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Supporting Information

Transparent Films from CO_2-Based Polyunsaturated Poly(ether carbonate)s: A Novel Synthesis Strategy and Fast Curing

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Materials and methods

Materials: All reagents were purchased from commercial suppliers and used as received. The deuterated solvents were also used as obtained from the supplier.

Double metal cyanide (DMC) catalyst: The DMC catalyst based on zinc hexacyanocobaltate was prepared according to the following procedure of example 6 in patent WO-A 01/80994. A solution of zinc chloride (6.485 kg) in distilled water (23.9 kg) and tert-butanol (3.4 kg) was circulated at 50°C in a loop reactor. A solution of potassium hexacyanocobaltate (0.65 kg) in distilled water (8.0 kg) was metered into the reactor. Directly thereafter a mixture of tert-butanol (0.144 kg), polypropylene glycol 1000 (0.685 kg) and distilled water (6.5 kg) was metered in. The dispersion was circulated for 90 min. Part of the dispersion (58 kg) was filtered in a membrane filter press. A scrubbing solution (65 wt % tert-butanol, 33.7 wt% water, 1.3 wt% polypropyleneglycol 1000, 44 kg) was applied. After drying for 5.5 hours under reduced pressure the filter cake had a residual moisture content of around 3%.

NMR spectroscopy: A Bruker AV III (^{1}H, 400 MHz) and Bruker AV II (^{1}H, 400 MHz) was used for recording the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra. Chemical shifts are quoted relative to tetramethylsilane (TMS).

IR spectroscopy: FT-IR spectra were recorded on a Bruker Alpha-P FT-IR Spectrometer (Bruker Optics) equipped with a diamond probe. All samples were scanned 24 times with a resolution of 4 cm^{-1}. The data were collected in the range of 4000 – 400 cm^{-1} and evaluated using OPUS 7.0 (Bruker Optics) software. A background spectrum was recorded prior to every measurement.

Gel permeation chromatography (GPC): The number- and weight-average molecular weight (M_n and M_w, respectively) of the obtained polyunsaturated polyethercarbonates were determined by gel permeation chromatography (GPC). The procedure was in accordance with DIN 55672-1: "Gel permeation chromatography, Part 1 - Tetrahydrofuran as the eluting agent" (SECurity GPC System from PSS Polymer Service, flow rate 1.0 ml·min^{-1}; columns: 2×PSS SDV linear M, 8×300 mm, 5 µm; RID detector). Polystyrene samples of known molecular weight were used for calibration, and the chromatogram was referenced against the absolute mass determined by mass spectroscopy. The PDI was calculated as the ratio of M_w to M_n.

Rheometry: The rheological analysis of polyunsaturated polyethercarbonates was performed on a Parr Rheometer MCR501. For viscosity measurements a cone-plate measuring system with a diameter of 25 mm, an angle of 1° and a truncation of 50 µm was used. The shear rate was increased from 0.01 to 1000 s^{-1} in 60 increments whereby a constant shear rate as applied for 10 seconds each. The viscosity was calculated as the average of the 60 measurements.

Differential scanning calorimetry (DSC): The glass transition point (T_g) was determined by using DSC. The phase behaviour was characterized by using a Perkin-Elmer Pyris 6 differential scanning calorimeter. A sample of the polymer (*ca*. 10 mg) was placed into the sample holder. The latter was placed into a flow of argon, and the temperature was adjusted to 25°C. Then, the sample was heated to 100°C at 20°C·min^{-1}, held at 100°C for 10 min, cooled to -80°C (-10°C·min^{-1}) and held there for 10 min. Then, the sample was heated three times to 100°C at a rate of 10°C·min^{-1}, kept at 100°C for 2 min, cooled to -80°C (-10°C·min^{-1}) and held at this temperature for 2 min. The glass transition temperature or the melting point is given as the inflection point of the heat flow curve in the third heating cycle.

Thermogravimetric analysis (TGA): The TGA traces were recorded on a Mettler Toledo Gas Controller GC20 with STRe System. A sample of the polymer (*ca*. 30 mg) was placed into the sample holder. The latter was placed into a flow of argon, and the temperature was adjusted to 25°C. Then, the sample was heated to 600°C at a rate of 10°C·min^{-1}.

Synthesis and characterization of polyunsaturated polyethercarbonates

Representative procedure for the multicomponent polymerization of CO_2, propylene oxide, maleic anhydride, and allylglycidylether (3a-c): A high pressure reactor (300 mL, Parr Instrument) equipped with a gas entrainment stirrer was charged with DMC catalyst (16 mg) and α,ω-dihydroxy polypropylene oxide (1000 g·mol^{-1}, f = 2, 20.0 g). The reactor was closed, the mixture stirred at 800 rpm, purged with argon and heated to 130°C. The reactor was then pressurized with carbon dioxide to 15 bar. Thereafter, the pressure was maintained at 15 bar by feeding CO_2. A mixture of maleic anhydride and propylene oxide (**3a** = 7/93 wt%; **3b** = 14/86 wt%; **3c** = 26/74 wt%) was added in three pulses of 2.0 g (1 mL·min^{-1}) each, and the mixture was stirred for 20 minutes after each pulse. Then, the temperature was adjusted to 100°C. After the temperature and pressure had been stable for at least 5 minutes, 24 g

(1 mL·min^{-1}) of maleic anhydride and propylene oxide mixture (**3a** = 7/93 wt%; **3b** = 14/86 wt%; **3c** = 26/74 wt%) was added. Subsequently, 30 g of allylglycidylether and propylene oxide mixture (**3a** = 7/93 wt%; **3b** = 15/85 wt%; **3c** = 30/70 wt%) was added (1 mL·min^{-1}). After the addition of monomers had been completed, the mixture was stirred for another 60 min. Subsequently, the reaction mixture was cooled to room temperature, the excess pressure released, the liquid phase collected and the volatiles removed in a thin film evaporator. The polyethercarbonate was obtained as a clear liquid.

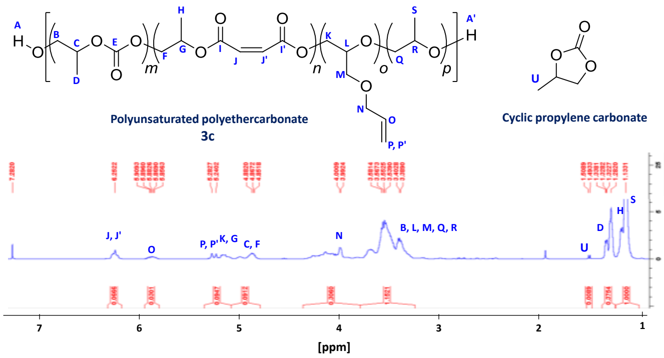

Figure S1. ^{1}H-NMR spectrum of the crude product mixture of polyunsaturated polyethercarbonate **3c** containing trace amounts of cyclic propylene carbonate and assignment of the signals; the spectrum is representative for the series of polyunsaturated polyethercarbonates

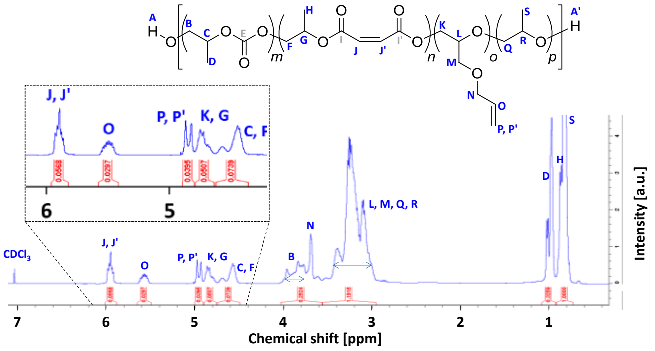

Figure S2. ^{1}H-NMR spectrum of polyunsaturated polyethercarbonate **3c** after the sample had been passed through a thin-film evaporator and assignment of the signals; the spectrum is representative for the series of polyunsaturated polyethercarbonates

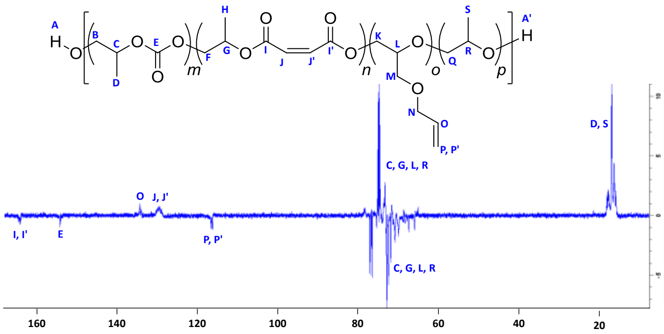

Figure S3. ^{13}C-{^{1}H} NMR spectrum polyunsaturated polyethercarbonate **3c** and assignment of the signals

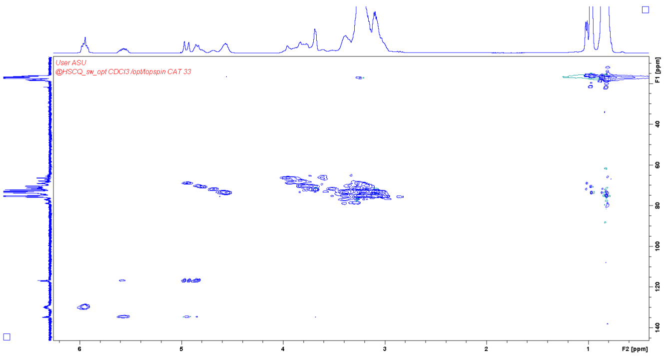

Figure S4. HSQC-NMR spectrum of polyunsaturated polyethercarbonate **3c**

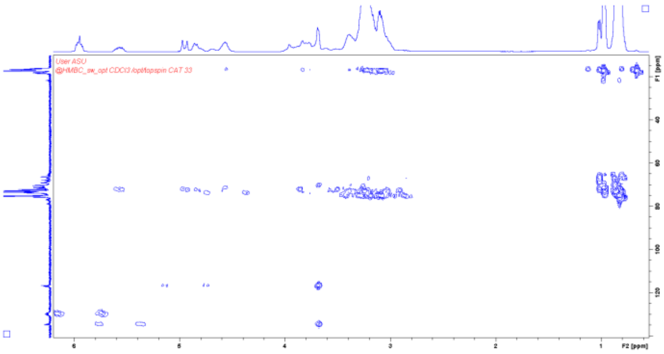

Figure S5. HMBC-NMR spectrum of polyunsaturated polyethercarbonate **3c**

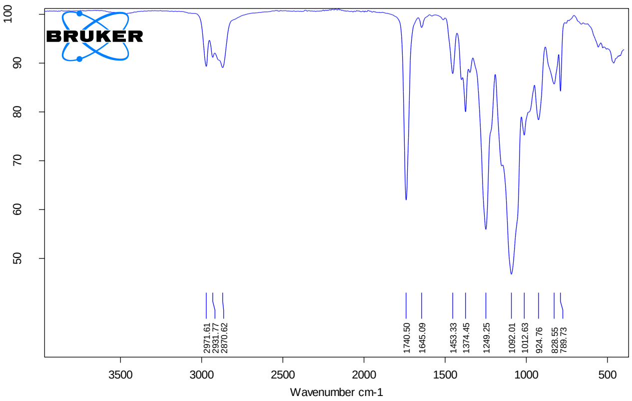

Figure S6. IR spectrum of polyunsaturated polyethercarbonate **3c**

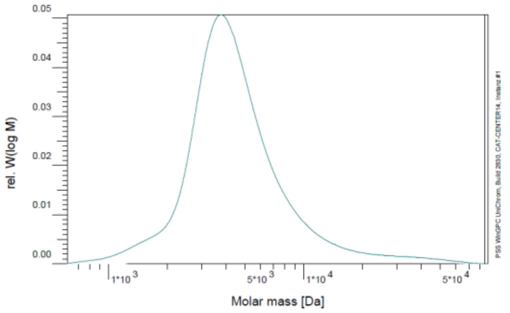

Figure S7. GPC trace of polyunsaturated polyethercarbonate **3c**

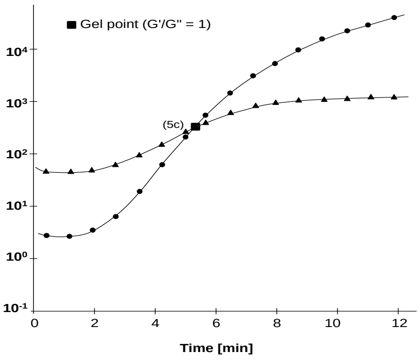

Figure S8. Viscoelastic behavior of polyunsaturated polyethercarbonate **3c** during irradiation with UV-light

Procedure for the multicomponent polymerization of CO_2, propylene oxide, maleic anhydride, and allylglycidylether (4): A high pressure reactor (300 mL, Parr Instrument) equipped with a gas entrainment stirrer was charged with DMC catalyst (16 mg) and α,ω-dihydroxy polypropylene oxide (1000 $g\cdot mol^{-1}$, f = 2, 20.0 g). The reactor was closed, the mixture stirred at 800 rpm, purged with argon and heated to 130°C. The reactor was then pressurized with carbon dioxide to 15 bar. Thereafter, the pressure was maintained at 15 bar by feeding CO_2. Simultaneously, 1 g (0.5 $mL\cdot min^{-1}$) of a mixture of maleic anhydride and propylene oxide (26/74 wt%) and 1 g (0.5 $mL\cdot min^{-1}$) of a mixture of allylglycidylether and propylene oxide (30/70 wt%) was added *via* an HPLC pump into the reactor in three pulses each, and the mixture was stirred for 20 minutes after each pulse. Then, the temperature was adjusted to 100°C. After the temperature and pressure had been stable for at least 5 minutes, 27 g (0.5 $mL\cdot min^{-1}$) of a mixture of maleic anhydride/propylene oxide (26/74 wt%) and 27 g (0.5 $mL\cdot min^{-1}$) of a mixture of allylglycidylether/propylene oxide (30/70 wt%) was added simultaneously *via* two HPLC pumps into the reactor. After the addition of monomers had been completed, the mixture was stirred for another 60 min. Subsequently, the reaction mixture was cooled to room temperature, the excess pressure released, the liquid phase collected and the volatiles removed in a thin film evaporator. The polyethercarbonate was obtained as a clear liquid.

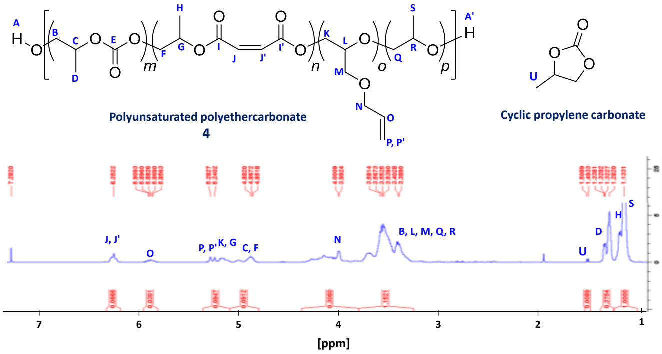

Figure S9. ^{1}H-NMR spectrum of the crude product mixture of polyunsaturated polyethercarbonate **4** containing trace amounts of cyclic propylene carbonate and assignment of the signals

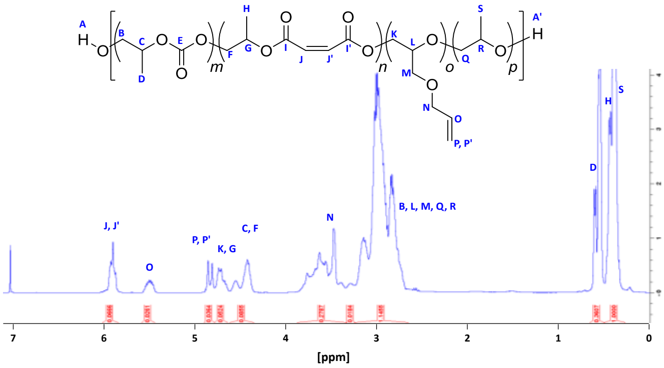

Figure S10. ^{1}H-NMR spectrum of polyunsaturated polyethercarbonate **4** and assignment of the signals

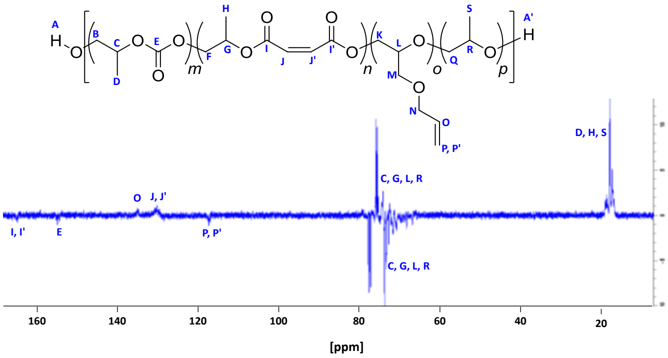

Figure S11. ^{13}C{^{1}H} NMR spectrum polyunsaturated polyethercarbonate **4** and assignment of the signals

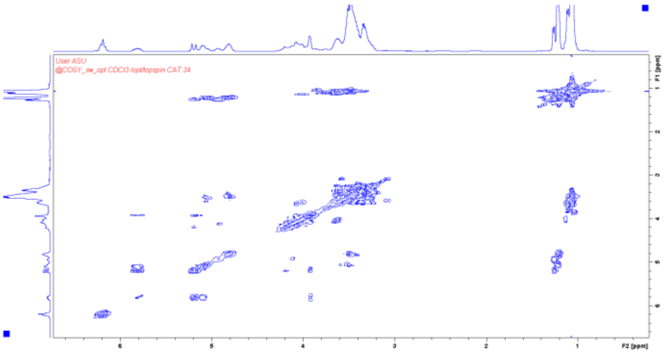

Figure S12. ^{1}H-^{1}H COSY NMR spectrum of polyunsaturated polyethercarbonate **4**

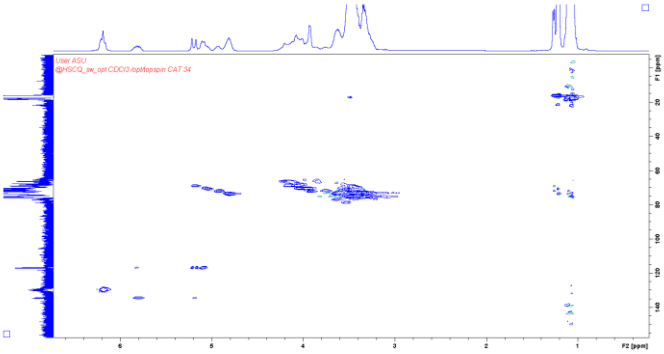

Figure S13. HSQC-NMR spectrum of polyunsaturated polyethercarbonate **4**

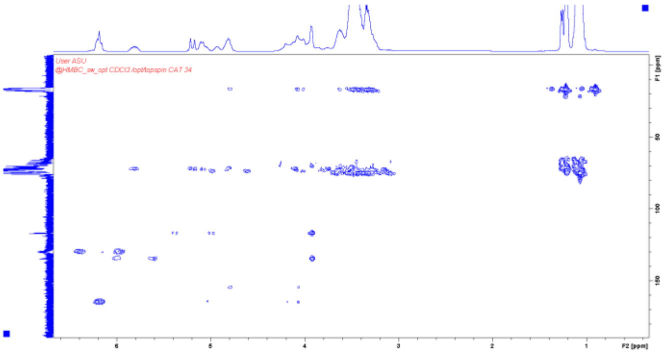

Figure S14. HMBC-NMR spectrum of polyunsaturated polyethercarbonate **4**

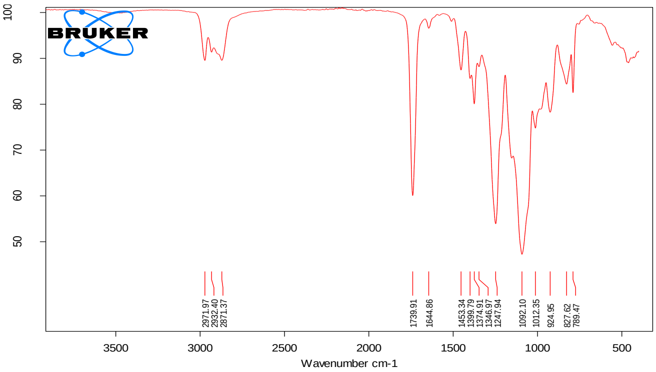

Figure S15. IR spectrum of polyunsaturated polyethercarbonate **4**

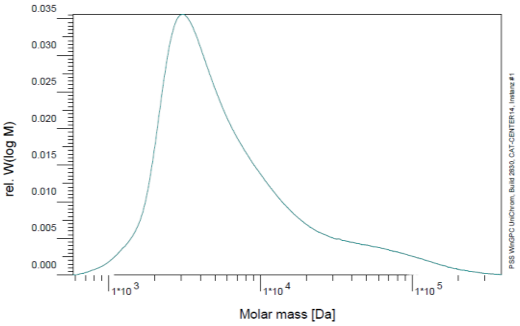

Figure S16. GPC trace of polyunsaturated polyethercarbonate **4**

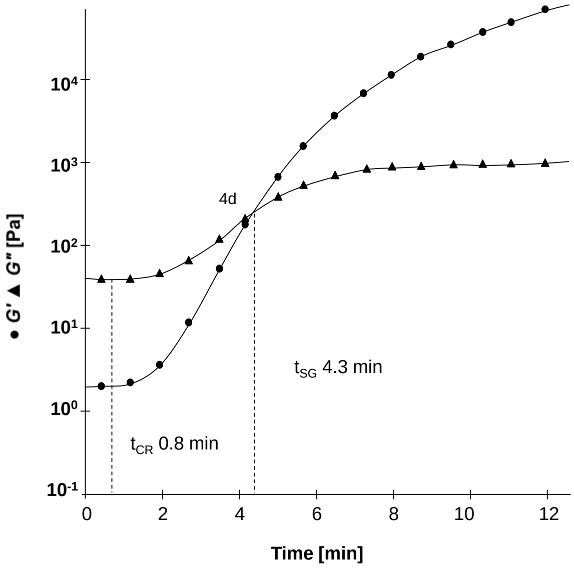

Figure S17. Viscoelastic behaviour of polyunsaturated polyethercarbonate **4** during irradiation with UV-light

Table S1. Microscopic and macroscopic properties of polyunsaturated polyethercarbonates

Entry	Sample	Archite-cture	Unsaturated moieties		η [Pa·s][b]	T_g [°C][c]	t_g [min][d]
			Maleate [mol%][a]	Allyl [mol%][a]			
1	**3a**	ABXBA	1.6	1.4	22.0	-43.1	9.3
2	**3b**	ABXBA	3.0	3.0	19.1	-45.2	6.6
3	**3c**	ABXBA	5.9	5.9	17.0	-47.4	5.3
4	**4**	AXA	6.0	5.8	21.1	-46.2	4.3

[a] Determined by ^{1}H-NMR spectroscopy; [b] Determined on rheometer using cone-plate measuring system at 25°C; [c] Determined on rheometer using plate-pate measuring system at 25°C; [d] Determined by differential scanning calorimetry.

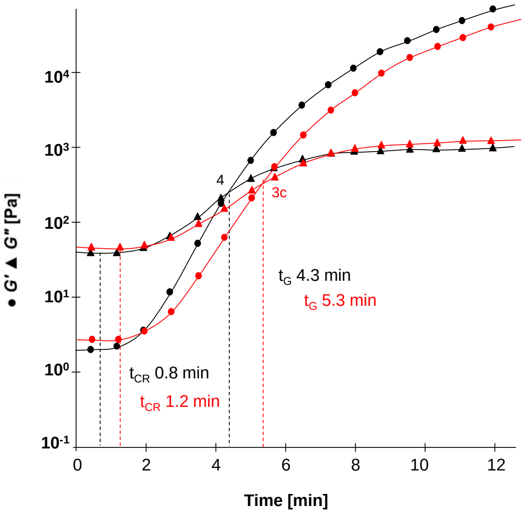

Figure S18. A comparison of the viscoelastic behaviour of polyunsaturated polyethercarbonates ***3c*** (red) and **4** (black) during irradiation with UV-light

Procedure for the stepwise multicomponent polymerization of CO$_2$, propylene oxide, maleic anhydride, and allylglycidylether (3c'): A high pressure reactor (300 mL, Parr Instrument) equipped with a gas entrainment stirrer was charged with DMC catalyst (16 mg) and α,ω-dihydroxy polypropylene oxide (1000 g·mol^{-1}, f = 2, 20.0 g). The reactor was closed, the mixture stirred at 800 rpm, purged with argon and heated to 100°C. The reactor was then pressurized with carbon dioxide to 15 bar. 1st portion of maleic anhydride/propylene oxide mixture (26/74 wt%, 15 g, 1 mL·min^{-1}) was added to the reaction mixture. After complete addition of 1st portion of maleic anhydride/propylene oxide mixture, the reaction mixture was stirred for 5 minutes and reaction sample was collected. Subsequently, 2nd portion of maleic anhydride/propylene oxide mixture (26/74 wt%, 15 g, 1 mL·min^{-1}) was added and reaction mixture was stirred for five minutes and a reaction sample was collected. Then, 1st and 2nd portion of allyl glycidyl ether/propylene oxide mixture (30/70 wt%, 15 g, 1 mL·min^{-1}) was added to the reaction mixture and a reaction sample was collected after each addition was complete. After the addition of monomers had been completed, the mixture was stirred for another 60 min. Subsequently, the reaction mixture was cooled to room temperature, the excess pressure released, the liquid phase collected and the volatiles removed in a thin film evaporator. The polyethercarbonate was obtained as a clear liquid.

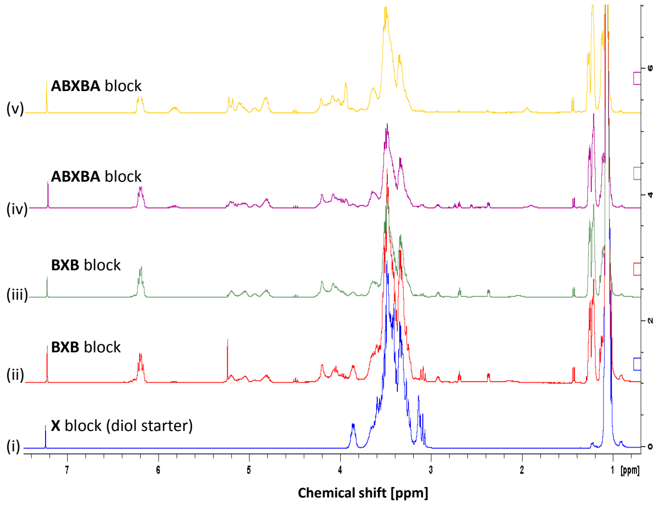

Figure S19. ^{1}H-NMR spectra of polyunsaturated polyethercarbonate **3c'** taken (i) *prior* to monomer addition; (ii) after addition of the 1st portion of PO/MA (26/74 wt%) mixture; (iii) after addition of the 2nd portion of PO/MA (26/74 wt%) mixture; (iv) after addition of the 1st portion of PO/AGE (30/70 wt%) mixture; (v) after addition of the 2nd portion of PO/AGE (30/70 wt%) mixture.

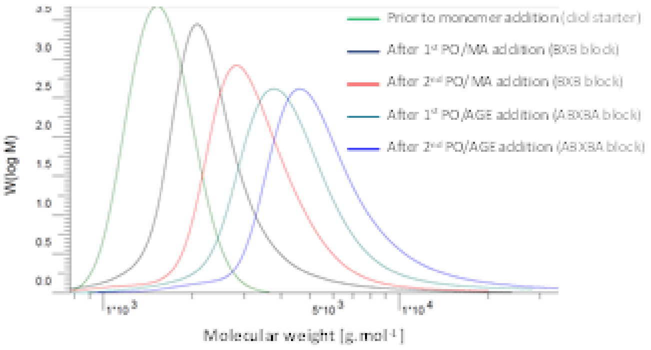

Figure S20. Respective GPC traces of polyunsaturated polyethercarbonate **3c'** taken after steps i to v.

Procedure for the stepwise multicomponent polymerization of CO$_2$, propylene oxide, maleic anhydride, and allylglycidylether (4'): A high pressure reactor (300 mL, Parr Instrument) equipped with a gas entrainment stirrer was charged with DMC catalyst (16 mg) and α,ω-dihydroxy polypropylene oxide (1000 g·mol^{-1}, f = 2, 20.0 g). The reactor was closed, the mixture stirred at 800 rpm, purged with argon and heated to 100°C. The reactor was then pressurized with carbon dioxide to 15 bar. 1st portion of maleic anhydride/propylene oxide mixture (26/74 wt%, 7.5 g, 1 mL·min^{-1}) and allyl glycidyl ether/propylene oxide mixture (30/70 wt%, 7.5 g, 1 mL·min^{-1}) was added simultaneously to the reaction mixture. Reaction mixture was stirred for five minutes and a reaction sample was collected after complete addition of 1st portion of maleic anhydride/propylene oxide and allyl glycidyl ether/propylene oxide mixture. Subsequently, 2nd, 3rd and 4th maleic anhydride/propylene oxide mixture (26/74 wt%, 7.5 g, 1 mL·min^{-1}) and allyl glycidyl ether/propylene oxide mixture (30/70 wt%, 7.5 g, 1 mL·min^{-1}) was added simultaneously to the reaction mixture. After each addition reaction mixture stirred for five minutes and a reaction sample was collected. After the addition of monomers had been completed, the mixture was stirred for another 60 min. Subsequently, the reaction mixture was cooled to room temperature, the excess pressure released, the liquid phase collected and the volatiles removed in a thin film evaporator. The polyethercarbonate was obtained as a clear liquid.

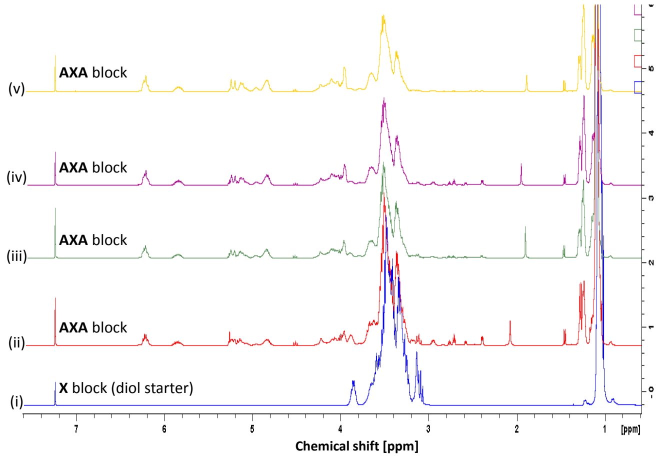

Figure S21. ^{1}H-NMR spectra of polyunsaturated polyethercarbonate **3c'** taken; (i) prior to monomer addition; (ii) after addition of 1st portion of PO/MA (26/74 wt%) and PO/AGE (30/70 wt%) mixture; (iii) after addition of 2nd portion of PO/MA (26/74 wt%) and PO/AGE (30/70 wt%) mixture; (iv) after addition of 3rd portion of PO/MA (26/74 wt%) and PO/AGE (30/70 wt%) mixture; (v) after addition of 4th portion of PO/MA (26/74 wt%) and PO/AGE (30/70 wt%) mixture

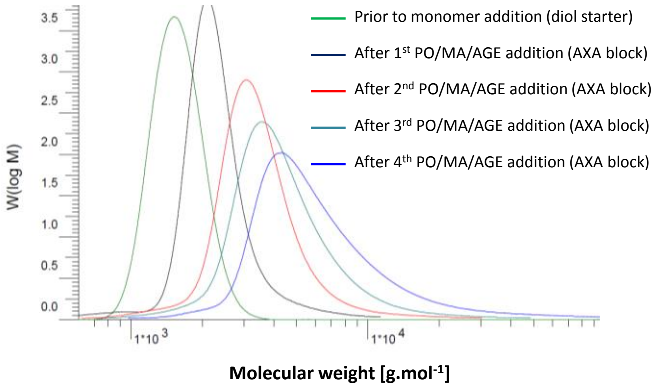

Figure S22. GPC traces of polyunsaturated polyethercarbonate **4'** taken after each addition of monomers mixture.