

Supporting Information

Ethylene-free Synthesis of Polyethylene Copolymers and Block Copolymers

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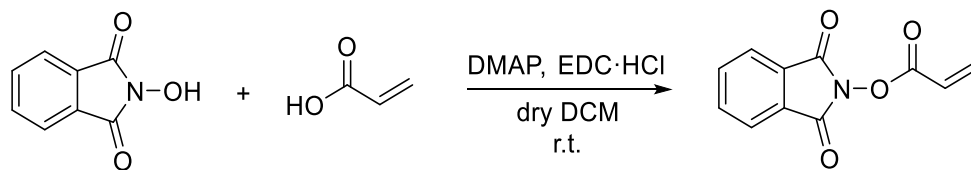
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Table of Contents

Monomer Synthesis	1
Free Radical Polymerization of <i>N</i> -(acryloyloxy)phthalimide	3
Copolymerization of <i>N</i> -(acryloyloxy)phthalimide and OEGMEA	6
RAFT Block Copolymerization with BPTT	8
Synthesis of <i>S</i> -benzyl <i>S'</i> -propyltrithiocarbonate (BPTT)	19
Decarboxylation procedure	21
Photochemically-induced decarboxylation method	21
Photochemically-induced decarboxylation of poly[<i>N</i> -(acryloyloxy)phthalimide] with phenylsilane.....	21
Photochemically-induced decarboxylation of poly[<i>N</i> -(acryloyloxy)phthalimide]- <i>block</i> -poly[oligo(ethylene glycol) methyl ether acrylate] with phenylsilane.....	22
Photochemically-induced decarboxylation of poly[<i>N</i> -(acryloyloxy)phthalimide]- <i>block</i> -poly[oligo(ethylene glycol) methyl ether acrylate] with tributyltin hydride.....	31
Photochemically-induced decarboxylation of poly[<i>N</i> -(acryloyloxy)phthalimide]- <i>block</i> -poly[2-methoxyethyl acrylate]	34
Thermally-induced decarboxylation method.....	36
Thermally-induced decarboxylation of poly[<i>N</i> -(acryloyloxy)phthalimide] with phenylsilane.....	36
Thermally-induced decarboxylation of poly[<i>N</i> -(acryloyloxy)phthalimide] with tributyltin hydride.....	37
Thermally-induced decarboxylation of poly[<i>N</i> -(acryloyloxy)phthalimide]- <i>co</i> -oligo(ethylene glycol) methyl ether acrylate] with phenylsilane	38
Thermally-induced decarboxylation of poly[<i>N</i> -(acryloyloxy)phthalimide]- <i>block</i> -poly[oligo(ethylene glycol) methyl ether acrylate] with phenylsilane.....	41
Thermally-induced decarboxylation of poly[<i>N</i> -(acryloyloxy)phthalimide]- <i>block</i> -poly[oligo(ethylene glycol) methyl ether acrylate] with tributyltin hydride.....	48
Thermally-induced decarboxylation of poly[<i>N</i> -(acryloyloxy)phthalimide]- <i>block</i> -poly(2-methoxyethyl acrylate).....	51

Monomer Synthesis



^1H NMR (400 MHz, $\text{DCM-}d_2$): δ /ppm = 8.24 - 7.27 (m, 4H, $\text{C}_{\text{aromatic}}\text{H}$), 6.73 (d, $J = 17.3$, 1.0 Hz, 1H, $\text{C}_{\text{vinyl}}\text{H}$), 6.40 (dd, $J = 17.3$, 10.7 Hz, 1H, $\text{C}_{\text{vinyl}}\text{H}$), 6.22 (d, $J = 10.7$, 1.0 Hz, 1H, $\text{C}_{\text{vinyl}}\text{H}$).

^{13}C NMR (400 MHz, $\text{DCM-}d_2$): δ /ppm = 161.16 ($\text{C}_{\text{vinyl}}\text{COO}$), 161.85 (NCO), 136.19 (C_{vinyl}), 134.90 ($\text{C}_{\text{aromat.}}$), 128.86 (C_{vinyl}), 123.89 ($\text{C}_{\text{aromat.}}$), 122.92 ($\text{C}_{\text{aromat.}}$).

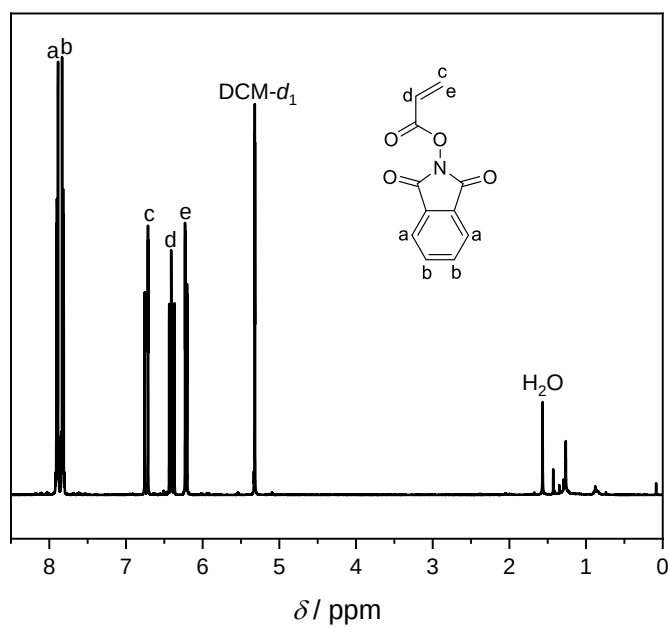


Figure S1: ^1H NMR spectrum of *N*-(acryloyloxy)phthalimide. Solvent: $\text{DCM-}d_2$.

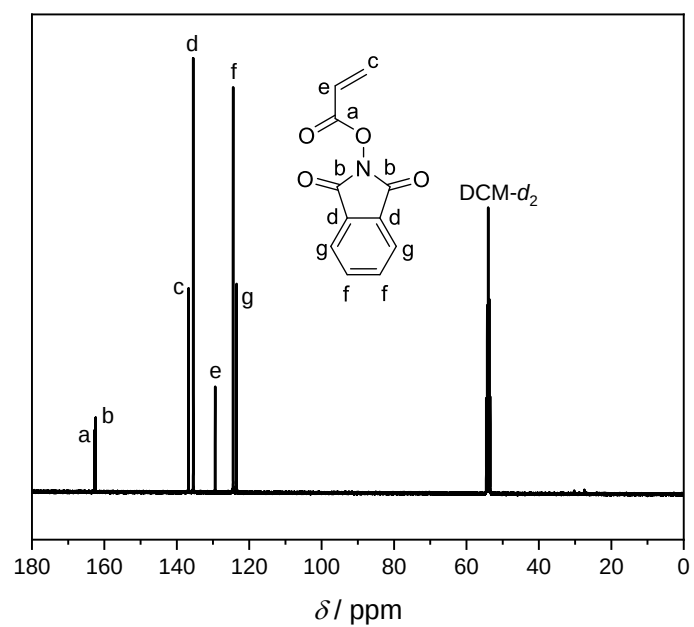
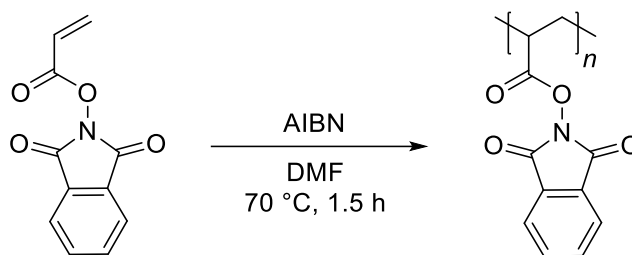


Figure S2: ^{13}C NMR spectrum of *N*-(acryloyloxy)phthalimide. Solvent DCM-d_2 .

Free Radical Polymerization of *N*-(acryloyloxy)phthalimide



^1H NMR (400 MHz, $\text{DCM-}d_2$): δ /ppm = 7.66 (m, 4H, $\text{C}_{\text{aromatic}}\text{H}$), 3.69 – 3.39 (m, 1H, $\text{C}_{\text{backbone}}\text{HCOON}$) 2.43 (s, 2H, $\text{C}_{\text{backbone}}\text{H}_2$).

Table S1

	M_n^* (g mol^{-1})	$\bar{D}^*$	DP^*	$M_n^\dagger$ (g mol^{-1})	$DP^\dagger$	$M_{n, \text{theo.}}$ (g mol^{-1})	$\text{conv.}^\#$ (%)
P1	8300	2.25	39	8250	38	27.130	30
P2	2500	1.22	11	1600	7	1600	> 90
P3	5600	1.56	26	6700	30	27.130	25
P4	28.300	1.75	2.17	-	-	57.400	-

*estimated by SEC with DMAc as eluent; † estimated by ^1H NMR spectroscopy; $^\#$ conversion estimated by ^1H NMR spectroscopy.

Table S2 **P1**

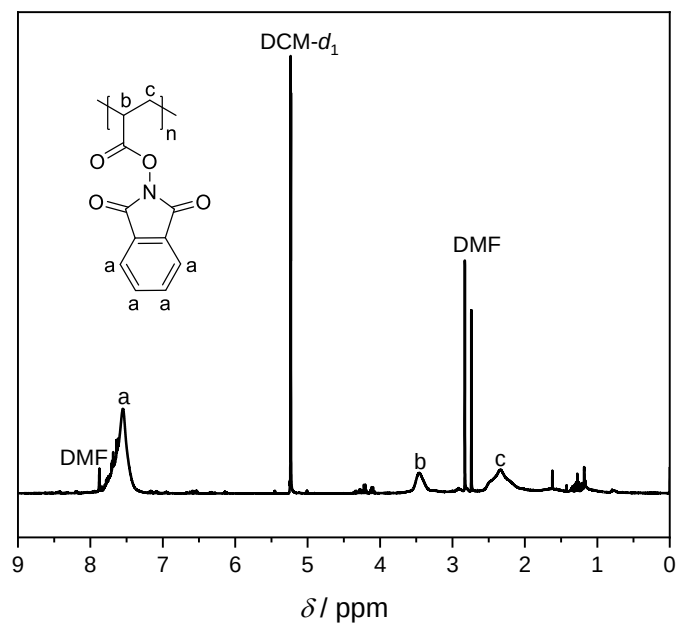
	mass [mg]	[mmol]	eq.
<i>N</i>-(acryloyloxy)phthalimide	400	1.84	125
AIBN	2.43	0.01	1.00
DMF	0.75 mL	/	/

Table S3 P2

	mass [mg]	[mmol]	eq.
<i>N</i> -(acryloxyloxy)phthalimide	260	1.20	7.00
AIBN	30.0	0.18	1.00
DMF	2.0 mL	/	/

Table S4 P3

	mass [mg]	[mmol]	eq.
<i>N</i> -(acryloxyloxy)phthalimide	500	2.3	125
AIBN	3.00	0.018	1.00
DMF	2.5 mL	/	/

Figure S3: ^1H NMR spectrum of PAP (P1). Solvent DCM-d_2 .

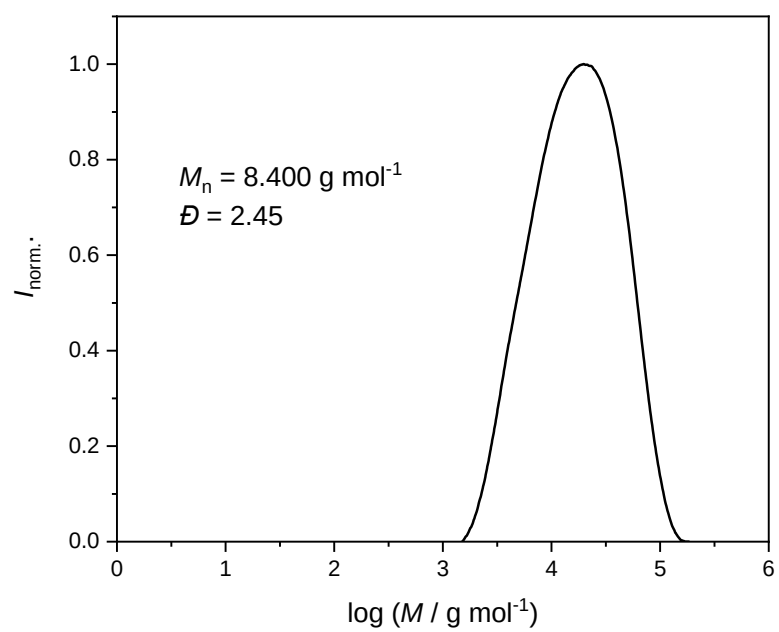
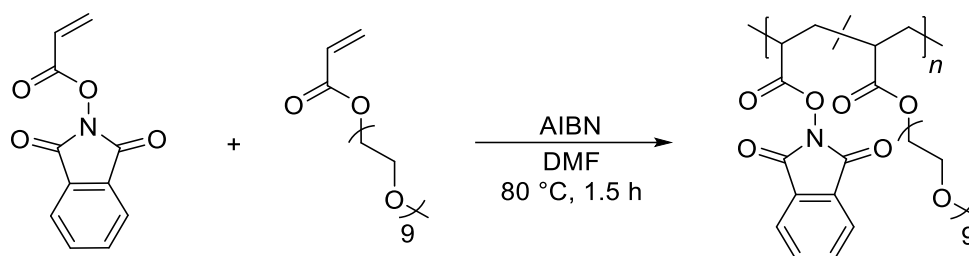


Figure S4: SEC trace of PAP (**P1**) with DMAc as eluent. $M_n = 8400 \text{ g mol}^{-1}$, $D = 2.45$.

Copolymerization of *N*-(acryloyloxy)phthalimide and OEGMEA



^1H NMR (400 MHz, CDCl_3): δ /ppm = 7.82 (m, 4H, $\text{C}_{\text{aromatic}}\text{H}$), 4.19 (m, 2H, COOCH_2), 3.79 - 3.46 (m, 32H, $(\text{OCH}_2\text{CH}_2\text{O})_8$), 3.36 (s, 3H, CH_2OCH_3), 2.64 - 1.15 (m, 3H, $\text{C}_{\text{backbone}}\text{H}$).

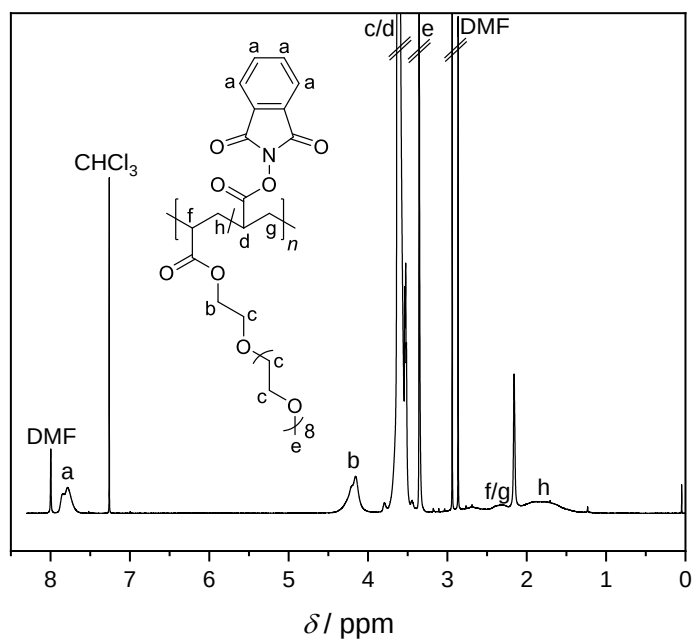


Figure S5: ^1H NMR spectrum of $\text{P}(\text{AP-co-OEGMEA})$ (**P4**). Solvent CDCl_3 .

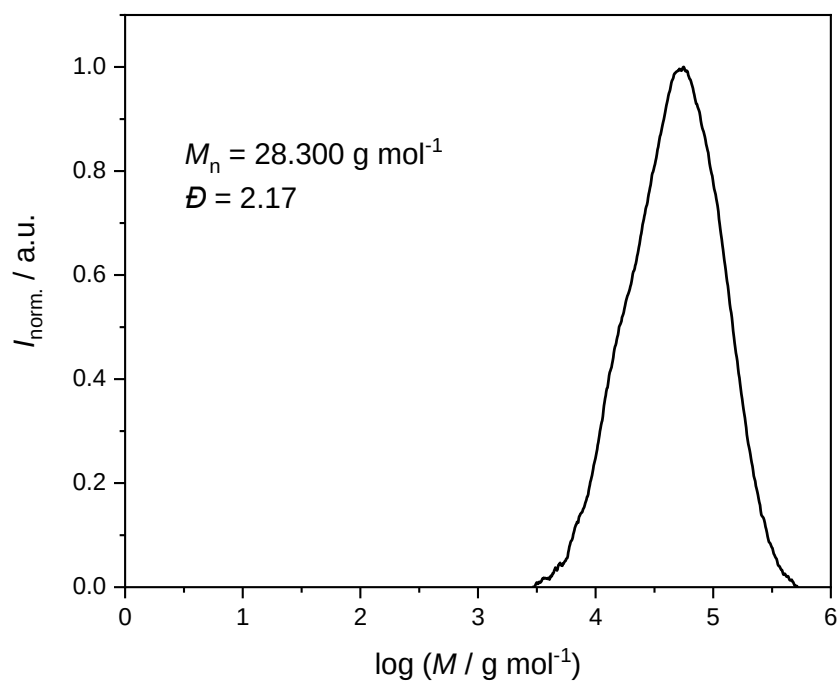


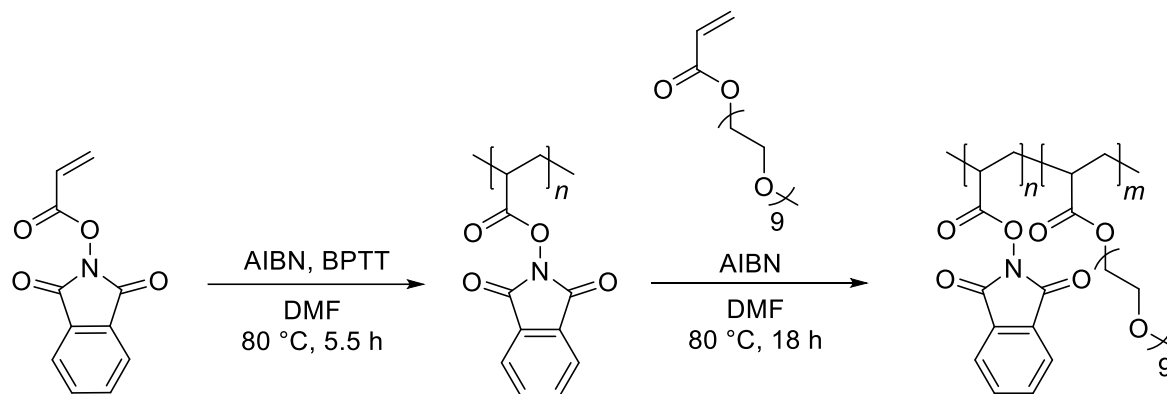
Figure S6: SEC trace of P(AP-co-OEGMEA) (**P4**) with DMAc as eluent. $M_n = 28.300 \text{ g mol}^{-1}$, $\text{Đ} = 2.17$.

Table S5 **P4**

	mass [mg]	[mmol]	eq.
N-(acryloxyloxy)phthalimide	150	0.69	12
OEGMEA	1000	2.08	38
AIBN	3.40	0.02	1.00
DMF	1.5 mL	/	/

RAFT Block Copolymerization with BPTT

Block copolymerization of *N*-(acryloyloxy)phthalimide and oligo(ethylene glycol) methyl ether acrylate



^1H NMR (400 MHz, $\text{DCM-}d_2$): δ / ppm = 8.13 (m, 4H, $\text{C}_{\text{aromatic}}\text{H}$), 4.44 (s, 2H, COOCH_2), 3.88 (m, 32H, $(\text{OCH}_2\text{CH}_2)_8$), 3.64 (s, 3H, CH_3), 2.97 – 2.42 (m, 1H, $\text{COOC}_{\text{backbone}}\text{H}$), 2.12 (m, 2H, $\text{C}_{\text{backbone}}\text{H}$).

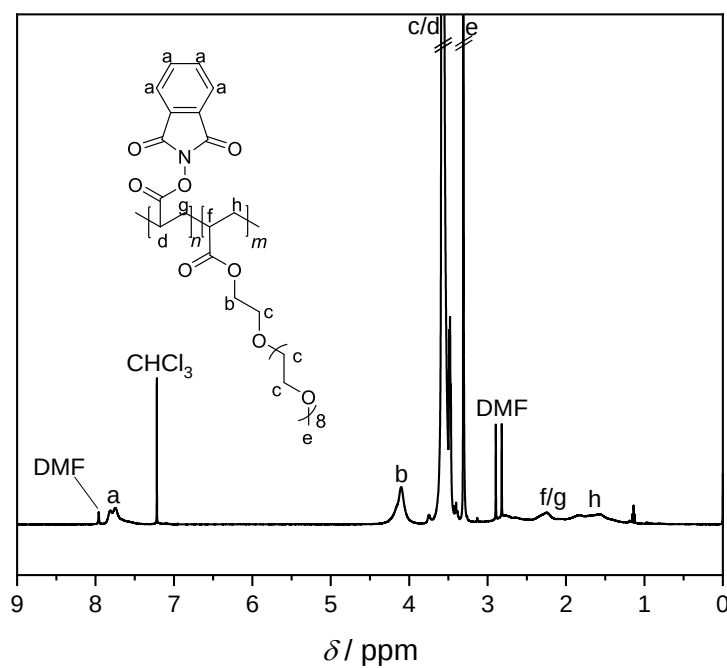


Figure S7 ^1H NMR spectrum of PAP-block-POEGMEA (**P5**). Solvent: CDCl_3 .

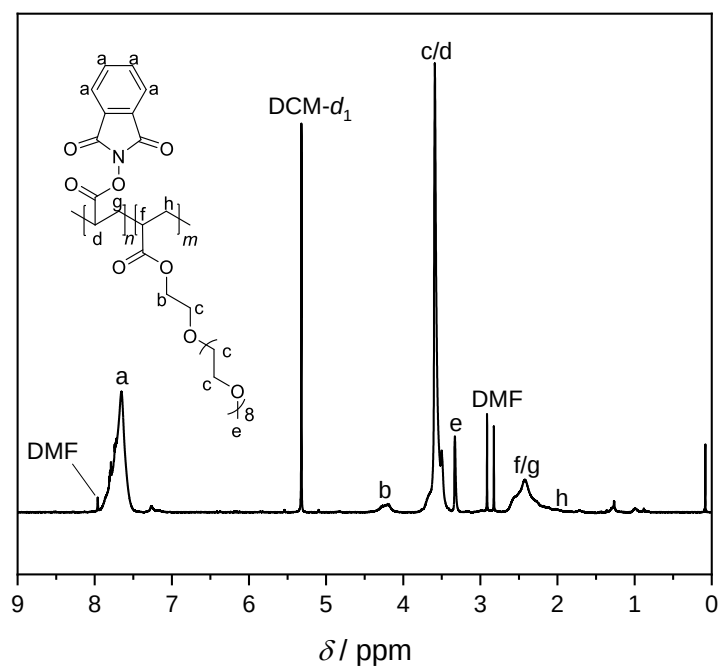


Figure S8 ^1H NMR spectrum of PAP-block-POEGMEA (**P6**). Solvent: $\text{DCM-}d_2$.

Table S6

	$M_{\text{n, phth.}}^*$ (g mol^{-1})	$M_{\text{n, phth.}}^\dagger$ (g mol^{-1})	$M_{\text{n, phth., theo.}}$ (g mol^{-1})	$M_{\text{n, block}}^*$ (g mol^{-1})	$M_{\text{n, block}}^\dagger$ (g mol^{-1})	$M_{\text{n, block, theo.}}$ (g mol^{-1})	$\text{conv.}^\#$ (%)	D^*_{block}
P5	3400	4220	4340	17.500	20.640	52.340	30	2.25
P6	5000	6180	6510	5400	7620	7950	60	1.62
P7	4000	6180	6510	5200	7620	7950	60	1.56
P10	3800	5210	6510	9500	10.000	28.340	20	1.75
P11	4700	3690	6510	8500	9450	28.340	24	1.64

*estimated by SEC with DMAc as eluent; † estimated by ^1H NMR spectroscopy; $^\#$ conversion of OEGMEA monomer, estimated by ^1H NMR spectroscopy.

Table S7 **P5**

	mass [mg]	[mmol]	eq.
<i>N</i>-(acryloxyloxy)phthalimide	200	0.92	20.0
AIBN	0.76	0.005	0.1
BPTT	11.2	0.05	1.0
OEGMEA	2212	4.61	100
DMF	2.0 mL	/	/

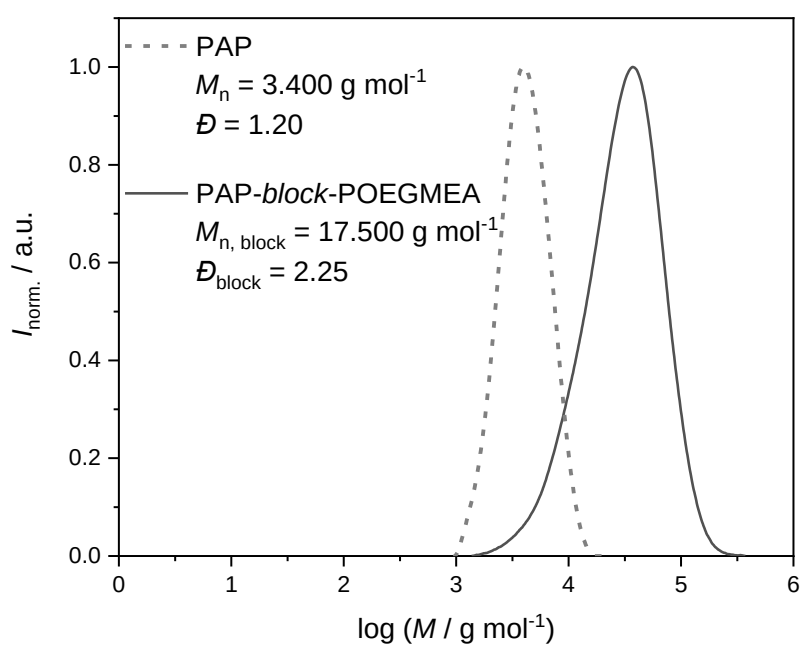
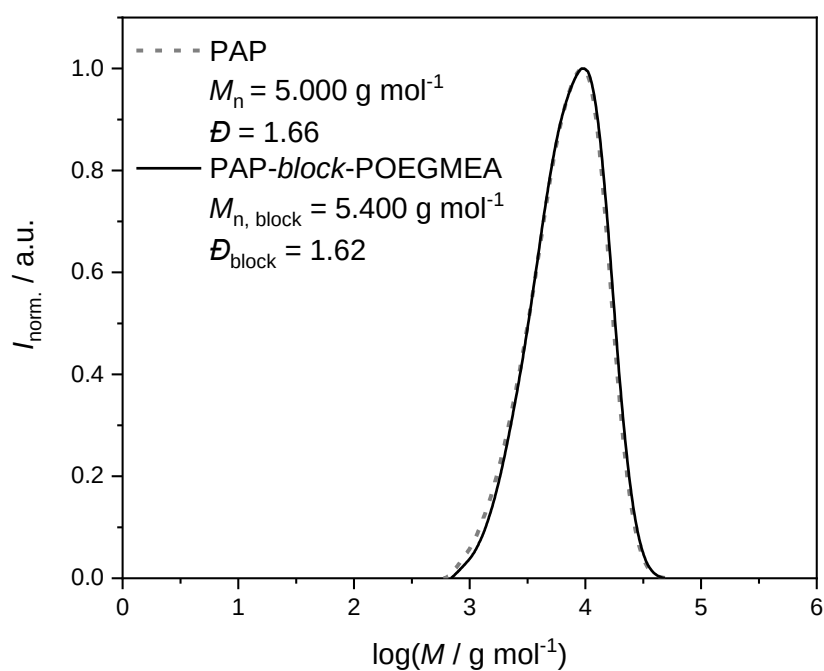


Figure S9: Comparison of the SEC traces of PAP and PAP-block-POEGMEA (**P5**) with DMAc as eluent.
 $M_{n, \text{phthalimide}} = 3400 \text{ g mol}^{-1}$, $\mathcal{D} = 1.20$; $M_{n, \text{block}} = 17.500 \text{ g mol}^{-1}$, $\mathcal{D} = 2.25$.

Table S8 P6/P7

	mass [mg]	[mmol]	eq.
<i>N</i>-(acryloxyloxy)phthalimide	750	3.46	30.0
AIBN	1.89	0.01	0.1
BPTT	27.9	0.12	1.0
OEGMEA	276	0.57	5.0
DMF	1.0 mL	/	/

Figure S10: Comparison of SEC traces of PAP and PAP-*block*-POEGMEA (**P6**) with DMAC as eluent.

$M_{n, \text{phthalimide}} = 5000 \text{ g mol}^{-1}$, $\bar{D} = 1.66$; $M_{n, \text{block}} = 5400 \text{ g mol}^{-1}$, $\bar{D} = 1.62$.

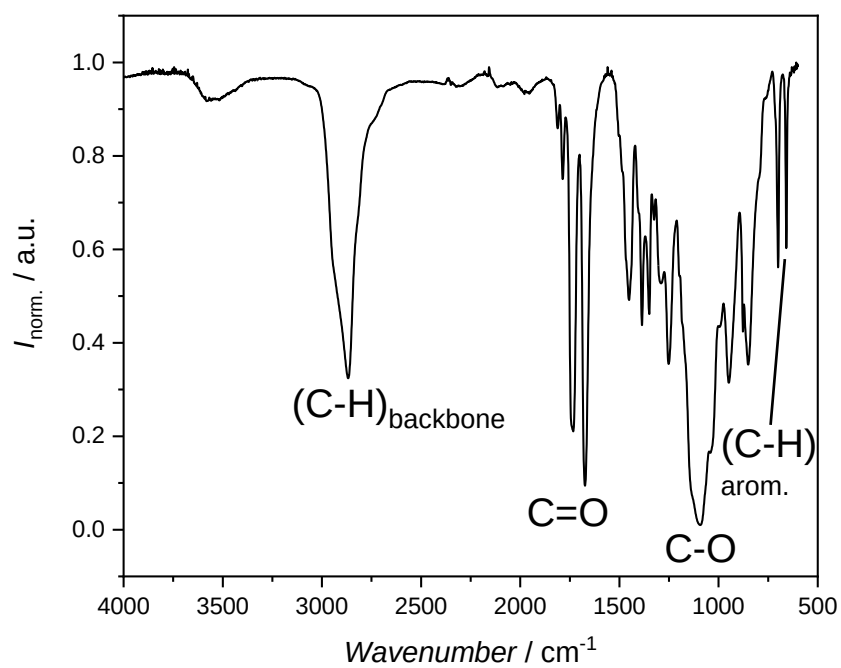


Figure S11: ATR-IR spectrum of PAP-block-POEGMEA (**P5**)

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2870$ (C-H of backbone), 1670-1737 (C=O of ester), 1085 (C-O of ether), 659-701 ($\text{C}_{\text{aromatic}}\text{-H}$).

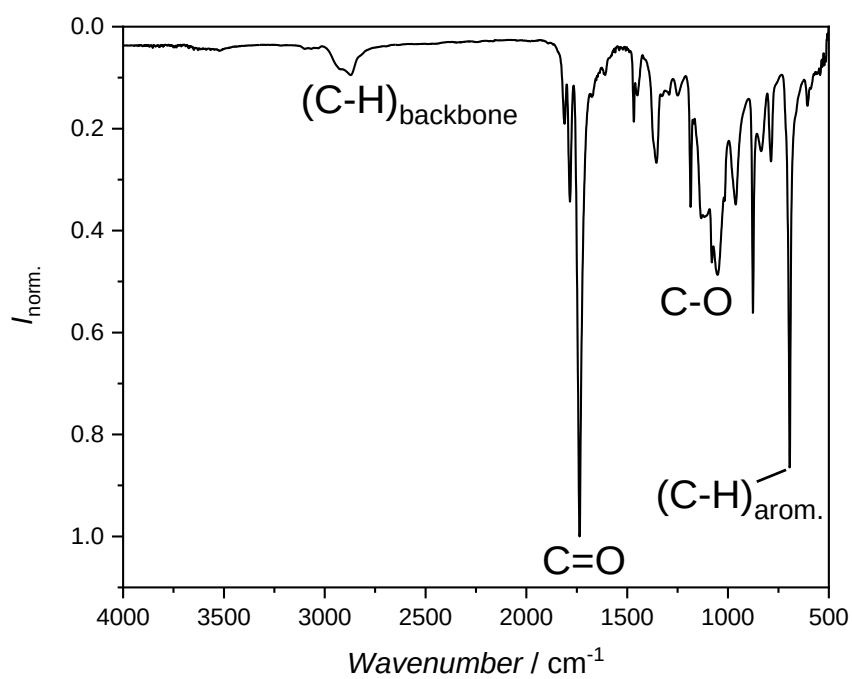


Figure S12: ATR-IR spectrum of PAP-block-POEGMEA (**P6**)

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2898$ (C-H of backbone), 1738-1782 (C=O of ester), 1048 (C-O of ether), 693 ($\text{C}_{\text{aromatic}}\text{-H}$).

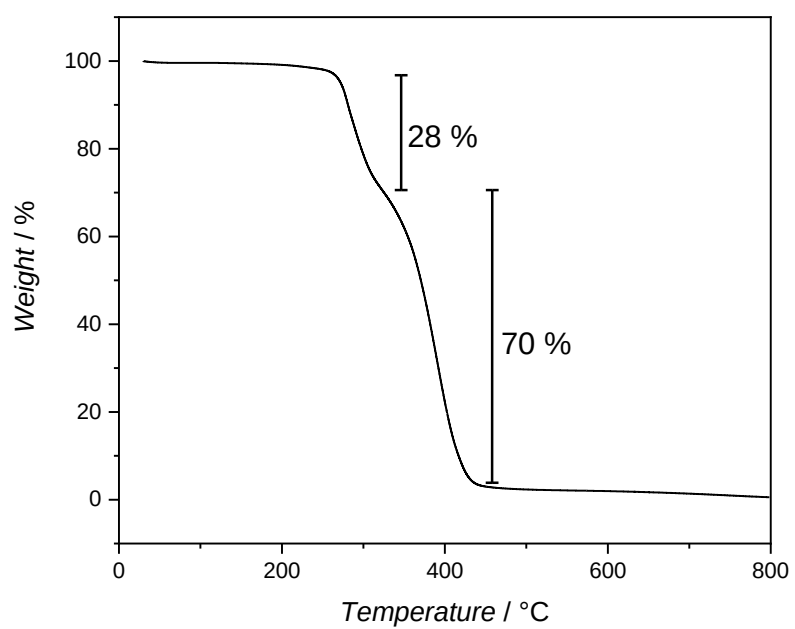


Figure S13: Thermogravimetric analysis of PAP-block-POEGMEA (**P5**).

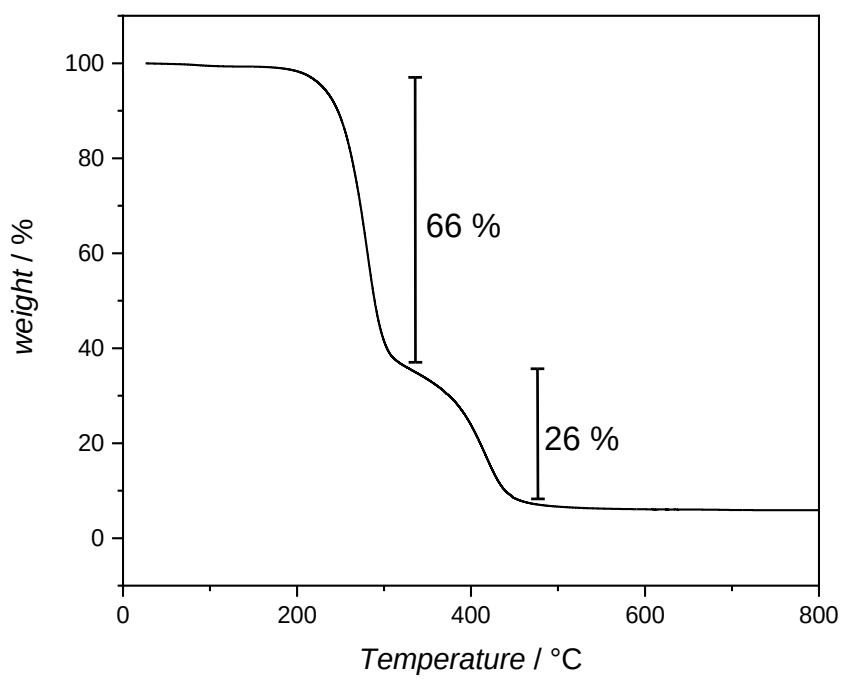


Figure: S14 Thermogravimetric analysis of PAP-block-POEGMEA (**P6**).

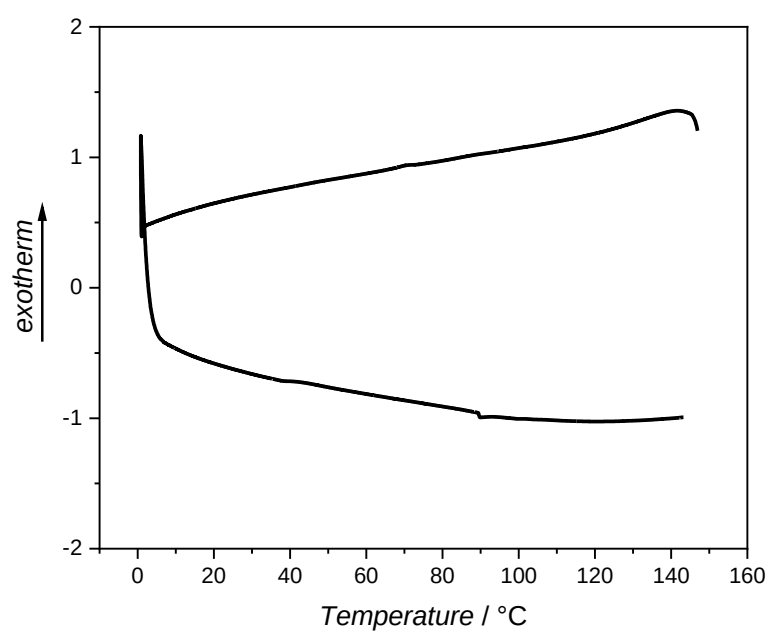
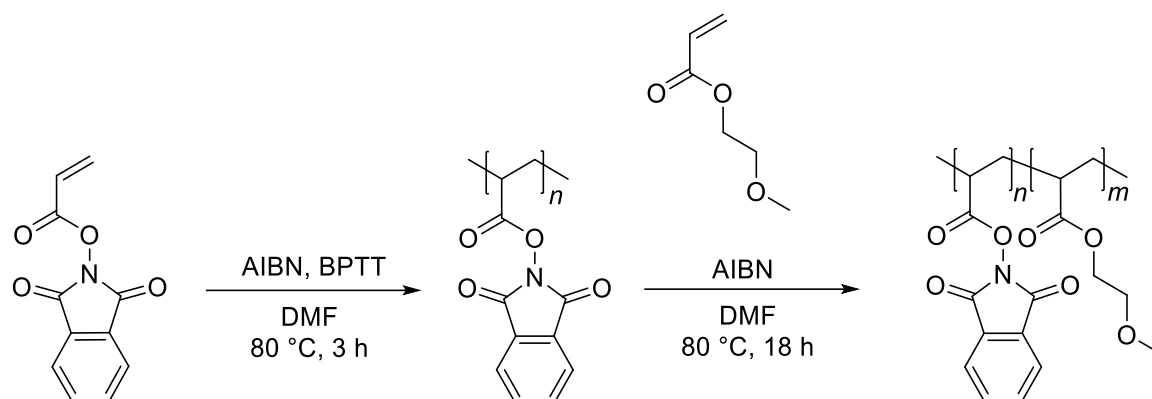


Figure S15: DSC characterization of PAP-block-POEGMEA, heating rate 10 K min^{-1} .

Block copolymerization of *N*-(acryloyloxy)phthalimide and 2-methoxyethyl acrylate



^1H NMR (400 MHz, DCM-d_2): δ /ppm = 7.71 (m, 4H, $\text{C}_{\text{aromatic}}\text{H}$), 4.18 (s, 2H, COOCH_2), 3.56 (s, 3H, $\text{COOCH}_2\text{CH}_2$, CHCOO), 3.34 (s, 3H, CH_3), 2.39 (s, 2H, $\text{C}_{\text{backbone}}\text{H}$), 1.80 (s, 2H, $\text{C}_{\text{backbone}}\text{H}$).

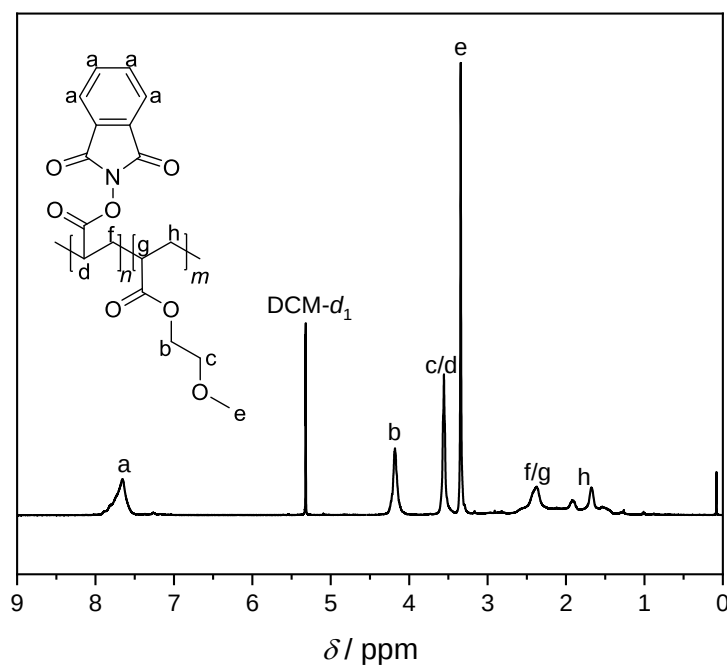


Figure S16: ^1H NMR spectrum of PAP-block-PMEA (**P9**). Solvent: DCM-d_2 .

Table S9

	$M_{n, \text{phth.}}^*$ (g mol ⁻¹)	$M_{n, \text{phth.}}^\dagger$ (g mol ⁻¹)	$M_{n, \text{phth.,}}^{\text{theo.}}$ (g mol ⁻¹)	$M_{n, \text{block}}^*$ (g mol ⁻¹)	$M_{n, \text{block}}^\dagger$ (g mol ⁻¹)	$M_{n, \text{block,}}^{\text{theo.}}$ (g mol ⁻¹)	$\text{conv.}^\#$ (%)	$\bar{D}^*_{\text{block}}$
P8	4600	4200	6510	8100	9660	13.000	68	1.57
P9	4900	4600	6510	7000	9020	13.000	84	1.80

*estimated by SEC with DMAc as eluent; [†]estimated by ¹H NMR spectroscopy; [#]conversion of MEA monomer, estimated by ¹H NMR spectroscopy.

Table S10 P8/P9

	mass [mg]	[mmol]	eq.
<i>N</i>-(acryloxyloxy)phthalimide	200	0.92	30.0
AIBN	0.50	0.003	0.1
BPTT	7.45	0.03	1.0
MEA	200	1.54	50.0
DMF	0.5 mL	/	/

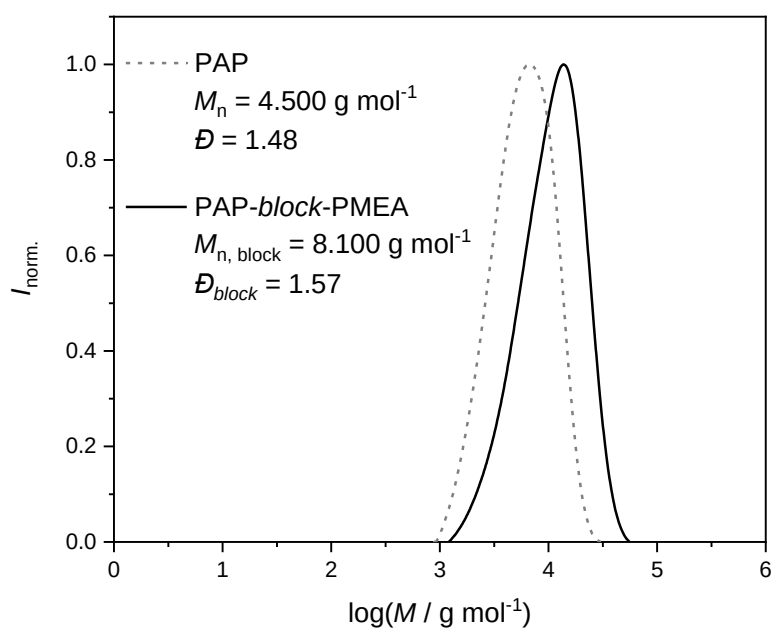


Figure S17: Comparison of SEC trace of PAP and PAP-block-PMEA (P8) with DMAc as eluent.
 $M_{n, \text{phthalimide}} = 4.500 \text{ g mol}^{-1}$, $\bar{D} = 1.48$; $M_{n, \text{block}} = 8.100 \text{ g mol}^{-1}$, $\bar{D} = 1.57$.

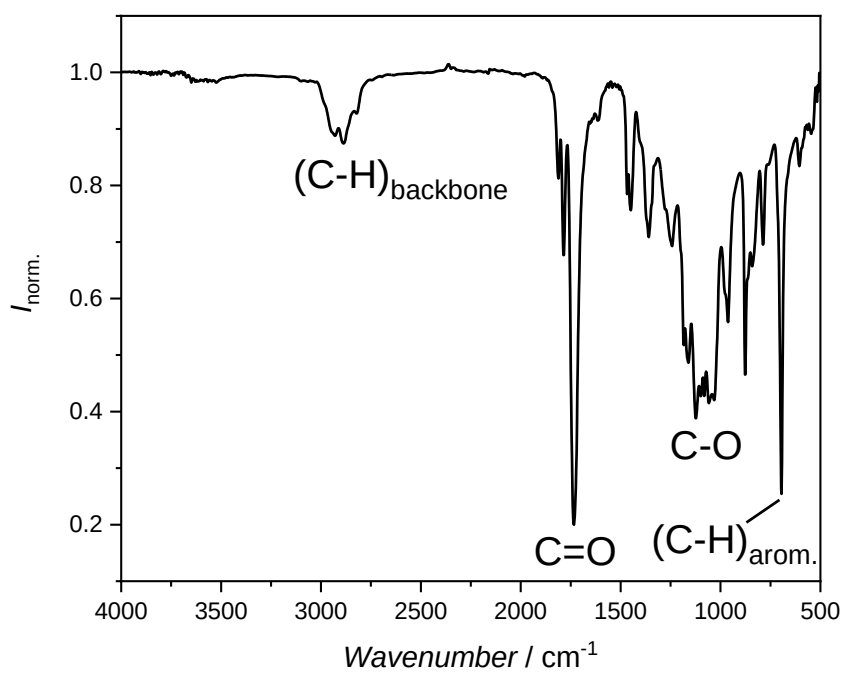
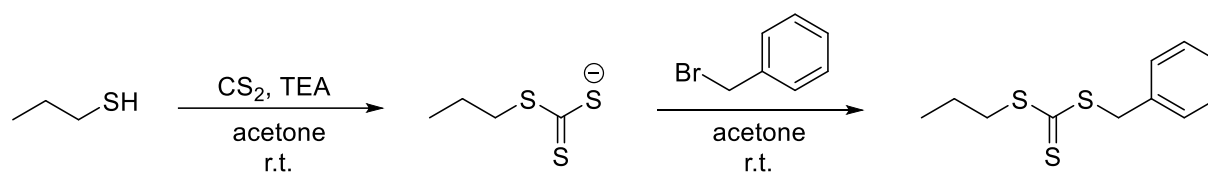


Figure S18: ATR-IR spectrum of PAP-block-PMEA (**P9**).

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2880$ (C-H of backbone), 1738-1809 (C=O of ester), 1096 (C-O of ether), 696 ($\text{C}_{\text{aromatic}}\text{H}$).

Synthesis of *S*-benzyl *S'*-propyltrithiocarbonate (BPTT)



In a 25 mL round bottom flask propanethiol (0.30 g, 3.94 mmol, 1.00 eq.) and triethylamine (0.40 g, 3.94 mmol, 1.00 eq.) were dissolved in 6 mL of acetone and carbon disulfide (0.75 g, 9.85 mmol, 2.5 eq.) was added dropwise while stirring. After 30 minutes, benzyl bromide (0.84 g, 4.95 mmol, 1.25 eq.) dissolved in 2 mL of acetone was added dropwise and the reaction was stirred for 2 hours. Subsequently, 20 mL of DCM were added and the reaction mixture was washed with water, HCl, and brine. The combined organic phases were dried with MgSO₄ and concentrated using a rotatory evaporator.

¹H NMR (400 MHz, DCM-*d*₂): δ /ppm = 7.42 - 7.23 (m, 5H, C_{aromatic}H), 4.63 (s, 2H, SCH₂C_{aromatic}), 3.45 – 3.32 (m, 2H, CH₃CH₂CH₂S) 1.75 (m, 2H, CH₃CH₂CH₂S), 1.02 (t, *J* = 7.4 Hz, 3H, CH₃CH₂CH₂S).

¹³C NMR (400 MHz, DCM-*d*₂): δ /ppm = 135.91, 131.91 – 126.79 (m), 41.79, 39.46, 22.14, 13.78.

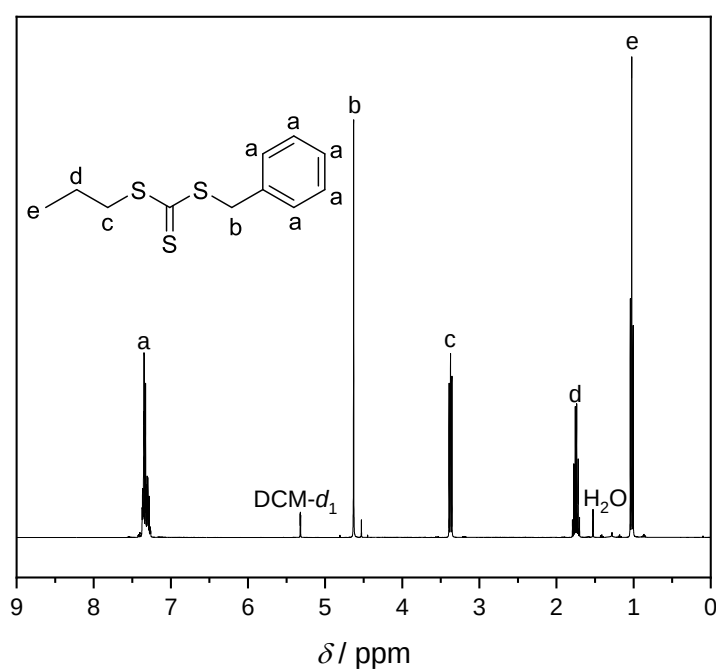


Figure S19: ¹H NMR spectrum of *S*-benzyl *S'*-propyltrithiocarbonate. Solvent: DCM-*d*₂.

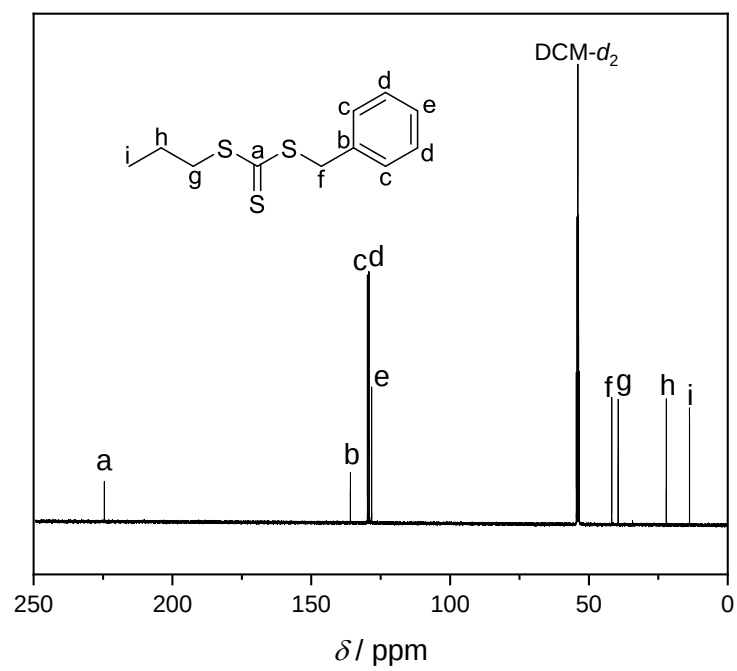
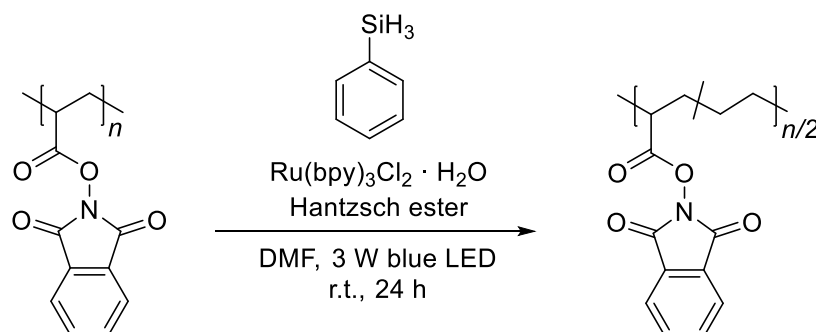


Figure S20: ^{13}C NMR spectrum of S-benzyl S'-propyltrithiocarbonate. Solvent: DCM- d_2 .

Decarboxylation procedure

Photochemically-induced decarboxylation method

Photochemically-induced decarboxylation of poly[N-(acryloyloxy)phthalimide] with phenylsilane



^1H NMR (400 MHz, DMSO-d_6): δ / ppm = 7.73 – 7.38 (m, 4H, $\text{C}_{\text{aromatic}}\text{H}$), 3.69 - 3.03 (m, 1H, CHCOON), 2.82 – 2.21 (s, 2H, $\text{C}_{\text{backbone}}\text{H}$), 1.99 - 0.38 (m, 2H, $\text{C}_{\text{backbone}}\text{H}_2$).

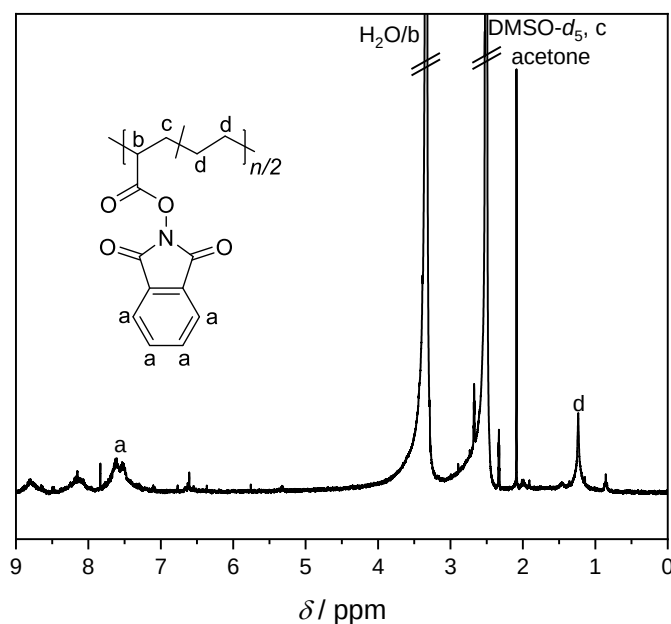
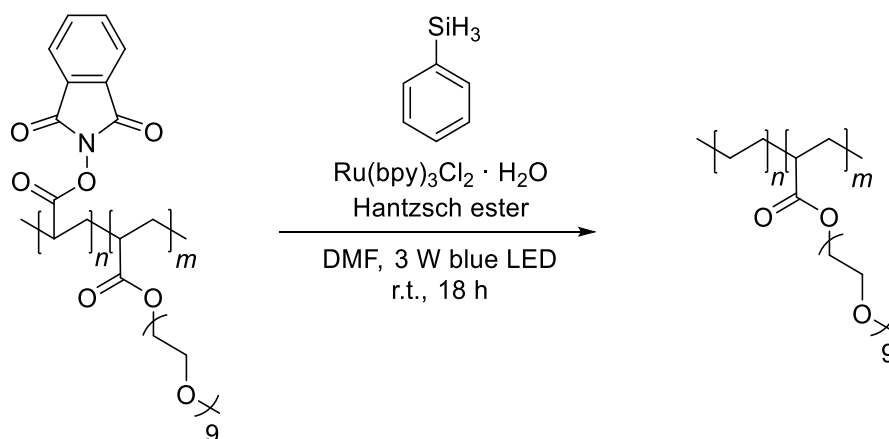


Figure S21: ^1H NMR spectrum of poly[N-(acryloyloxy)phthalimide] (**P1**) after photochemically-induced decarboxylation. Solvent DMSO-d_6 .

Photochemically-induced decarboxylation of poly[*N*-(acryloyloxy)phthalimide]-*block*-poly[oligo(ethylene glycol) methyl ether acrylate] with phenylsilane



^1H NMR (400 MHz, DCM-d_2): δ /ppm = 4.18 (s, 2H, $\text{COOCH}_2\text{CH}_2\text{O}$), 3.73 – 3.54 (m, 34H, $\text{CH}_2(\text{CH}_2\text{CH}_2\text{O})_{8-9}$), 3.33 (s, 3H, $\text{CH}_2\text{CH}_2\text{OCH}_3$), 1.58 (s, 3H, $\text{C}_{\text{backbone, OEGMEA}}\text{H}$), 1.26 (s, 98H, CH_2 , PE).

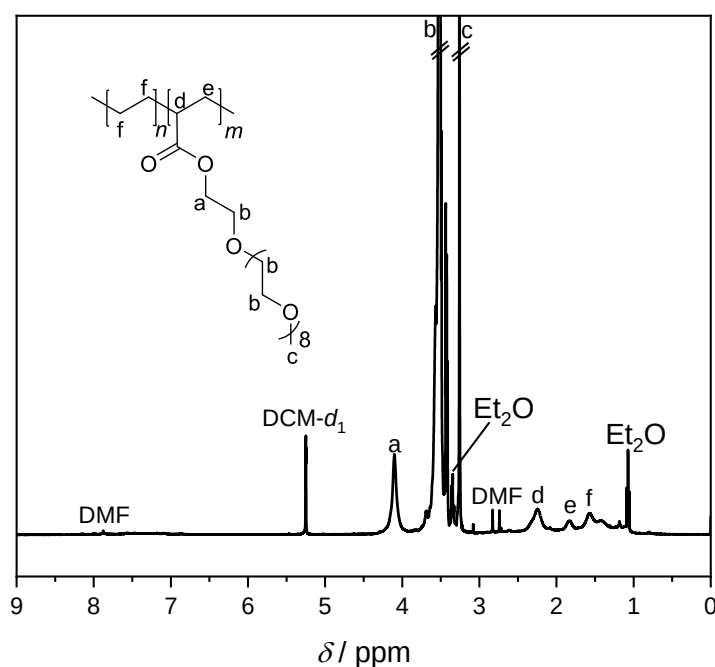


Figure S22: ^1H NMR spectrum of PAP-*block*-POEGMEA (**P5**) after photochemically-induced decarboxylation. Solvent: DCM-d_2 .

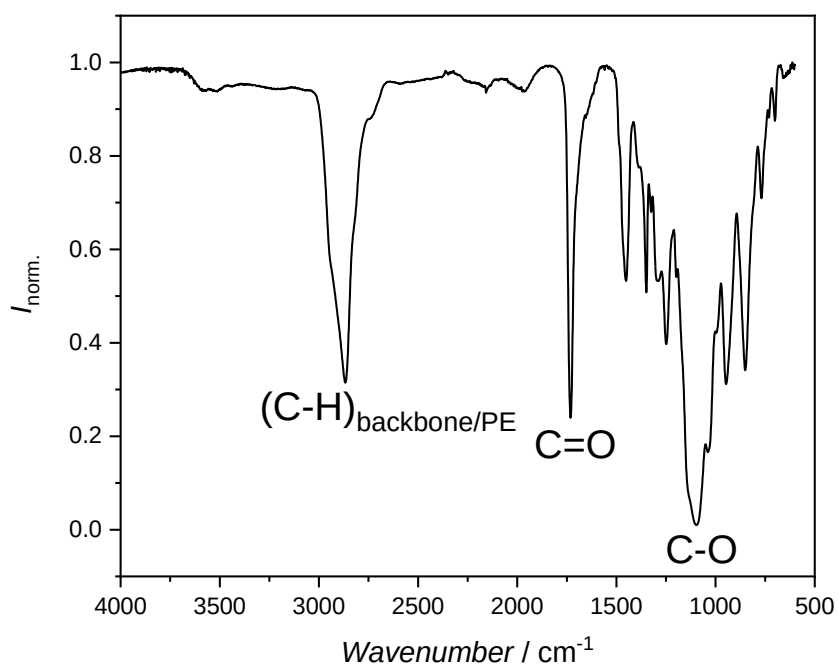


Figure S23: ATR-IR spectrum of PAP-block-POEGMEA (**P5**) after photochemically-induced decarboxylation.

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2865$ (C-H of backbone), 1731 (C=O of ester), 1100 (C-O of ether).

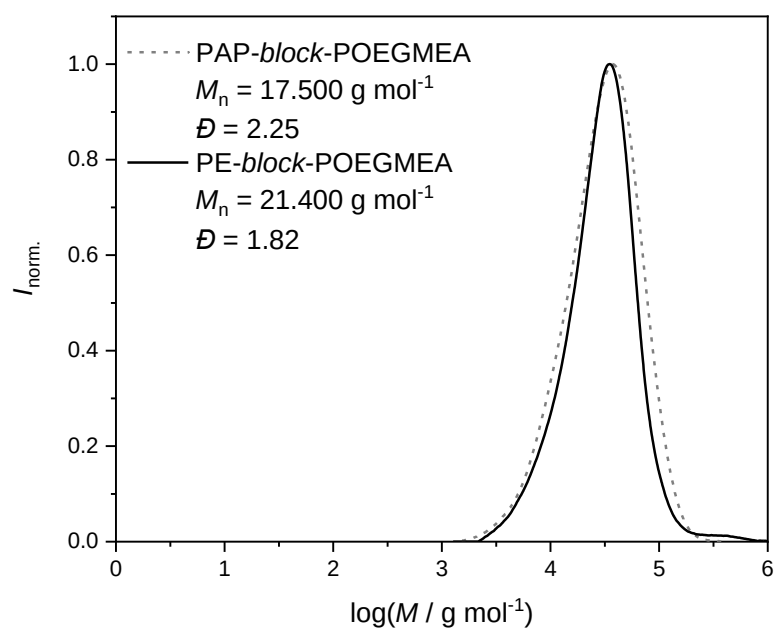


Figure S24: Comparison of SEC traces of PAP-*block*-POEGMEA (**P5**) with DMAc as eluent before and after photochemically-induced decarboxylation. $M_n, \text{PAP-}i\text{block-POEGMEA} = 17.500 \text{ g mol}^{-1}$, $\text{Đ} = 2.25$;
 $M_n, \text{PE-}i\text{block-POEGMEA} = 21.400 \text{ g mol}^{-1}$, $\text{Đ} = 1.82$.

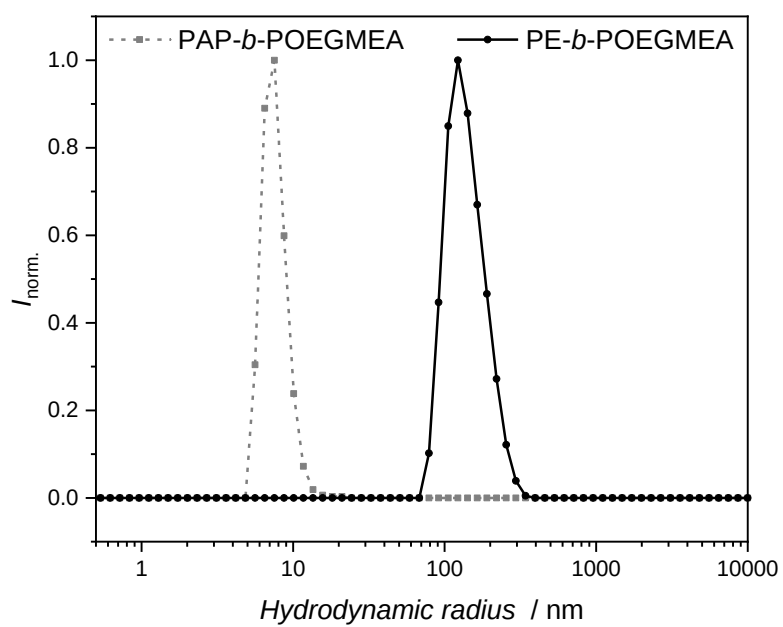


Figure S25: DLS characterization of PAP-*block*-POEGMEA (**P5**) before (grey) and after (black) photochemically-induced decarboxylation.

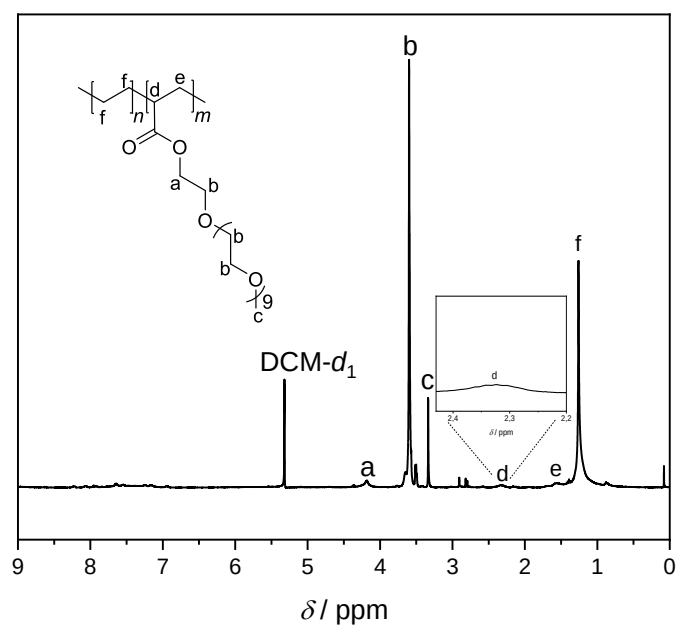


Figure S26: ^1H NMR spectrum of PAP-block-POEGMEA (P6) after photochemically-induced decarboxylation. Solvent: DCM-d_2 .

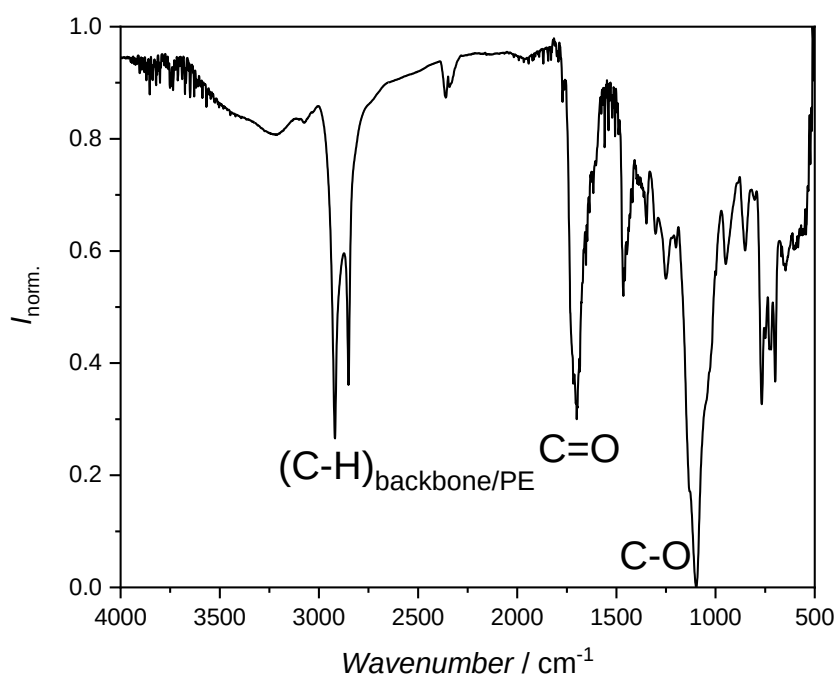


Figure S27: ATR-IR spectrum of PAP-block-POEGMEA (**P6**) after photochemically-induced decarboxylation.

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2924 - 2853$ (C-H of backbone), 1707 (C=O of ester), 1105 (C-O of ether).

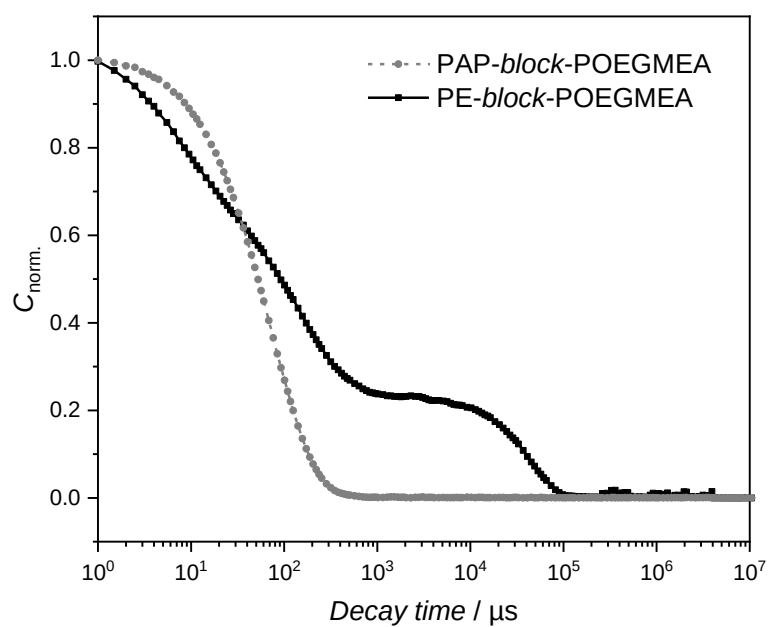


Figure S28: DLS autocorrelation data of PAP-*block*-POEGMEA (**P6**) before and after decarboxylation.

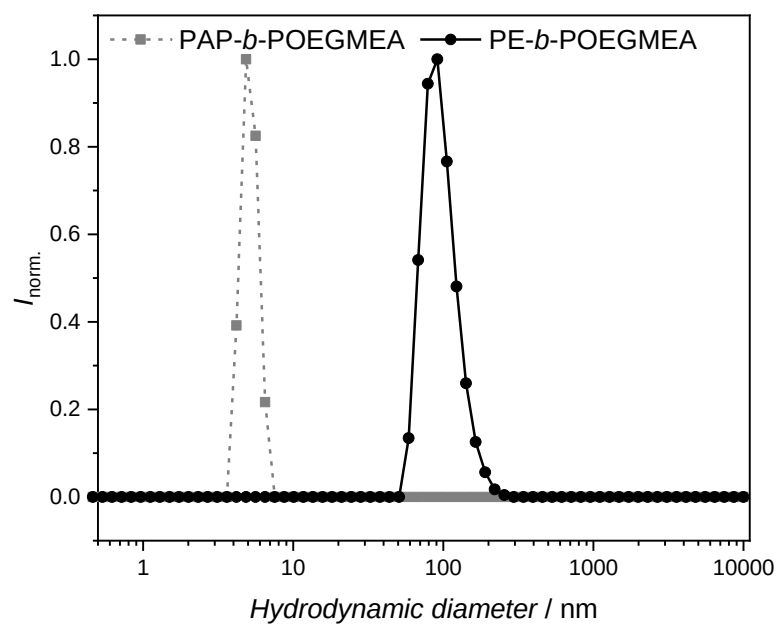


Figure S29: DLS measurement of PAP-*block*-POEGMEA (**P6**) before (grey) and after (black) photochemically-induced decarboxylation.

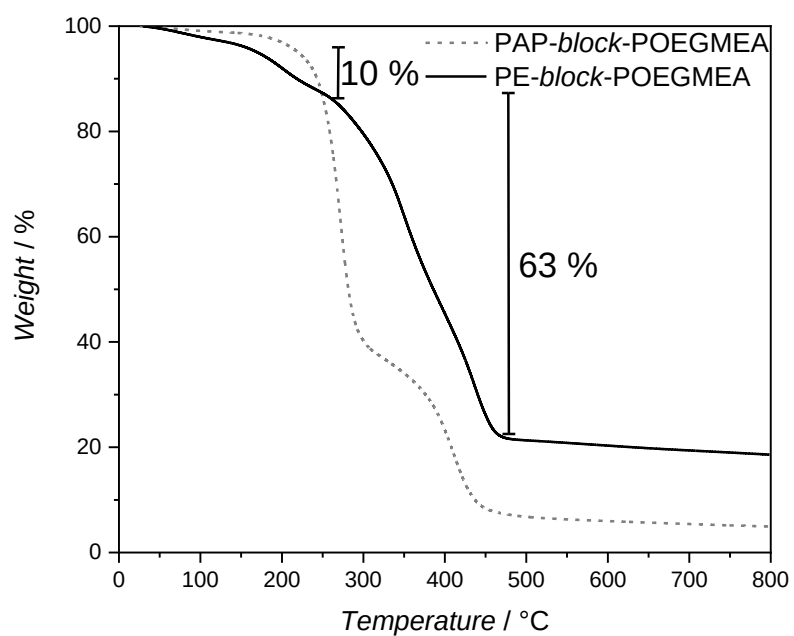


Figure S30: Thermogravimetric analysis of PAP-block-POEGMEA (**P6**) before (black) and after (grey) photochemically-induced decarboxylation.

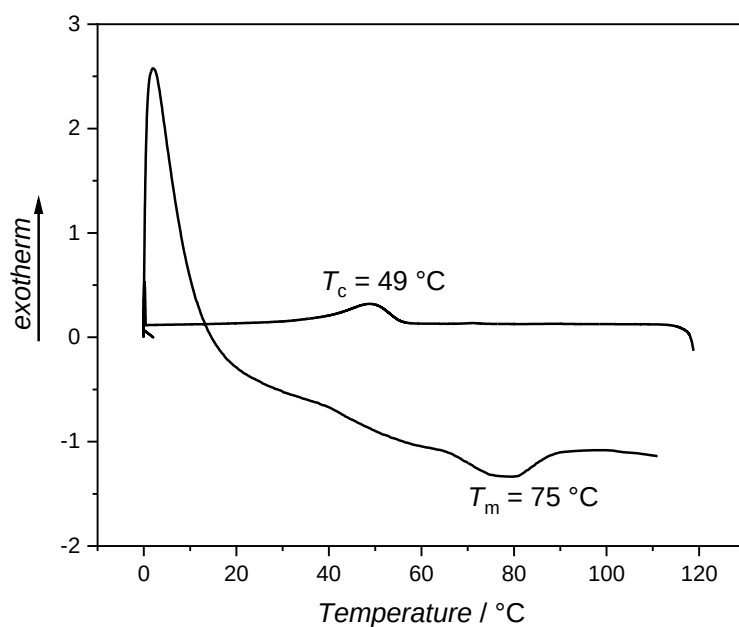


Figure S31: DSC characterization of PAP-block-POEGMEA (**P6**) after photochemically-induced decarboxylation. $T_m = 75\text{ }^{\circ}\text{C}$, $T_c = 49\text{ }^{\circ}\text{C}$. Heating/cooling rate: $10\text{ }^{\circ}\text{C min}^{-1}$.

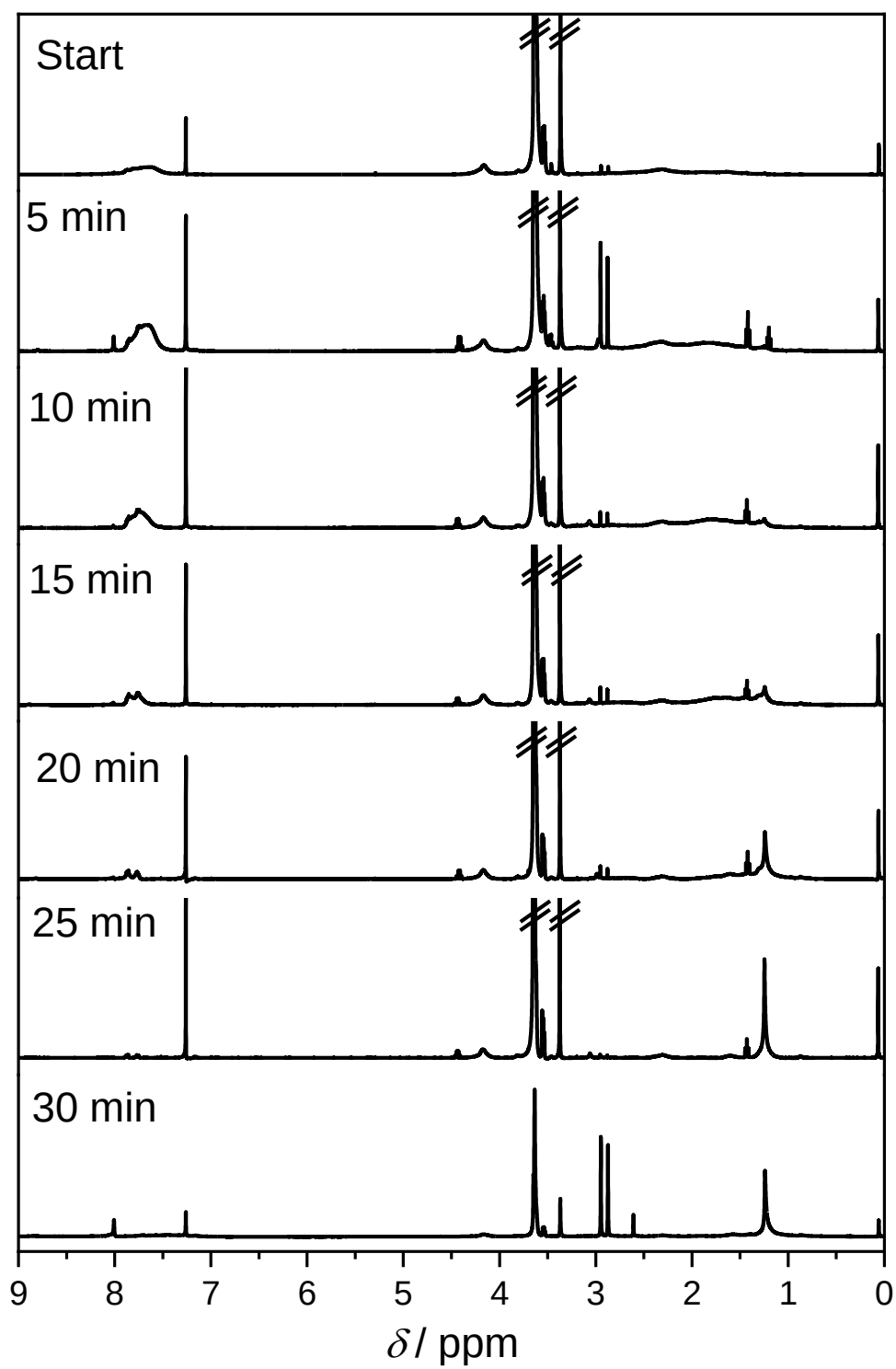
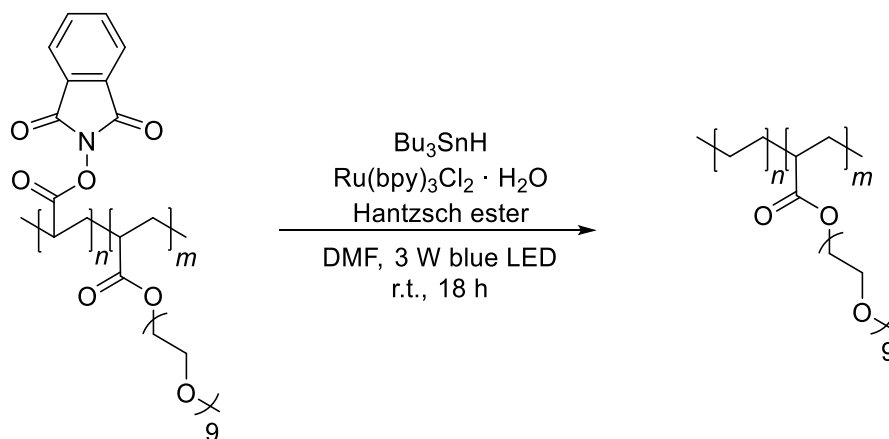


Figure S32: Reaction monitoring of photochemically-induced decarboxylation of PAP-b-POEGMEA (**P10**). Solvent: CDCl_3 .

Photochemically-induced decarboxylation of poly[*N*-(acryloyloxy)phthalimide]-*block*-poly[oligo(ethylene glycol) methyl ether acrylate] with tributyltin hydride



^1H NMR (400 MHz, DCM-d_2): δ/ppm = 4.18 (s, 2H, COOCH_2), 3.86 – 3.42 (m, 32H, $(\text{OCH}_2\text{CH}_2)_8$), 3.34 (s, 3H, CH_3), 2.33 (s, 1H, $\text{C}_{\text{backbone}}\text{H}$), 1.71 (s, 2H, $\text{C}_{\text{backbone}}\text{H}_2$), 1.26 (s, 2H, CH_2 , PE).

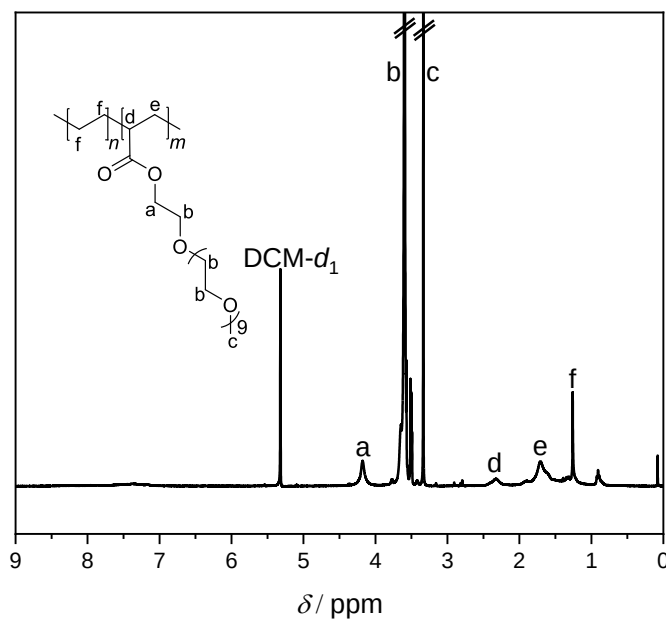


Figure 33: ^1H NMR spectrum of PAP-block-POEGMEA (**P10**) after photochemically-induced decarboxylation with tributyltin hydride as H-donor. Solvent: DCM-d_2 .

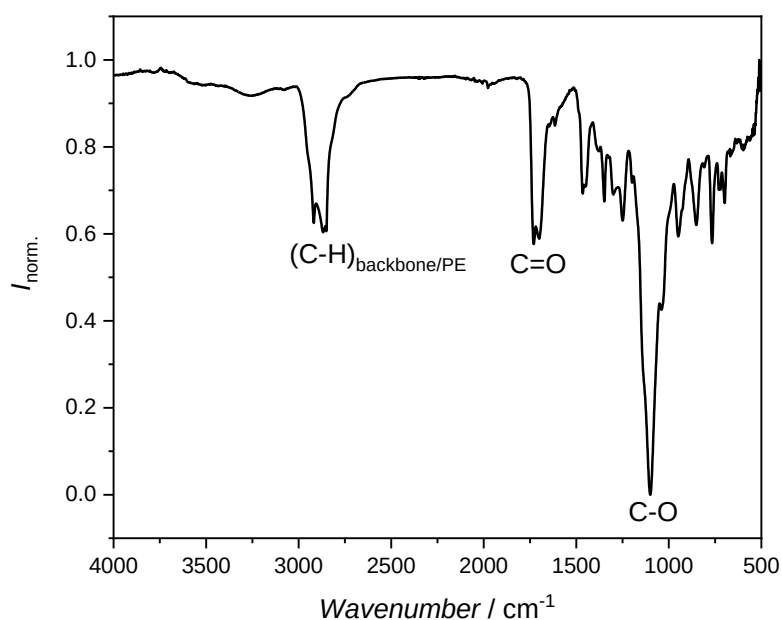


Figure 34: ATR-IR spectrum of PAP-block-POEGMEA (**P10**) after photochemically-induced decarboxylation with tributyltin hydride as H-donor.

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2917 - 2866$ (C-H of backbone), 1728 (C=O of ester), 1102 (C-O of ether).

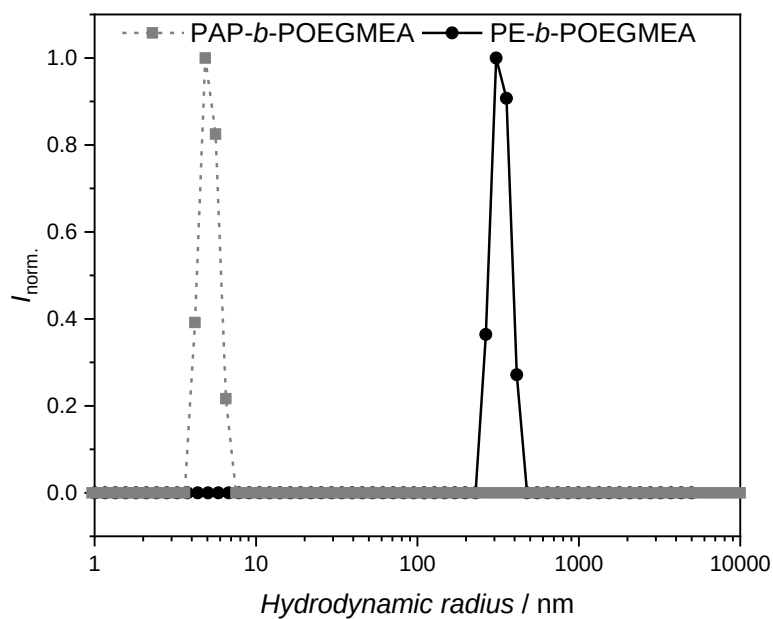


Figure 35: DLS measurement of PAP-block-POEGMEA (**P10**) before (grey) and after (black) photochemically-induced decarboxylation.

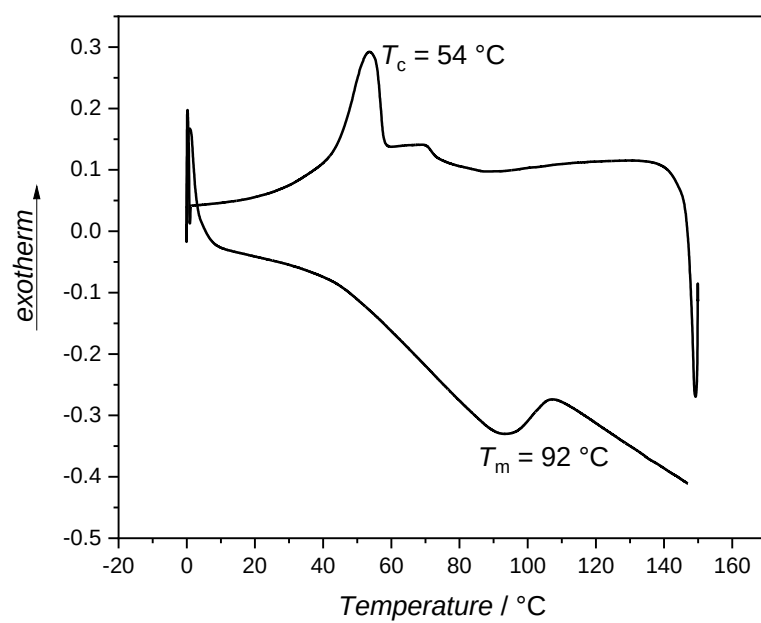
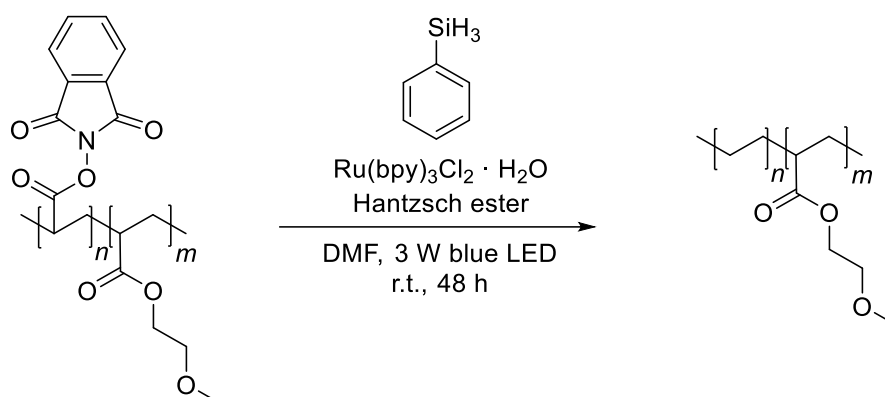


Figure 36: DSC characterization of PAP-block-POGEMEA (**P10**) after photochemically-induced decarboxylation with tributyltin hydride as H-donor. $T_m = 92\text{ °C}$, $T_c = 54\text{ °C}$. Heating/cooling rate: 10 °C min^{-1} .

PE-*block*-PMEA

Photochemically-induced decarboxylation of poly[*N*-(acryloyloxy)phthalimide]-*block*-poly[2-methoxyethyl acrylate]



Results:

^1H NMR (400 MHz, DCM-d_2): δ/ppm = 4.18 (m, 2H, $\text{COOCH}_2\text{CH}_2\text{O}$), 3.34 (m, 2H, $\text{COOCH}_2\text{CH}_2\text{O}$), 3.34 (s, 3H, OCH_3), 2.65 – 1.42 (m, 3H, $\text{C}_{\text{backbone}}\text{H}$), 1.24 (m, 2H, CH_2PE).

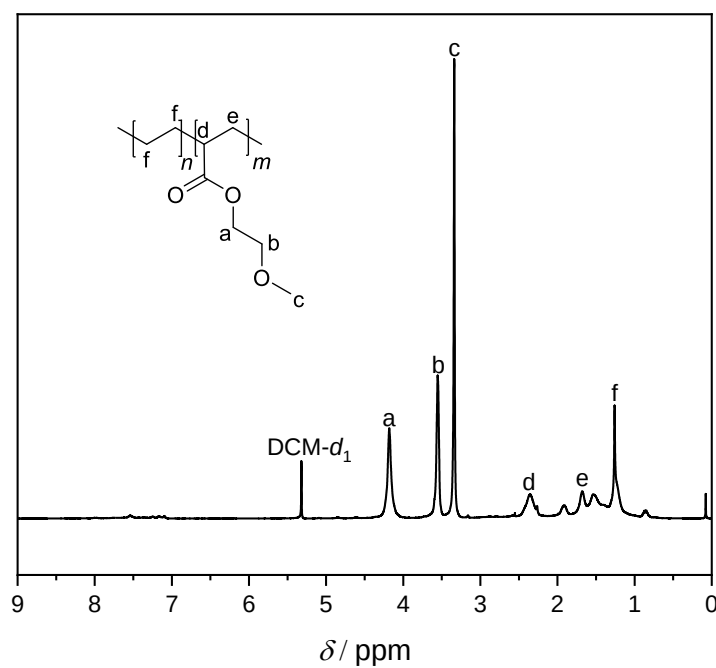


Figure S37: ^1H NMR spectrum of PAP-*block*-PMEA (**P8**) after photochemically-induced decarboxylation. Solvent: DCM-d_2 .

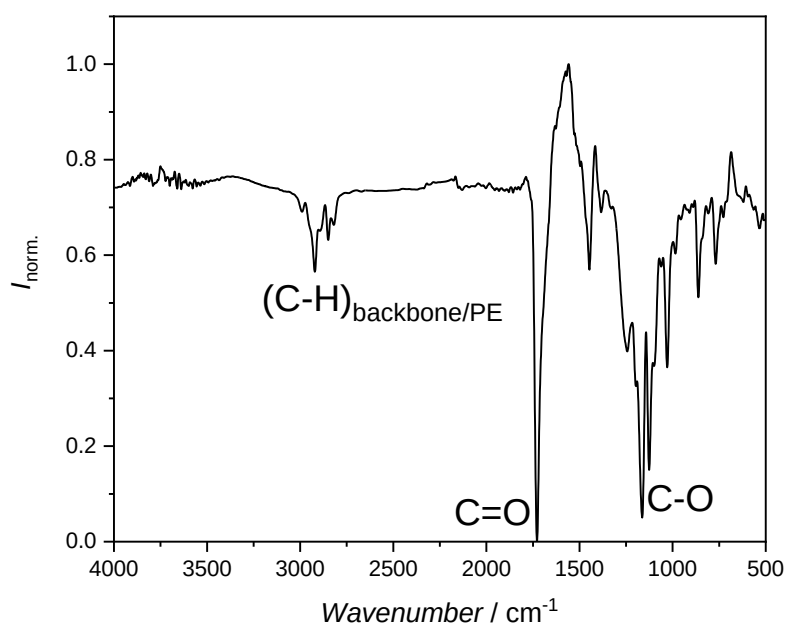
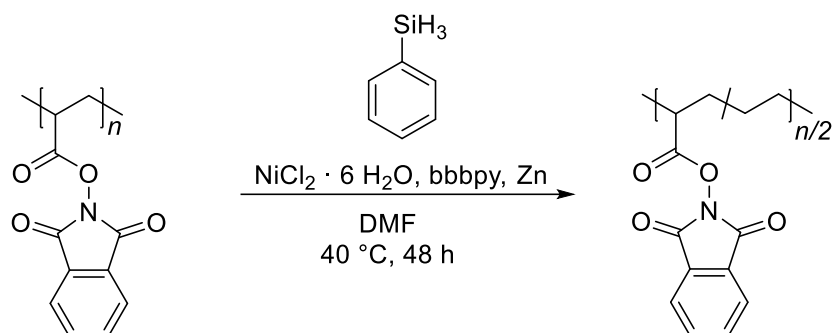


Figure S38: ATR-IR spectrum of PAP-block-POEGMEA (**P6**) after photochemically-induced decarboxylation.

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2914 - 2848$ (C-H of backbone), 1725 (C=O of ester), 1159 (C-O of ether).

Thermally-induced decarboxylation method

Thermally-induced decarboxylation of poly[N-(acryloyloxy)phthalimide] with phenylsilane



^1H NMR (400 MHz, DMF-d_7): $\delta/\text{ppm} = 7.77 - 6.64$ (m, 4H, $\text{C}_{\text{aromatic}}\text{H}$), 3.68 - 3.09 (m, 1H, CHCOON), 1.99 - 0.38 (m, 2H, $\text{C}_{\text{backbone}}\text{H}_2$).

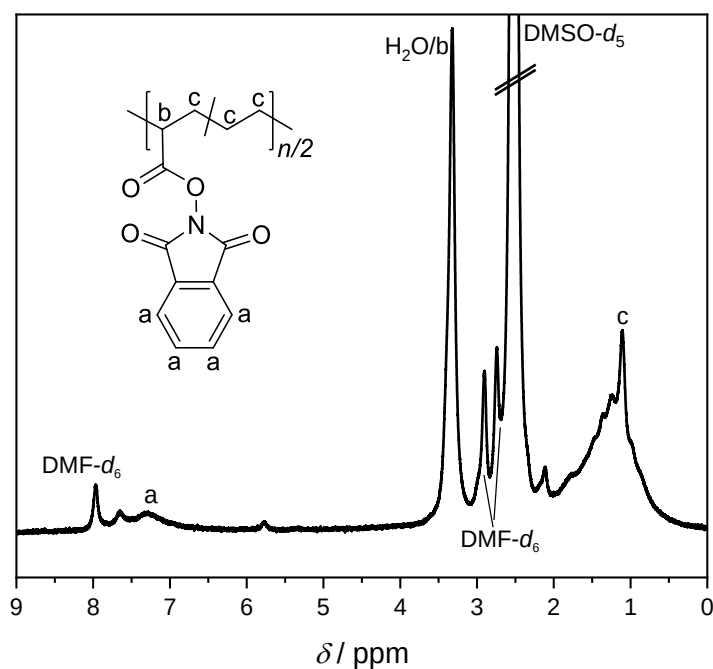
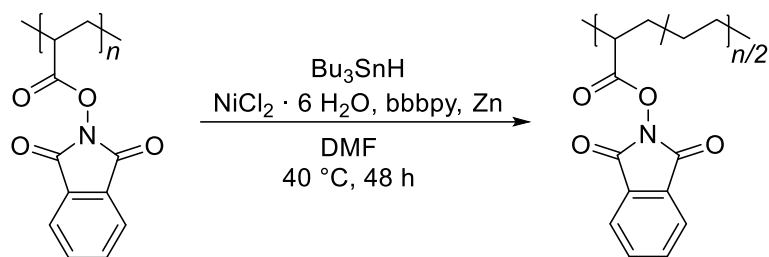


Figure S39: ^1H NMR spectrum of poly[N-(acryloyloxy)phthalimide] (**P1**) after thermally-induced decarboxylation. Solvent: DMF-d_7 .*

*The polymer featured low solubility in common solvents tested (DCM, toluene, petrol ether, acetone). Best solubility was obtained in a mixture of DMSO and DMF at elevated temperature.

Thermally-induced decarboxylation of poly[*N*-(acryloyloxy)phthalimide] with tributyltin hydride



^1H NMR (400 MHz, $\text{DMF-}d_7$): $\delta/\text{ppm} = 7.96 - 7.17$ (m, 4H, $\text{C}_{\text{aromatic}}\text{H}$), 4.82 - 3.12 (m, 1H, NOOCHCH_2), 2.67 - 0.44 (m, 2H, NOOCHCH_2).

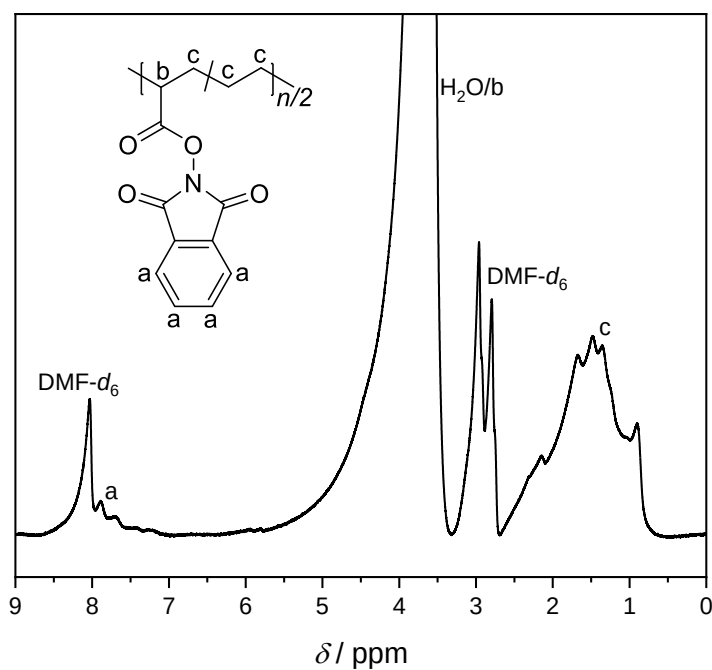
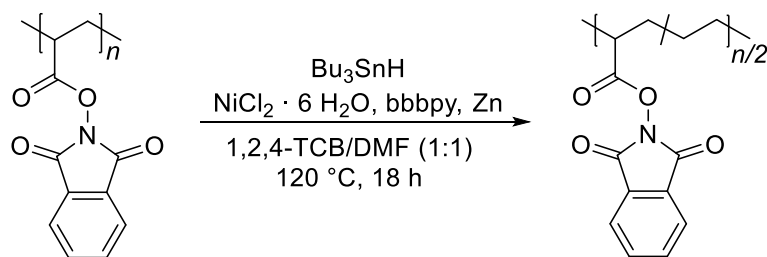


Figure S40: ^1H NMR spectrum of poly[*N*-(acryloyloxy)phthalimide] (**PI**) after thermally-induced decarboxylation with tributyltin hydride. Solvent: $\text{DMF-}d_7$.*

*Like stated on page S36 the polymer obtained from the decarboxylation featured low solubility and the ^1H NMR was therefore measured in deuterated DMF since the reaction was performed in this solvent.

Thermally-induced decarboxylation of poly[*N*-(acryloyloxy)phthalimide] with tributyltin hydride in DMF/1,2,4-TCB at 120 °C



^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ/ppm = 7.68 (m, 4H, $\text{C}_{\text{aromatic}}\text{H}$), 3.33 (m, 1H, NOOCHCH_2), 1.38 (m, 2H, CH_2).

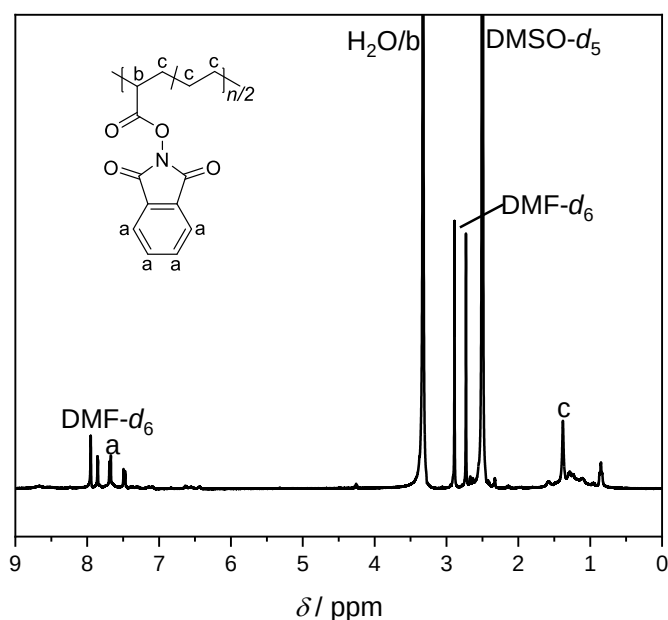
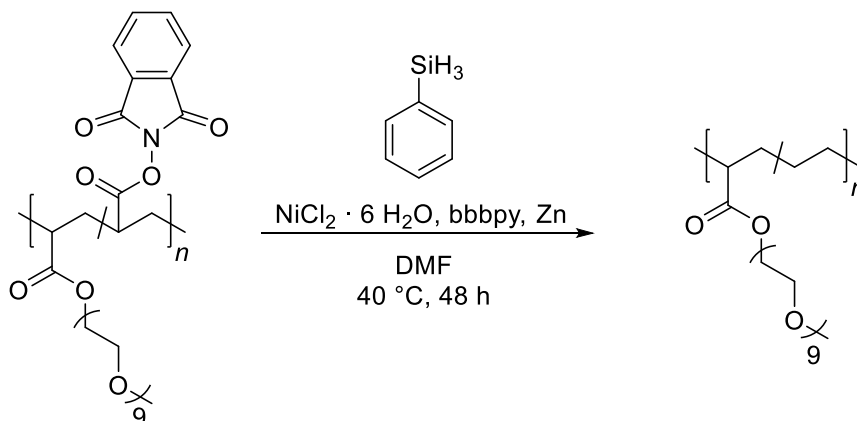


Figure 41: ^1H NMR spectrum of poly[*N*-(acryloyloxy)phthalimide] (PI) after thermally-induced decarboxylation with tributyltin hydride in DMF/1,2,4TCB (1:1) at 120 °C. Solvent: $\text{DMSO}-d_5$, DMF- d_7 .*

*Like stated on page S36 the polymer obtained from the decarboxylation featured low solubility and the ^1H NMR was therefore measured in deuterated DMF since the reaction was performed in this solvent. NMR sample could not be dissolved in deuterated 1,2-dichlorobenzene for additional ^1H NMR analysis.

Thermally-induced decarboxylation of poly[*N*-(acryloyloxy)phthalimide-co-oligo(ethylene glycol) methyl ether acrylate] with phenylsilane



^1H NMR (400 MHz, CDCl_3): $\delta/\text{ppm} = 4.18$ (s, 2H, COOCH_2), 3.93 - 3.49 (m, 32H, $(\text{OCH}_2\text{CH}_2\text{O})_8$), 3.37 (s, 3H, $(\text{OCH}_2\text{CH}_2\text{O})_8\text{CH}_3$), 2.3 (m, 1H, CHCOO), 2.09 – 0.51 (m, $\text{C}_{\text{backbone}}\text{H}_2$).

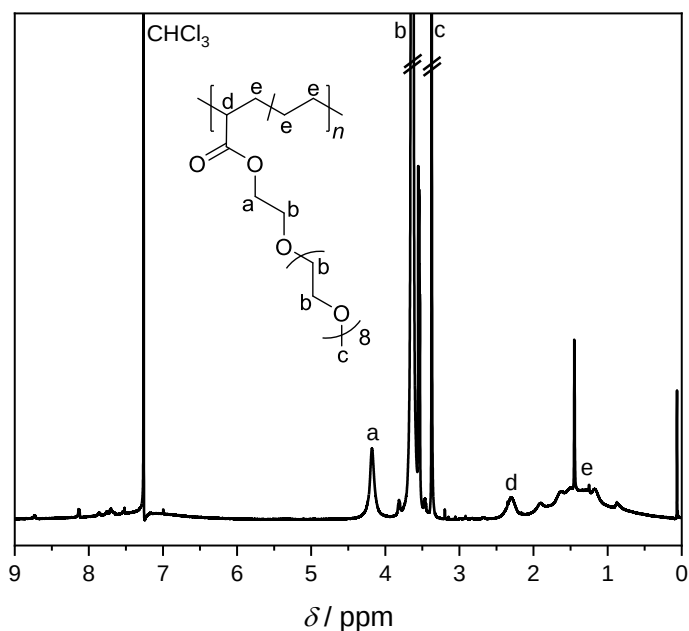


Figure S42: ^1H NMR spectrum of $\text{P}(\text{AP-co-OEGMEA})$ (**P4**) after thermally-induced decarboxylation. Solvent: CDCl_3 .

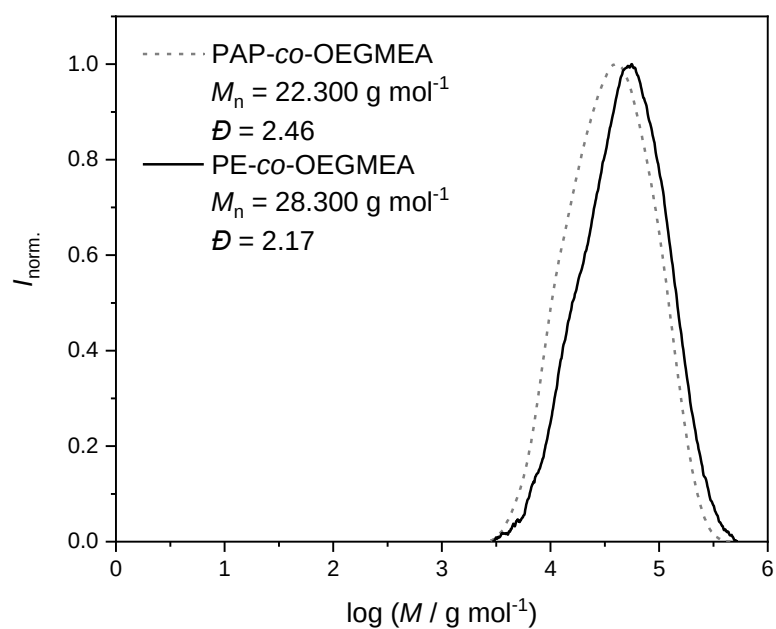
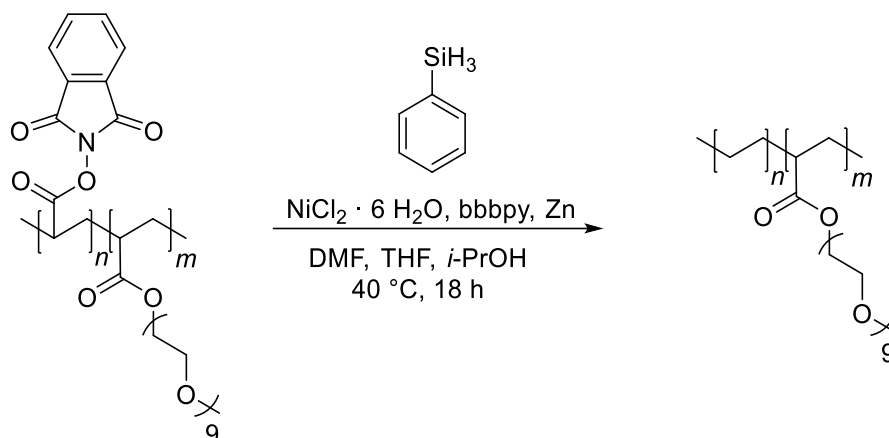


Figure S43: Comparison of the SEC traces of P(AP-co-OEGMEA) (**P4**) before (grey) and after (black) thermally-induced decarboxylation with DMAc as eluent. M_n , PAP-co-OEGMEA = 28300 g mol⁻¹, $\text{Đ} = 2.17$; M_n , PE-co-OEGMEA = 22300 g mol⁻¹, $\text{Đ} = 2.46$.

Thermally-induced decarboxylation of poly[*N*-(acryloyloxy)phthalimide]-*block*-poly[oligo(ethylene glycol) methyl ether acrylate] with phenylsilane



^1H NMR (400 MHz, CDCl_3): δ /ppm = 4.18 (s, 2H, $\text{COOCH}_2\text{CH}_2\text{O}$), 3.73 – 3.54 (m, 34H, $\text{CH}_2(\text{CH}_2\text{CH}_2\text{O})_{8-9}$), 3.33 (s, 3H, $\text{CH}_2\text{CH}_2\text{OCH}_3$), 2.26 (s, 1H, $\text{C}_{\text{backbone, OEGMEA}}\text{H}$), 1.89 (s, 2H, $\text{C}_{\text{backbone, OEGMEA}}\text{H}$), 1.58 (s, 98H, CH_2 , PE).

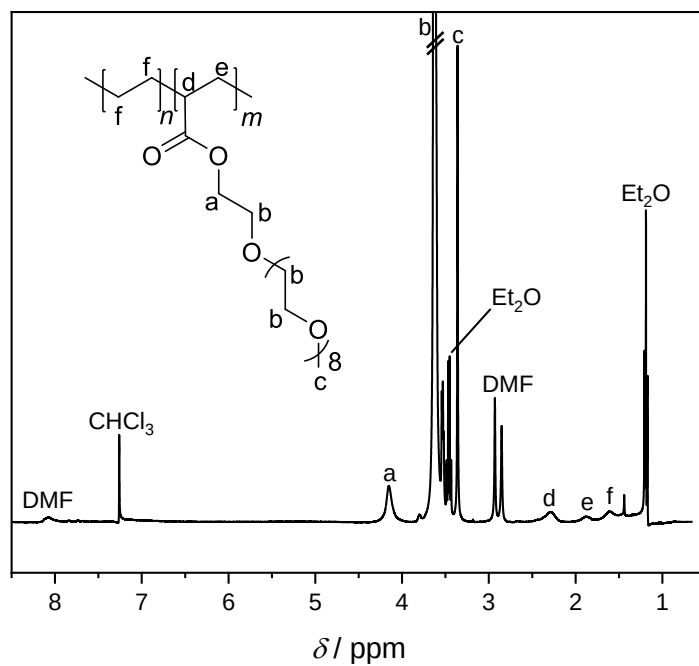


Figure S44: ^1H NMR spectrum of PAP-*block*-POEGMEA (**P5**) after thermally-induced decarboxylation. Solvent: CDCl_3 .

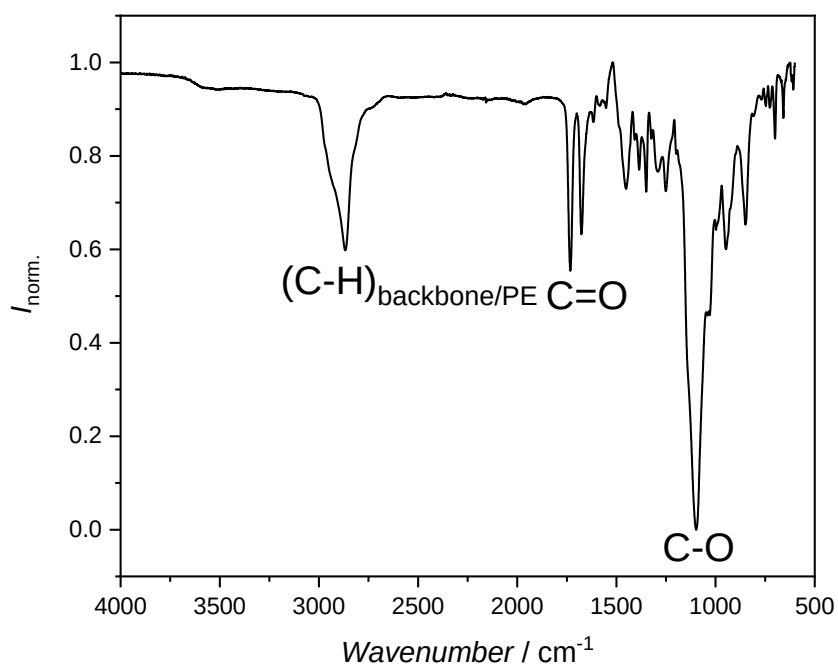


Figure S45: ATR-IR spectrum of PAP-block-POEGMEA (**P5**) after thermally-induced decarboxylation.

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2869$ (C-H of backbone), 1677-1731 (C=O of ester), 1102 (C-O of ether).

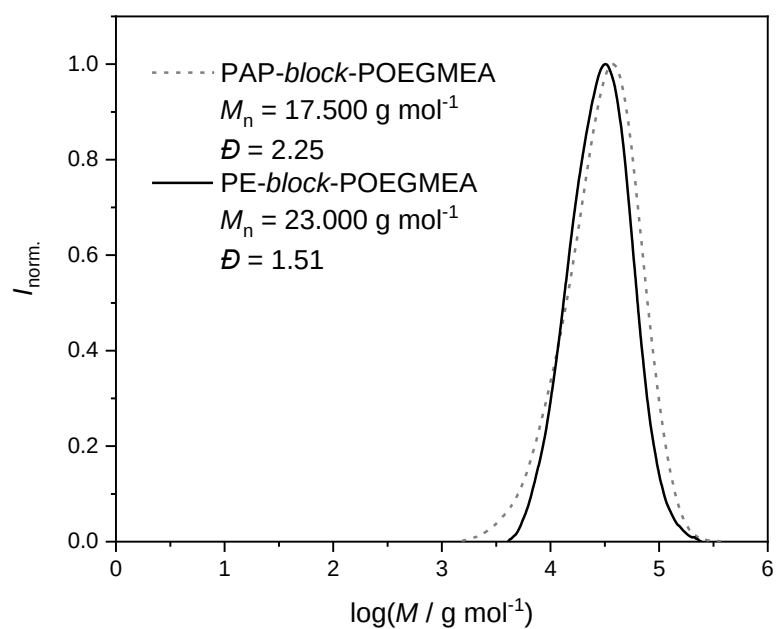


Figure S46: Comparison of SEC traces of PAP-*block*-POEGMEA (**P5**) before (grey) and after (black) thermally-decarboxylation with DMAc as eluent. $M_{n, \text{PAP-}i\text{block-POEGMEA}} = 17.500 \text{ g mol}^{-1}$, $\text{Đ} = 2.25$; $M_{n, \text{PE-}i\text{block-POEGMEA}} = 23.000 \text{ g mol}^{-1}$, $\text{Đ} = 1.51$.

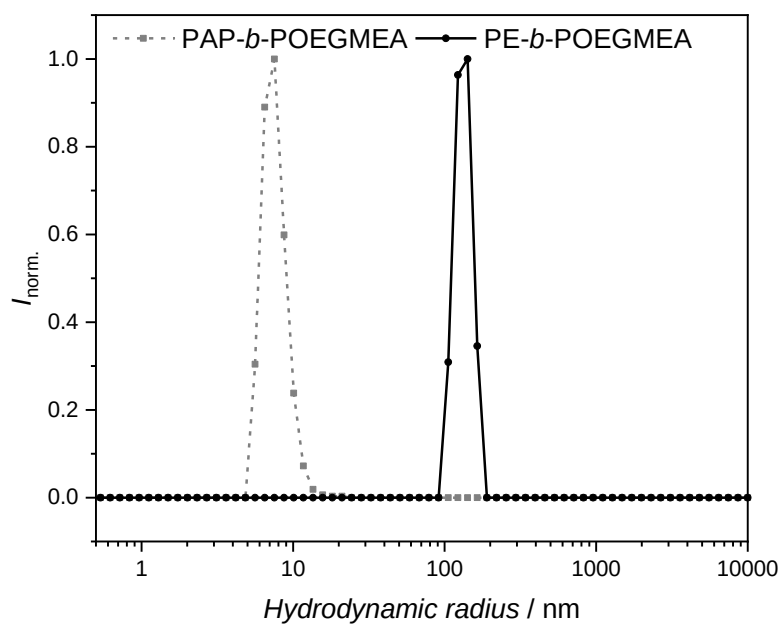


Figure S47: DLS characterization of PAP-*block*-POEGMEA (**P5**) before (grey) and after (black) thermally-induced decarboxylation.

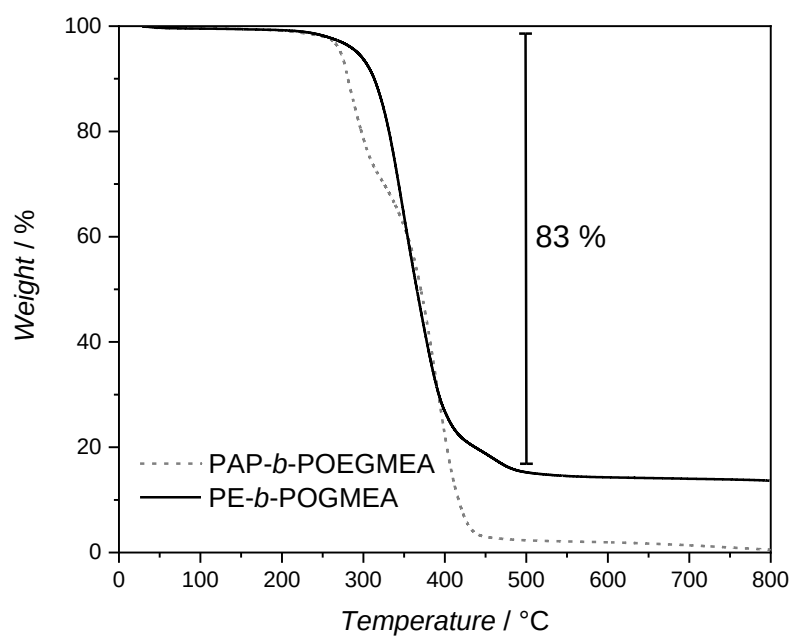


Figure S48: Thermogravimetric analysis of PAP-*b*-POEGMEA (P5) before (grey) and after (black) thermally-induced decarboxylation.

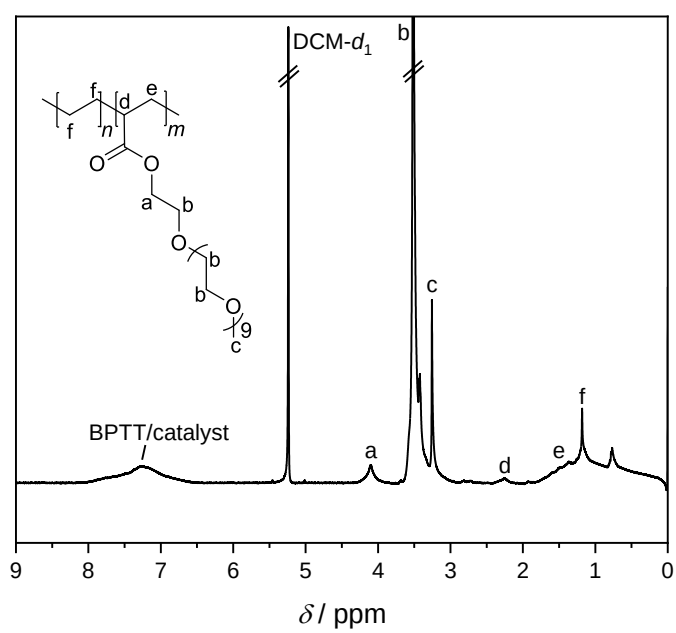


Figure S49: ¹H NMR spectrum of PAP-*b*-POEGMEA (P7) after thermally-induced decarboxylation. Solvent: DCM-*d*₂.

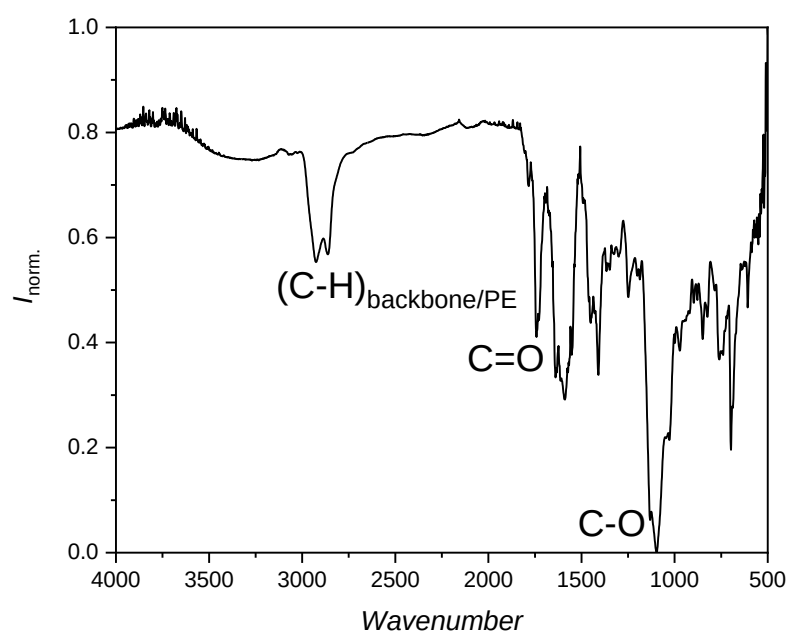


Figure S50: ATR-IR spectrum of PAP-block-POEGMEA (**P7**) after thermally-induced decarboxylation.

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2930 - 2858$ (C-H of backbone), 1744 (C=O of ester), 1102 (C-O of ether).

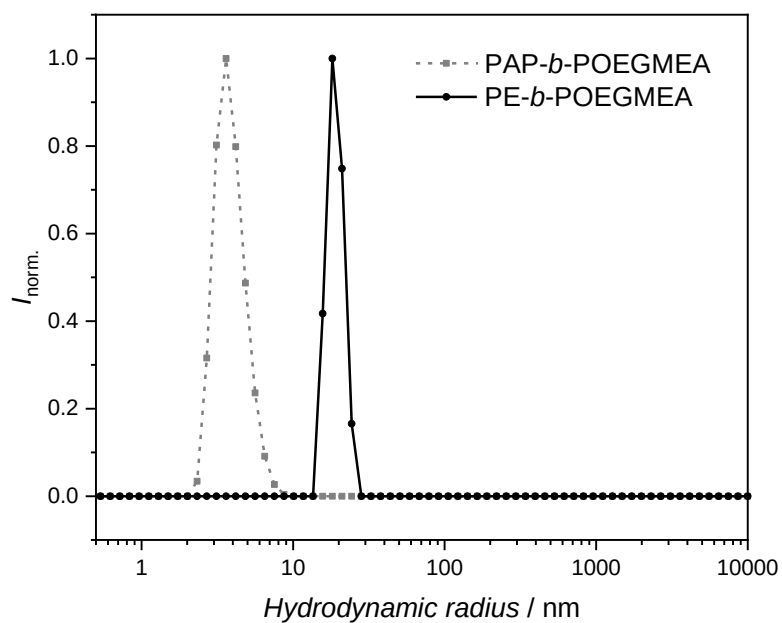


Figure S51: DLS characterization of PAP-block-POEGMEA (**P7**) before (grey) and after (black) thermally-induced decarboxylation.

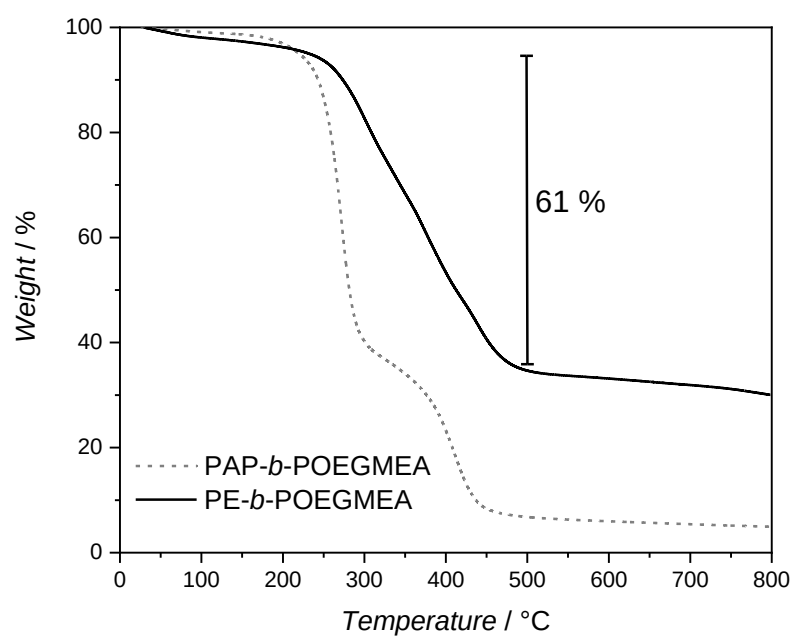


Figure S52: Thermogravimetric analysis of PAP-block-POEGMEA (**P7**) before (grey) and after (black) thermally-induced decarboxylation.

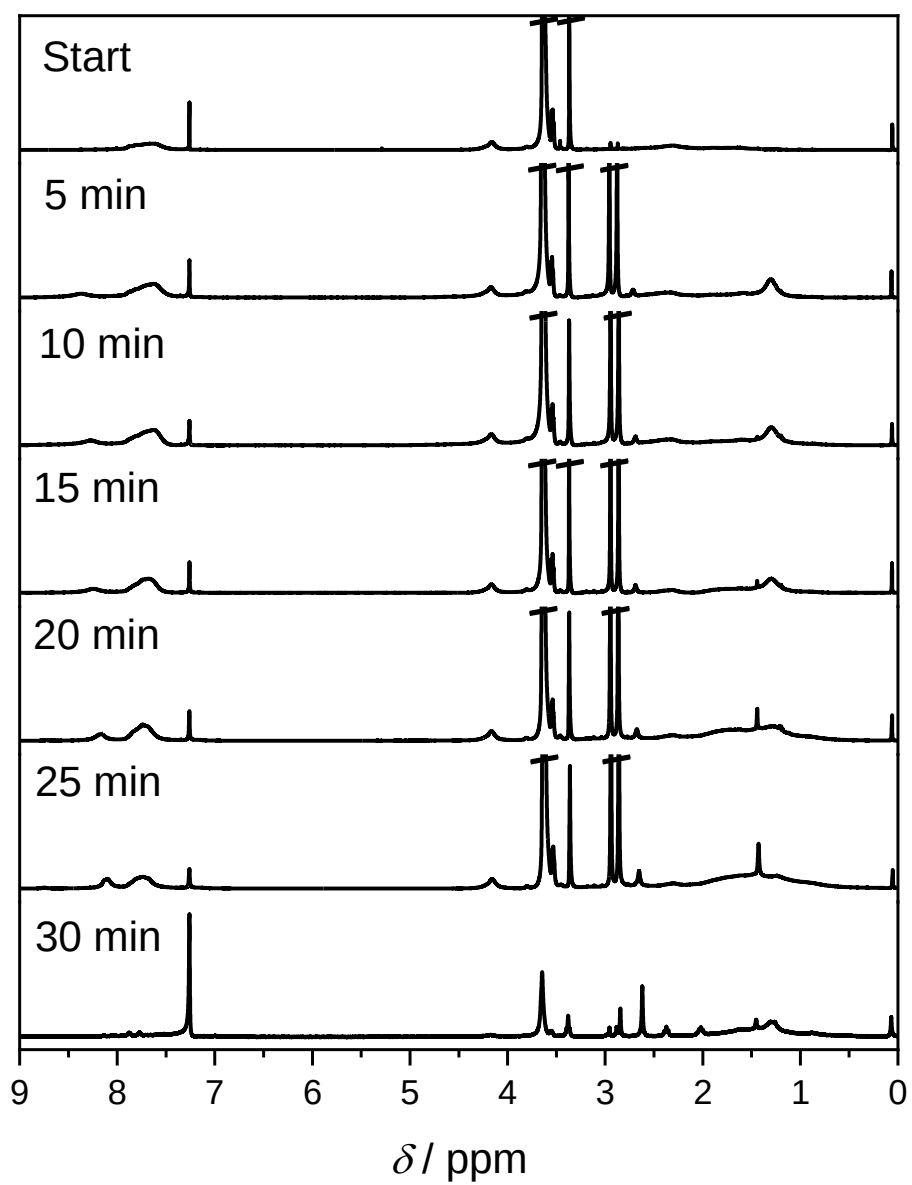
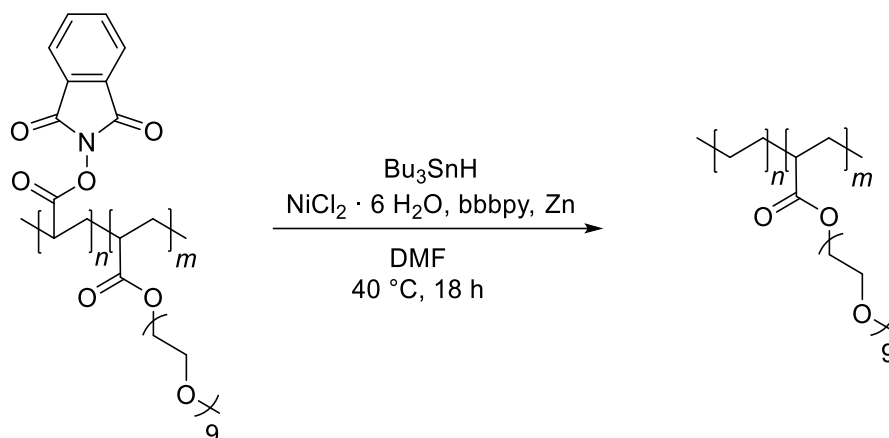


Figure S53: Reaction monitoring of thermally-induced decarboxylation of PAP-b-POEGMEA (**P11**). Solvent: CDCl_3 .

Thermally-induced decarboxylation of poly[*N*-(acryloyloxy)phthalimide]-*block*-poly[oligo(ethylene glycol) methyl ether acrylate] with tributyltin hydride



^1H NMR (400 MHz, CDCl_3): $\delta/\text{ppm} = 4.17$ (s, 2H, $\text{COOCH}_2\text{CH}_2\text{O}$), 3.59 (m, 34H, $\text{CH}_2(\text{CH}_2\text{CH}_2\text{O})_8$), 3.34 (s, 3H, $\text{CH}_2\text{CH}_2\text{OCH}_3$), 2.32 (s, 1H, $\text{C}_{\text{backbone}}$, OEGMEA H), 1.77 (s, 2H, $\text{C}_{\text{backbone}}$, OEGMEA H), 1.46 (s, 2H, CH_2 , PE).

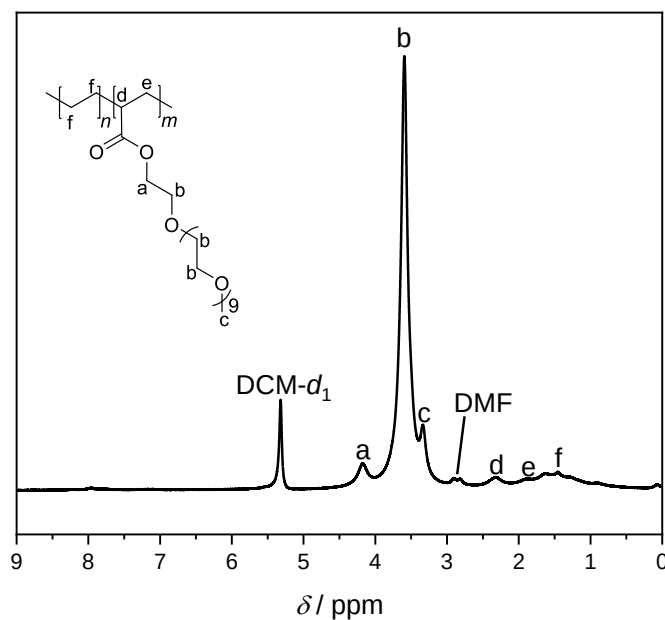


Figure 54: ^1H NMR spectrum of PAP-block-POEGMEA (**P11**) after thermally-induced decarboxylation with tributyltin hydride. Solvent: DCM-d_2 .

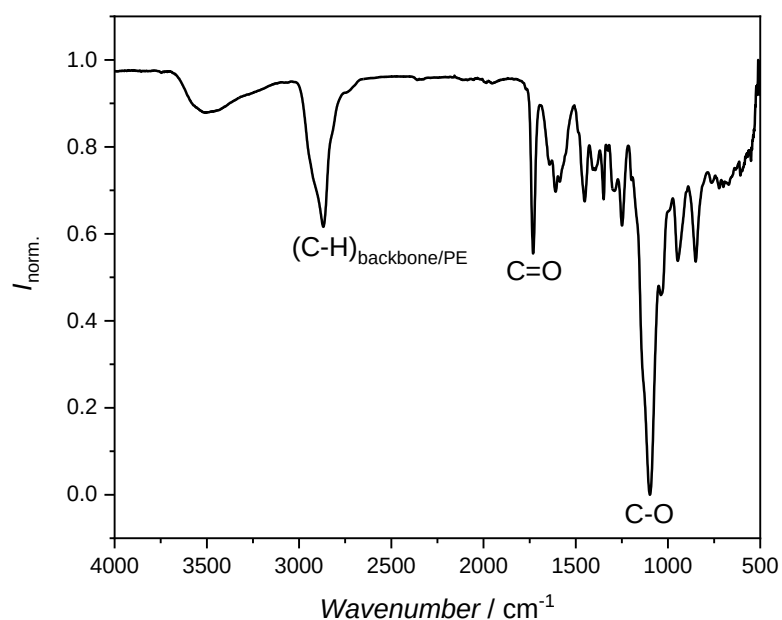


Figure 55: ATR-IR spectrum of PAP-block-POEGMEA (**P11**) after thermally-induced decarboxylation with tributyltin hydride.

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2872$ (C-H of backbone), 1730 (C=O of ester), 1098 (C-O of ether).

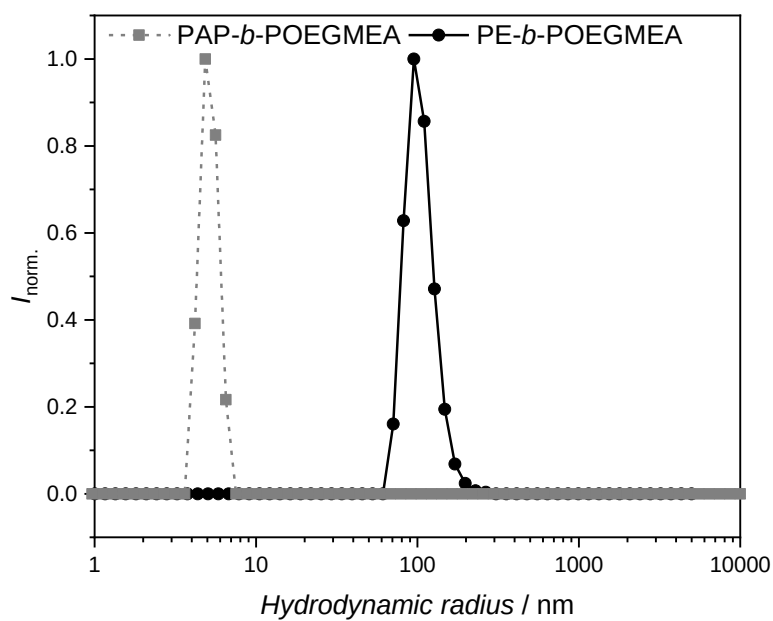


Figure 56: DLS characterization of PAP-block-POEGMEA (**P11**) before (grey) and after (black) thermally-induced decarboxylation with tributyltin hydride.

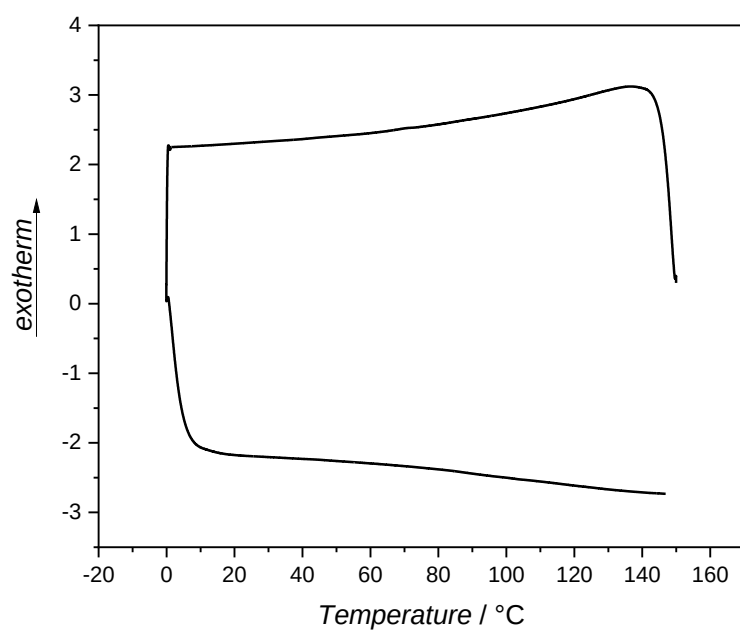
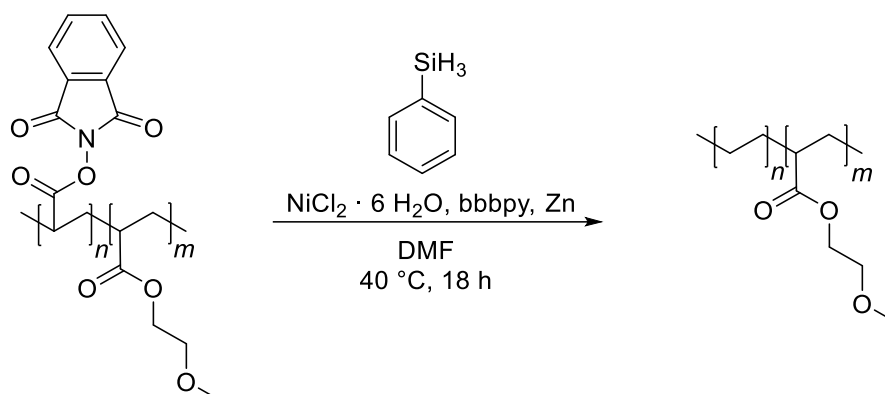


Figure S57: DSC characterization of PAP-block-POEGMEA (**P7**) after thermally-induced decarboxylation with tributyltin hydride as H-donor.

PE-*block*-PMEA

Thermally-induced decarboxylation of poly[*N*-(acryloyloxy)phthalimide]-*block*-poly(2-methoxyethyl acrylate)



^1H NMR (400 MHz, DCM-d_2): δ/ppm = 4.19 (m, 2H, $\text{COOCH}_2\text{CH}_2\text{O}$), 3.38 (m, 2H, $\text{COOCH}_2\text{CH}_2\text{O}$), 3.35 (s, 3H, OCH_3), 2.71 – 1.45 (m, 3H, $\text{C}_{\text{backbone}}\text{H}$), 1.23 (m, 2H, CH_2PE).

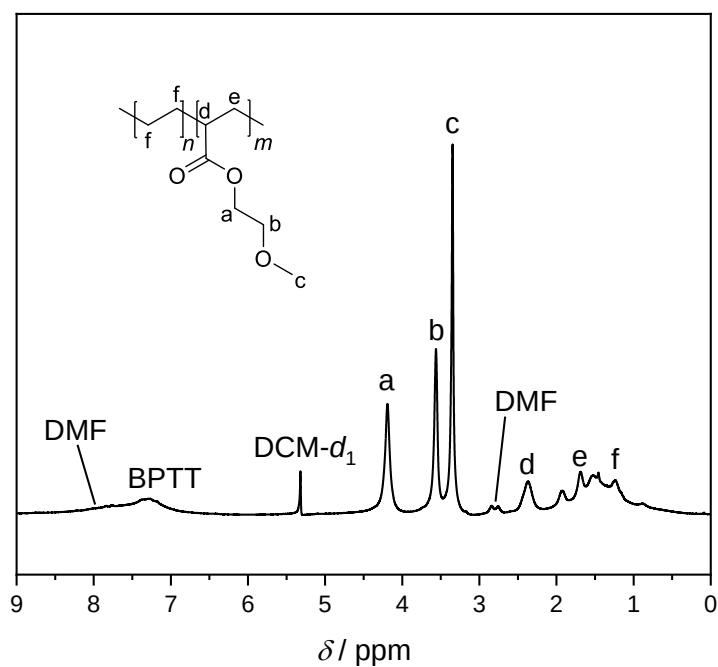


Figure S58: ^1H NMR spectrum of PAP-*block*-PMEA (**P9**) after thermally-induced decarboxylation. Solvent: DCM-d_2 .

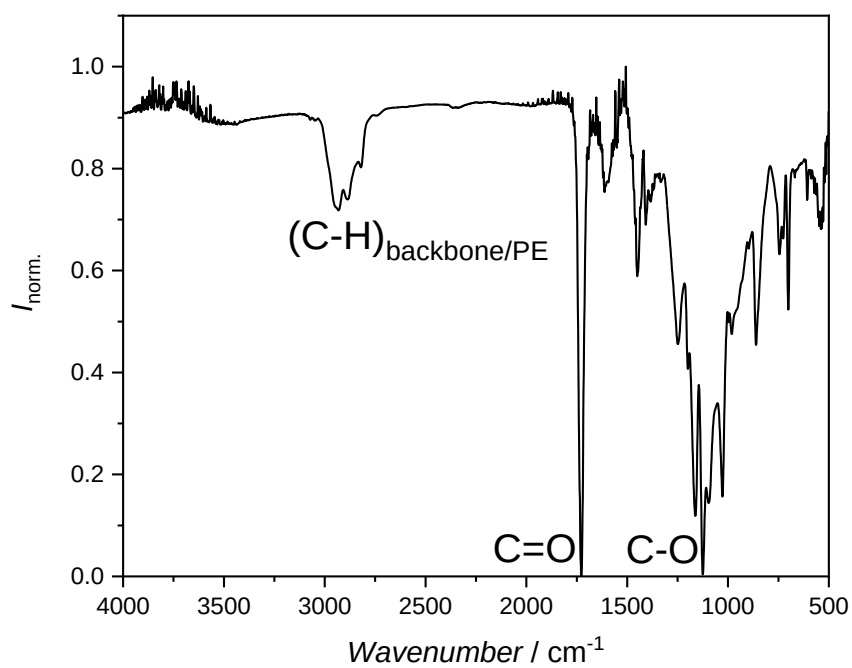


Figure S59: ATR-IR spectrum of PAP-block-PMEA (**P9**) after thermally-induced decarboxylation.

FT-IR (ATR): $\nu / \text{cm}^{-1} = 2924$ (C-H of backbone), 1731 (C=O of ester), 1128 (C-O of ether).