})
60	4	4	/
180	15	7	10600
300	22	13	13100
420	25	16	13400

5   Instrumentation

Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker System 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient (^{1}H: 600.13 MHz, ^{13}C: 150.90 MHz). All measurements were carried out in deuterated solvents. The chemical shift (δ) is recorded in parts per million (ppm) and relative to the residual solvent protons. Coupling constants (J) were calculated in Hertz (Hz). *MestReNova* 12.0 software was used to analyze the spectra. The signals were quoted as follows: s = singlet, bs =broad singlet, d = doublet, t = triplet and m = multiplet.

Size-Exclusion Chromatography

The SEC measurements were conducted on a *PSS* SECurity^2 system consisting of a *PSS* SECurity Degasser, *PSS* SECurity TCC6000 Column Oven (35 °C), *PSS* SDV Column Set (8x150 mm 5 µm Precolumn, 8x300 mm 5 µm Analytical Columns, 100000 Å, 1000 Å and 100 Å) and an *Agilent* 1260 Infinity Isocratic Pump, *Agilent* 1260 Infinity Standard Autosampler, *Agilent* 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), *Agilent* 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL·min^{-1}. Narrow disperse linear poly(styrene) (M_n: 266 g·mol^{-1} to 2.52·10^6 g·mol^{-1}) and poly(methyl methacrylate) (M_n: 202 g·mol^{-1} to 2.2·10^6 g·mol^{-1}) standards (*PSS* ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in *PSS* WinGPC UniChrom software (version 8.2).

SEC/HRESI-MS measurements

Spectra were recorded on a Q Exactive Plus (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the m/z range 74- 1822 using premixed calibration solutions (Thermo Scientific) and for the high mass mode in the m/z range of 600-8000 using ammonium hexafluorophosphate solution. A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 10 and 0 were applied, respectively. The capillary temperature was set to 320 °C, the S-lens RF level was set to 150, and the aux gas heater temperature was set to 125 °C. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a temperature controlled column department (TCC 3000). An aliquot (100 µL) of a polymer solution with a concentration of 2 mg·mL^{-1} in THF was separated on two mixed bed size exclusion chromatography columns

(Agilent, Mesopore 250 × 4.6 mm, particle diameter 3 µm) with a precolumn (Mesopore 50 × 7.5 mm) operating at 30 °C. THF at a flow rate of 0.30 mL·min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to an UV detector (VWD 3400, Dionex), and a RI-detector (RefractoMax520, ERC, Japan) in a setup described earlier.[3] 0.27 mL·min^{-1} of the eluent were directed through the UV and RI-detector and 30 µL·min^{-1} were infused into the electrospray source after post-column addition of a 50 µM solution of sodium iodide in methanol at 20 µL·min^{-1} by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM).

6 References

(1)   Martiny, M.; Steckhan, E.; Esch, T. Cycloaddition Reactions Initiated by Photochemically Excited Pyrylium Salts. *Chem. Ber.* **1993**, *126*, 1671–1682. https://doi.org/10.1002/cber.19931260726.

(2)   Ogawa, K. A.; Goetz, A. E.; Boydston, A. J. Metal-Free Ring-Opening Metathesis Polymerization. *J. Am. Chem. Soc.* **2015**, *137* (4), 1400–1403. https://doi.org/10.1021/ja512073m.

(3)   Gruendling, T.; Guilhaus, M.; Barner-Kowollik, C. Fast and Accurate Determination of Absolute Individual Molecular Weight Distributions from Mixtures of Polymers via Size Exclusion Chromatography- Electrospray Ionization Mass Spectrometry. *Macromolecules* **2009**, *42* (17), 6366–6374. https://doi.org/10.1021/ma900755z.