Supplementary Information for

Vinyl mercaptoethanol as a reactive monomer for preparation of functional homo- and copolymers with (meth)acrylates

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Experimental part

Materials and Methods

All reagents and solvents were commercially purchased from Sigma-Aldrich, TCI Chemicals, and abcr, or were provided by BASF SE. All were used without further purification.

^{1}H-NMR spectra were measured with a Bruker spectrometer (300 MHz) equipped with an Avance I console, a dual ^{1}H and ^{13}C sample head and a 120 x BACS automatic sample changer and a Bruker spectrometer (400 MHz) equipped with an Avance III console, a BBO sample head and a 60 x BACS automatic sample changer. The chemical shifts of the peaks were determined by using the residual solvent signal as a reference and are given in ppm in comparison to TMS. Deuterated solvents were commercially purchased from EURISO-TOP GmbH.

Size-exclusion chromatography (SEC) of polymers was performed on an Agilent system (series 1200) equipped with a PSS degasser, a G1310A pump, a G1362A refractive index detector and a

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PSS GRAM 30 and 1000 column with DMAc (+ 0.21 wt.% LiCl) as eluent at a flow rate of 1 mL/min. The column oven was set to 40 °C and poly(methyl methacrylate) (PMMA) standards were used for calibration.

The differential scanning calorimetry (DSC) measurements were performed on a DSC 204 F1 Phoenix® from Netzsch under a nitrogen atmosphere with a heating rate of 10 K/min. The thermal gravimetric analysis (TGA) was carried under nitrogen using a Netzsch TG 209F1.

Simultaneous Thermal Analysis (STA) measurements were carried out using an Netzsch 449 F3 Jupiter® and Netzsch QMS 403 D Aëolos® with a quadrupole mass analyzer.

IR spectra were recorded on an Invenio S Fourier transform infrared spectrophotometer equipped with a platinum ATR setup from Bruker.

Nanoindentation measurements were conducted on the film surface using a diamond Berkovich tip by applying a max load of 1 mN or 0.3 mN. The apparatus used was a Nanoindenter G200 (KLA). The applied load was controlled and the resulting penetration depth was detected, so that hardness, Young modulus and creep can be determined from the load vs. displacemnet curve.

Film thickness and optical constants were determined by spectroscopic ellipsometry. Data were collected by a Woollam Alpha-SE® between 380 nm and 900 nm wavelength. For data analysis, CompleteEase® version 6.51 was used. The substrate is described with a Cauchy layer. To avoid backside-reflection, a tape was applied to the backside of the substrate. For fitting of the polymer, a layer was converted to a B-spline and fitted over the entire spectral range. An ideal model considering sample roughness was applied. Polymer layer thickness and optical constants were fitted simultaneously.

Synthetic procedures:

General procedure for the free radical homopolymerizations of vinyl mercaptoethanol (VME): Vinyl mercaptoethanol (12 g, 116 mmol) and azobisisobutyronitrile (AIBN) were mixed, and the resulting solution was split into 11 different vials. Every solution was purged for 20 min with nitrogen and immersed into a preheated oil bath. The different polymerizations were stopped at different time points to evaluate the kinetics of the reaction.

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Table S1: Temperatures and applied amounts of initiator for the free radical homopolymerizations.

Temperature [°C]	m_{AIBN} [mg]	n_{AIBN} [mmol]
55	19.0	0.1
55	37.8	0.2
55	189.0	1.2
65	19.1	0.1
65	189.0	1.2

General procedure for synthesis of a bigger batch of PVME (P1): Vinyl mercaptoethanol (10 g, 96 mmol) and AIBN (189 mg, 1.2 mmol) were added in a microwave vial and the solution was purged for 20 min with nitrogen. Afterwards the solution was stirred at 55 °C for 4 h. Then DMF was added, and the polymers were precipitated in ether, centrifuged, redissolved in DMF and precipitated in ether again. Finally, the polymers were dried under vacuum.

Synthetic procedure for the oxidation of polyVME to the sulfoxide: PolyVME (0.2 g, 1 eq.) and was dissolved in DMF (3 mL) and 50 wt.% H_2O_2-solution (1.3 g, 22 mmol, 10 eq.) was added and stirred for 24 h at rt. The polymer was precipitated in methanol, centrifuged and dried under vacuum.

Synthetic procedure for the oxidation of polyVME to the sulfone: PolyVME (0.2 g, 1 eq.) and a spatula tip of sodium tungstate were dissolved in DMF (3 mL) and 50 wt.% H_2O_2-solution (1.3 g, 22 mmol, 10 eq.) was added and stirred for 24 h at 60 °C. The polymer was precipitated in methanol, centrifuged and dried under vacuum.

Vinyl sulfonylethanol (VSE): Vinyl mercaptoethanol (30.00 g, 288 mmol, 1 eq.), sodium tungstate (0.04 g, 0.12 mmol, 0.0004 eq.) and hydroxyanisol (0.05 g, 0.40 mmol, 0.001 eq.) were dispersed in water (15 mL). Afterwards, 50% hydrogen peroxide solution (19.61 g, 288 mmol, 1 eq.) was added dropwise so that the temperature did not exceed 40 °C. The solution was further stirred for 1 h at 40 °C. Subsequently, 50% hydrogen peroxide solution (19.61 g, 288 mmol, 1 eq.) was added dropwise at 40 °C and the solution was stirred overnight at 60 °C. Finally, manganese oxide was added, the solution was centrifuged, and the solvent was removed in a continuous stream of air at 40 °C.

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^{1}H-NMR (300 MHz, DMSO-d$_6$): δ [ppm] = 6.93 (dd, J = 16.2, 9.8 Hz, 1H), 6.18 (dd, J = 12.7, 8.9 Hz, 2H), 5.06 (s, 1H), 3.74 (s, 2H), 3.24 (s, 2H).

^{13}C-NMR (75 MHz, DMSO-d$_6$) δ [ppm] = 138.09, 128.30, 56.19, 54.84.

Synthetic procedure for the for the free radical homopolymerization of VSE: VSE (4.0 g, 29.4 mmol, 1 eq.) and AIBN (50.0 mg, 0.30 mmol, 0.01 eq.) were added in microwave vial and purged with nitrogen for 20 min. The reaction was started by immersion of the solution into a preheated oil bath at 65 °C and was further stirred for 48 h. The polymer was then precipitated in methanol, centrifuged, dissolved in methoxy ethanol, and precipitated in methanol again. The polymer was dried under vacuum. Because of the low yields two batches had to be prepared for the characterization. The first batch was used for the determination of thermal properties and the second batch for SEC measurements and IR-spectroscopy measurements.

General procedure for the RAFT-homopolymerizations: Vinyl mercaptoethanol (1.0 g, 9.6 mmol, 1 eq.) was added to a 2*wt%* stock solution of AIBN (1.5 mg, 0.009 mmol, 0.01 eq.) in dioxane and the CTA (0.1 eq.). The reaction mixture was degassed for 20 min. Afterwards the reaction mixture was heated at 65 °C for 24 h and samples were taken at different time points to examine the kinetics of the reaction.

Table S2: Applied amounts of RAFT-agents for the RAFT-polymerizations.

RAFT-agent	m_{CTA} [mg]	n_{CTA} [mmol]
2-(((butylthio)carbonothioyl)thio)propanoic acid	24	0.1
4-cyano-4-(((ethylthio)carbonothioyl)thio)pentanoic acid	25	0.1

General procedure for the determination of the copolymerization parameters: Vinyl mercaptoethanol and comonomer 2 were dissolved in DMF (1 mL) in different ratios and a stock solution of AIBN in vinyl mercaptoethanol was added. The reaction mixtures were purged for 20 min with nitrogen and then immersed into a preheated oil bath 65 °C. After short reaction times (see Table S3) the polymers were precipitated, centrifuged, redissolved in DMF, and precipitated again. The polymers were dried under vacuum and characterized by NMR-spectroscopy.

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Table S3: Applied amounts of monomers and initiator, applied solvents and time for the determination of the copolymerization parameters.

Comonomer 2	No.	m_{VME} [g]	$m_{comonomer\ 2}$ [g]	m_{AIBN} [mg]	Solvent for precipitating	Time [min]
Styrene	1	2.66	1.36	3.12	Isopropanol	50
	2	2.35	1.65	3.12	Isopropanol	50
	3	2.02	2.00	3.12	Isopropanol	48
	4	1.35	2.67	3.12	Isopropanol	46
	5	1.01	3.00	3.12	Isopropanol	44
	6	0.66	3.34	3.12	Isopropanol	42
	7	0.50	3.51	3.12	Isopropanol	40
MMA	1	3.81	0.19	0.31	Diethyl ether	25
	2	3.66	0.36	0.31	Diethyl ether	20
	3	2.70	1.30	0.31	Diethyl ether	15
	4	2.04	2.00	0.31	Diethyl ether	12
	5	1.37	2.63	0.31	Diethyl ether	10
	6	1.04	3.00	0.31	Diethyl ether	7
	7	0.70	3.33	0.31	Diethyl ether	5
BA	1	3.77	0.23	0.31	Diethyl ether	16
	2	3.50	0.44	0.31	Diethyl ether	14
	3	2.45	1.52	0.31	Diethyl ether	12
	4	1.79	2.21	0.31	Diethyl ether	10
	5	1.16	2.85	0.31	Diethyl ether	8
VP	1	3.79	0.21	0.31	Diethyl ether	24
	2	3.61	0.40	0.31	Diethyl ether	22
	3	2.61	1.40	0.31	Diethyl ether	20
	4	1.93	2.07	0.31	Diethyl ether	18
	5	1.27	2.73	0.31	Diethyl ether	16
	6	0.61	3.37	0.31	Diethyl ether	12
VA	1	3.86	0.16	3.12	Diethyl ether	40
	2	2.83	1.16	3.12	Diethyl ether	40

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Comonomer 2	No.	m_{VME} [g]	$m_{comonomer\ 2}$ [g]	m_{AIBN} [mg]	Solvent for precipitating	Time [min]
	3	2.22	1.80	3.12	Diethyl ether	40
	4	1.15	2.85	3.12	Diethyl ether	40
	5	0.77	3.30	3.12	Diethyl ether	40
	6	0.62	3.43	3.12	Diethyl ether	40
	7	0.51	3.54	3.12	Diethyl ether	40

General procedure for the free radical copolymerization targeting higher conversions: Vinyl mercaptoethanol and comonomer 2 were dissolved in DMF (1 mL) and a stock solution of AIBN in vinyl mercaptoethanol was added. The reaction mixtures were purged for 20 min with nitrogen and then immersed into a preheated oil bath 65 °C, where they were kept for 4 h. Afterwards the polymers were precipitated, centrifuged, dissolved in DMF, and precipitated again. The polymers were dried under vacuum.

Table S4: Applied amounts of monomers and initiator for the copolymerizations with higher conversion.

		m_{VME} [g]	n_{VME} [mmol]	$m_{comonomer\ 2}$ [g]	$n_{comonomer\ 2}$ [mmol]	m_{AIBN} [mg]	n_{AIBN} [mmol]	Solvent for precipitating
P2	MMA	0.38	3.6	3.6	36.2	0.31	0.002	Methanol
P3	MMA	2.1	20.1	2.0	20.0	0.31	0.002	Methanol
P4	BA	1.8	17.2	2.2	17.2	0.31	0.002	THF

General procedure for the experiments on the RAFT copolymerization with BA: *N*-butyl acrylate, vinyl mercaptoethanol, a 5*wt%* stock solution of AIBN in DMF, a 20*wt%* stock solution of CTA I in DMF and a few drops of mesitylene as a standard were added into a microwave vial and purged with nitrogen for 20 min. Afterwards the reaction mixtures were stirred for 24 h at 65 °C. The polymers were precipitated in water:methanol-mixture (1:1), centrifuged, washed with water:methanol-mixture (1:1) and dried under vacuum.

Table S5: Applied amounts of monomers and initiator for the RAFT copolymerizations with BA.

	Ratio	m_{VME}	n_{VME}	m_{n-BA}	n_{n-BA}	m_{AIBN}	n_{AIBN}	m_{CTAI}	n_{CTAI}

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	VME:BA	[g]	[mmol]	[g]	[mmol]	[mg]	[mmol]	[mg]	[mmol]
R1	3:1	2.13	20.49	0.88	6.85	4.50	0.03	64.90	0.27
R2	2:1	1.86	17.89	1.15	8.97	4.60	0.03	64.50	0.27
R3	1:1	1.34	12.90	1.65	12.90	4.20	0.03	61.2	0.26
R4	0.5:1	0.87	8.39	2.14	16.72	4.10	0.02	60.10	0.25
R5	1:1	1.35	12.92	1.64	12.80	8.10	0.05	122.50	0.51
R6	1:1	1.34	12.90	1.65	13.83	2.08	0.02	30.70	0.13

General procedure for the experiments on the RAFT copolymerization with MMA: Methyl methacrylate, vinyl mercaptoethanol, a 5*wt%* stock solution of AIBN in DMF, a 20*wt%* stock solution of CTA I in DMF and a few drops of mesitylene as a standard were added into a microwave vial and purged with nitrogen for 20 min. Afterwards the reaction mixtures were stirred for 24 h at 65 °C. The polymers were precipitated in diethylether, centrifuged, washed with diethylether and dried under vacuum.

Table S6: Applied amounts of monomers and initiator for the RAFT copolymerizations with MMA.

	Ratio VME:MMA	m_{VME} [g]	n_{VME} [mmol]	m_{MMA} [g]	n_{MMA} [mmol]	m_{AIBN} [mg]	n_{AIBN} [mmol]	m_{CTAI} [mg]	n_{CTAI} [mmol]
R7	3:1	2.28	21.92	0.73	7.29	4.90	0.03	68.22	0.29
R8	2:1	2.03	19.46	0.97	9.72	4.72	0.03	71.80	0.30
R9	1:1	1.52	14.64	1.47	14.72	4.80	0.03	70.20	0.29
R10	0.5:1	1.03	9.89	1.98	19.76	4.80	0.03	71.50	0.30
R11	1:1	1.54	14.78	1.47	14.66	9.50	0.06	140.72	0.59
R12	1:1	1.53	14.71	1.46	14.62	3.06	0.02	35.10	0.15

RAFT polymerization of poly[vinyl mercaptoethanol] [PVME$_{62}$]: Vinyl mercaptoethanol (6.12 g, 58.8 mmol, 182 eq.), 20*wt%* stock solution of CTA I (76.8 mg, 0.32 mmol, 1 eq.) in DMF and 5*wt%* stock solution of AIBN (5.34 mg, 0.03 mmol, 0.1 eq.) in DMF, DMF (2.0 g) and a few drops mesitylene as a standard were added into a microwave vial and purged for 20 min with nitrogen. Afterwards the solution was heated to 65 °C and kept for 4 h. Then the polymer was

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precipitated in diethylether, centrifuged, dissolved in methanol and precipitated again in diethylther, centrifuged and dried under vacuum.

Synthesis of poly[vinyl mercaptoethanol-*block-n*-butyl acrylate] [PVME$_{62}$-*b*-PBA$_{83}$]: PVME$_{62}$ (253.5 mg, 0.038 mmol, 1 eq.), *n*-butyl acrylate (477.0 mg, 3.72 mmol, 100 eq.) and 5*wt%* stock solution of AIBN (0.87 mg, 0.005 mmol, 0.13 eq.) in DMF, DMF (1.25 g) and a few drops mesitylene as a standard were added into a microwave vial and purged for 20 min with nitrogen. Afterwards the solution was heated to 65 °C and kept for 4 h. Then the polymer was precipitated in water:methanol-mixture (1:1), centrifuged, washed with water:methanol-mixture (1:1) and dried under vacuum.

RAFT polymerization of poly[*n*-butyl acrylate] [PBA$_{92}$]: *N*-butyl acrylate (3.30 g, 25.7 mmol, 100 eq.), 20*wt%* stock solution of CTAI (61.86 mg, 0.26 mmol, 1 eq.) in DMF and 5*wt%* stock solution of AIBN (2.05 mg, 0.01 mmol, 0.05 eq.) in DMF, DMF (2.0 g) and a few drops mesitylene as a standard were added into a microwave vial and purged for 20 min with nitrogen. Afterwards, the solution was heated to 65 °C and kept for 4 h. Then the polymer was precipitated in water:methanol-mixture (1:1), centrifuged, washed with water:methanol-mixture (1:1) and dried under vacuum.

Synthesis of poly[*n*-butyl acrylate-*block*-vinyl mercaptoethanol] [PBA$_{92}$-*b*-PVME$_{21}$]: PBA$_{92}$ (249.8 mg, 0.02 mmol, 1 eq.), vinyl mercaptoethanol (863.8 mg, 8.28 mmol, 400 eq.) and 5*wt%* stock solution of AIBN (0.55 mg, 0.003 mmol, 0.17 eq.) in DMF, DMF (250.8 mg) and a few drops mesitylene as a standard were added into a microwave vial and purged for 20 min with nitrogen. Afterwards the solution was heated to 65 °C and kept for 4 h. Then the polymer was precipitated in water:methanol-mixture (1:1), centrifuged, washed with water:methanol-mixture (1:1) and dried under vacuum.

RAFT polymerization of poly[methyl methacrylate] [PMMA$_{96}$]: Methyl methacrylate (2.95 g, 29.5 mmol, 100 eq.), 20*wt%* stock solution of CTAII (76.8 mg, 0.29 mmol, 1 eq.) in DMF and 5*wt%* stock solution of AIBN (2.45 mg, 0.02 mmol, 0.1 eq.) in DMF, DMF (2.0 g) and a few drops mesitylene as a standard were added into a microwave vial and purged for 20 min with nitrogen.

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Afterwards, the solution was heated to 65 °C and kept for 4 h. Then the polymer was precipitated in diethylether, centrifuged, washed with diethylther and dried under vacuum.

Synthesis of poly[methyl methacrylate-*block*-vinyl mercaptoethanol] [PMMA$_{96}$-*b*-PVME$_{32}$]: PMMA$_{96}$ (501.0 mg, 0.05 mmol, 1 eq.), vinyl mercaptoethanol (1061.9 mg, 10.2 mmol, 200 eq.) and 5*wt%* stock solution of AIBN (0.89 mg, 0.005 mmol, 0.1 eq.) in DMF, DMF (2.0 g) and a few drops mesitylene as a standard were added into a microwave vial and purged for 20 min with nitrogen. Afterwards, the solution was heated to 65 °C and kept for 4 h. Then the polymer was precipitated in diethylether, centrifuged, washed with diethylether and dried under vacuum.

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Supporting data

Free radical homopolymerization
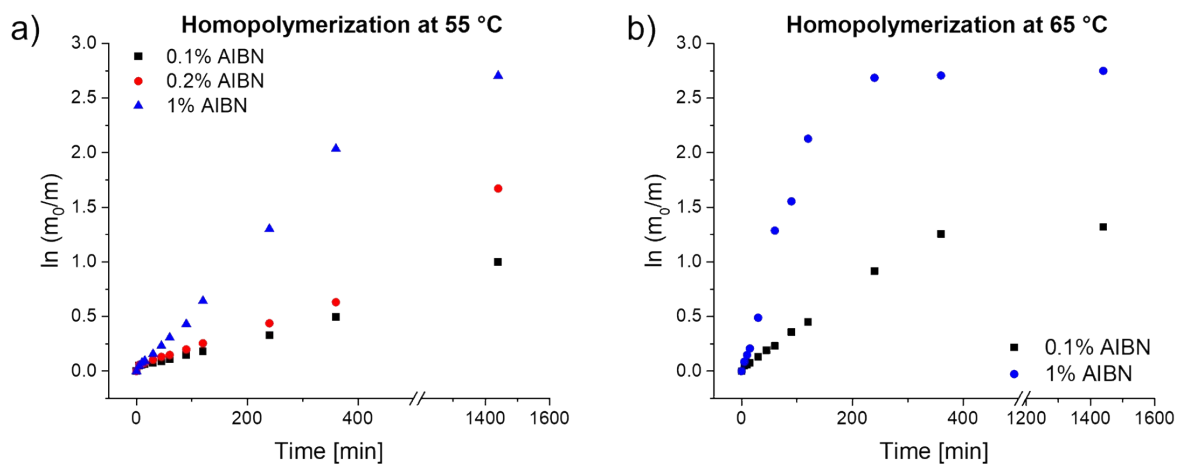
Figure S1: Ln (m_0/m) *vs.* reaction time for different polymerizations: a) homopolymerization of VME at 55 °C; b) homopolymerization of VME at 65 °C.
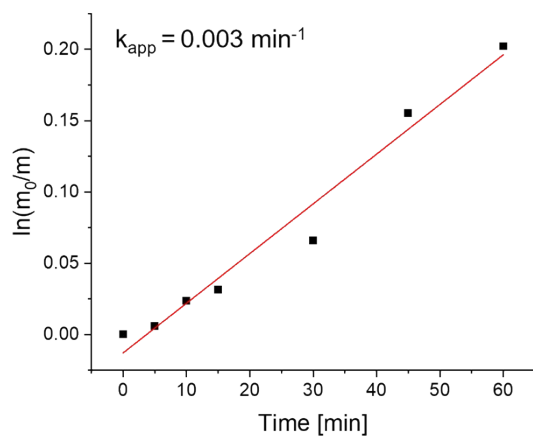
Figure S2: Ln (m_0/m) *vs.* reaction time for homopolymerization of MMA at 55 °C and 1% AIBN.

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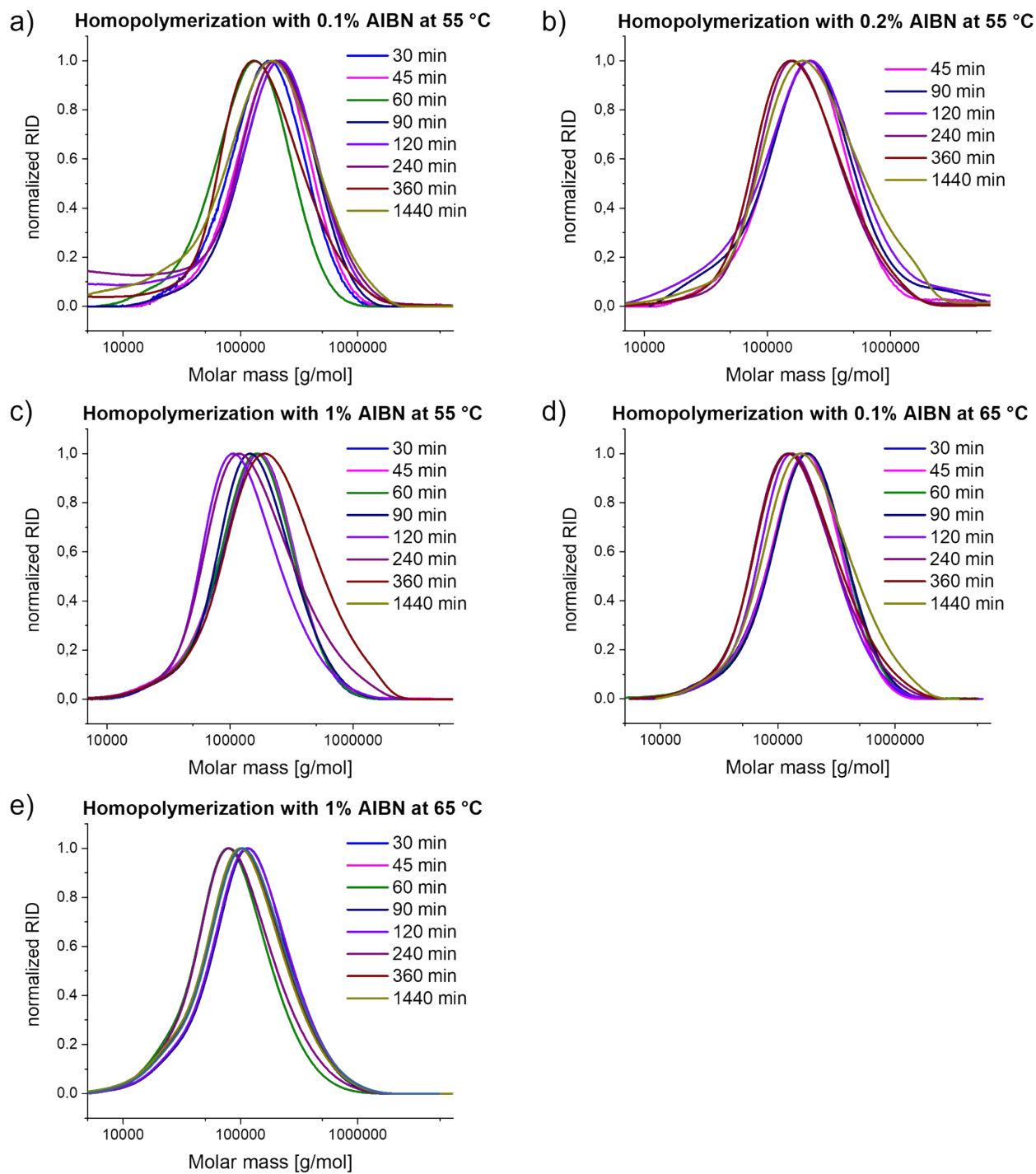
Figure S3: SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) traces of the kinetic samples taken after 30 min, 45 min, 60 min, 90 min, 120 min, 240 min, 360 min and 1440 min from the polymerization with a) 0.1 %, b) 0.2%, c) 1% AIBN at 55 °C and d) 0.1%, e) 1% AIBN at 65 °C.

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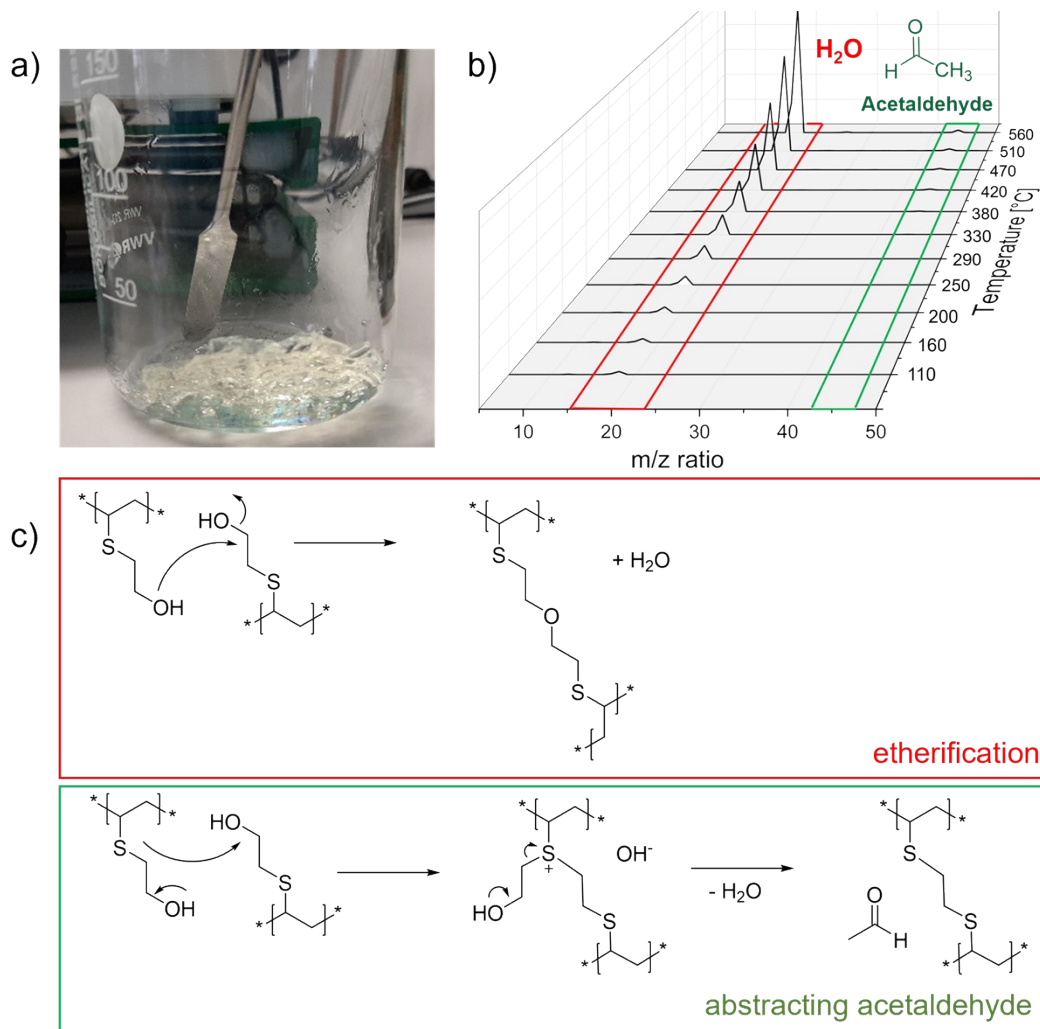
Figure S4: a) Picture of the generated gel b) STA-measurement (He) of the homopolymer c) Scheme of a possible mechanism of crosslinking.
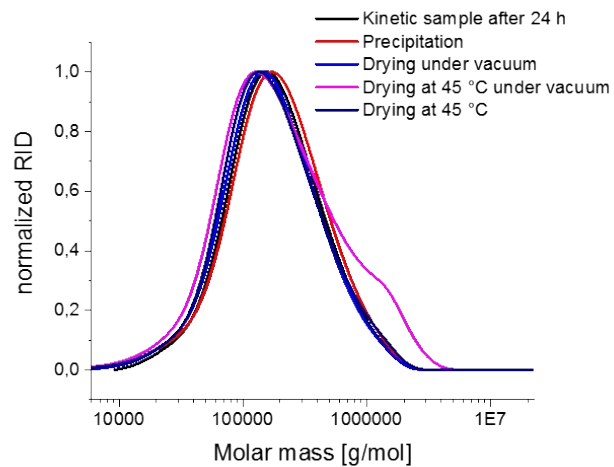
Figure S5: SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) traces for the investigation of different influencing variables on cross-linking.

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Copolymerization parameter

For the determination of the copolymerization parameters, the monomers were weighed in different ratios, dissolved in DMF, degassed for 10 min, and then polymerized at 65 °C. In order to use the Fineman-Ross method for the determination of the copolymer parameters, a conversion of less than 5% must be guaranteed, which in this case was verified with kinetics probes and the respective analysis by NMR spectroscopy. Before reaching a conversion of 5%, the polymerization was stopped by precipitating the polymers into a non-solvent. The polymers were then centrifuged, redissolved, and precipitated/centrifuged again and dried under vacuum. Due to the risk of crosslinking elevated temperatures were avoided during drying. The composition of the monomers (equation (1)) was determined by exact weighing, and the composition of the polymers (equation (2)) was determined by integrating the specific polymer signals for the various repeating units in ^{1}H-NMR spectra (see SI Figure S19). If these values are now plotted graphically according to equation (3), the values r_1 and r_2 can be determined from the slope and the intercept of the linear fits, respectively (see SI Figure S6/S7).

$$composition\ monomer\ f = \frac{[a]}{[b]} \tag{1}$$

$$composition\ polymer\ F = \frac{[A]}{[B]} \tag{2}$$

$$\frac{f(1-F)}{F} = -r_1\frac{f^2}{F} + r_2 \tag{3}$$

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Copolymerization VME-*co*-Styrene

a)

b) $f(1-F)/F = -0.04\ f^2/F + 5.88$
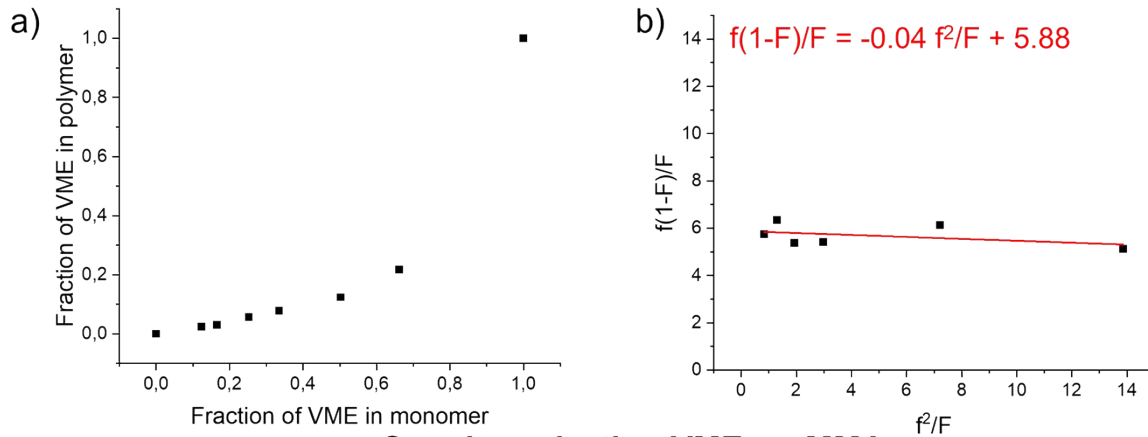
Copolymerization VME-*co*-MMA

c)

d) $f(1-F)/F = -0.07\ f^2/F + 0.48$
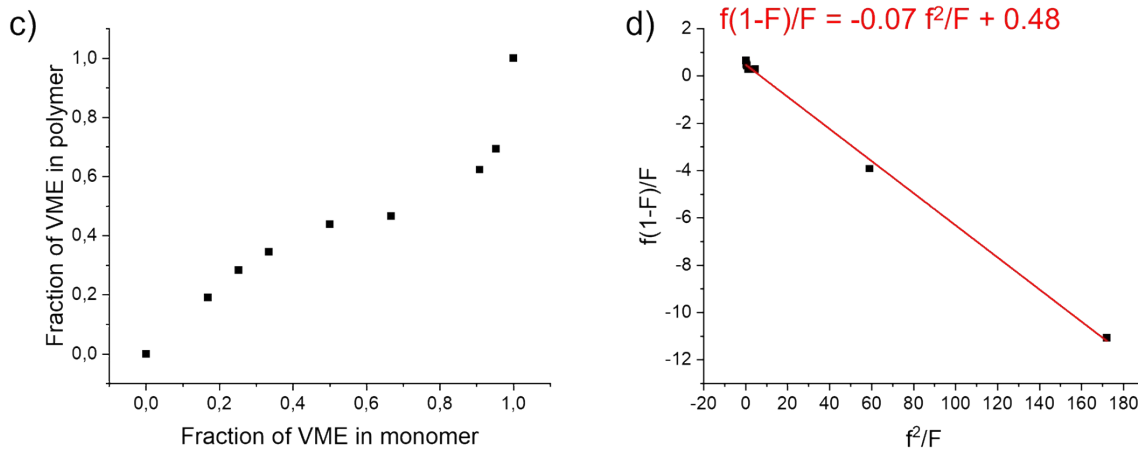
Copolymerization VME-*co*-BA

e)
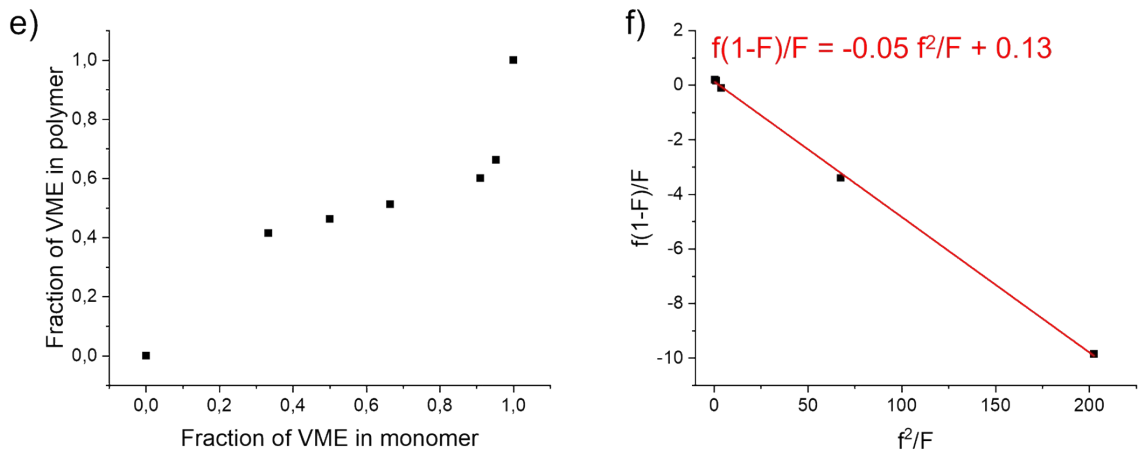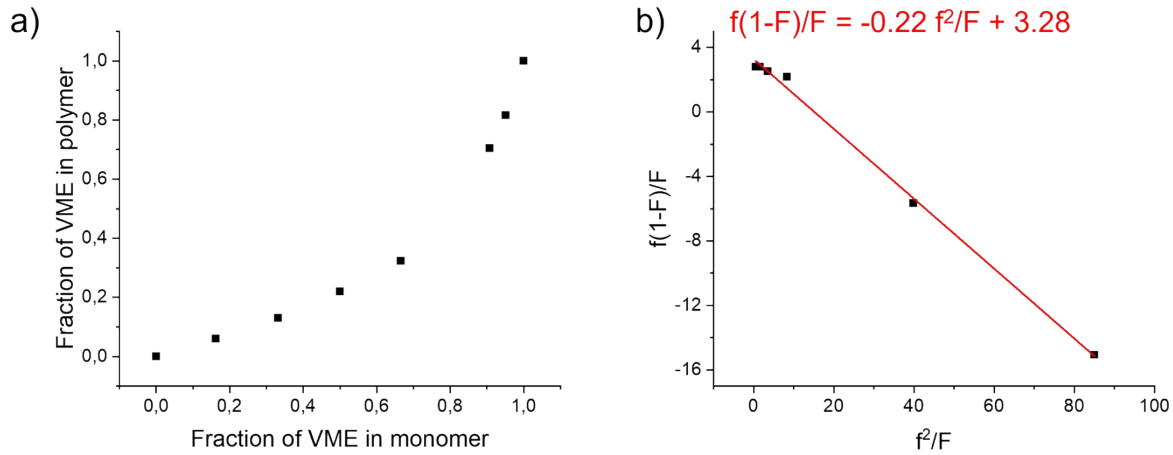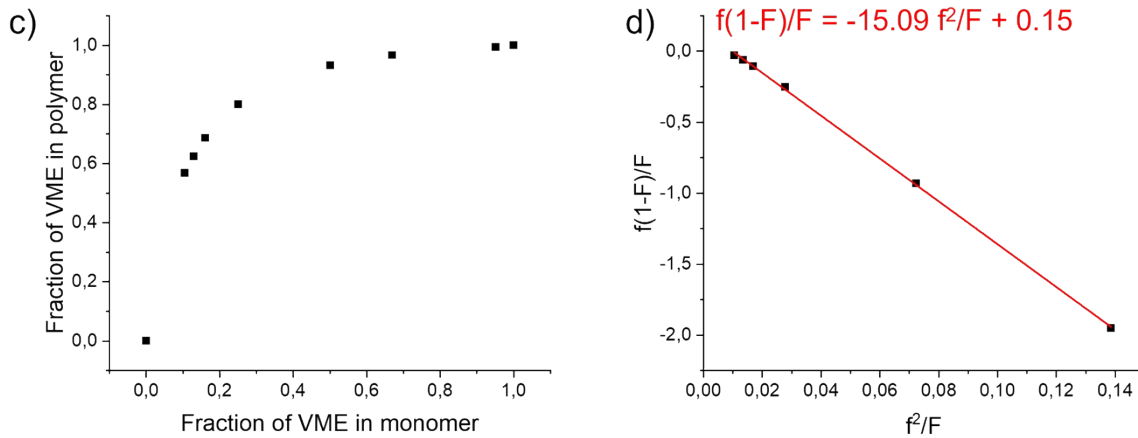
f) $f(1-F)/F = -0.05\ f^2/F + 0.13$

Figure S6: Determination of the copolymer parameters *via* Finemann-Ross method of the copolymerization of a/b) VME-*co*-Styrene c/d) VME-*co*-MMA e/f) VME-*co*-BA.

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Copolymerization VME-*co*-VP

a)

b)

f(1-F)/F = -0.22 f²/F + 3.28

Copolymerization VME-*co*-VA

c)

d)

f(1-F)/F = -15.09 f²/F + 0.15

Figure S7: Determination of the copolymer parameters *via* Finemann-Ross method of the copolymerization of a/b) VME-*co*-VP c/d) VME-*co*-VA.

From the copolymer parameters calculated for the copolymerization with styrene, the *Q*- and *e*-values could be determined *via* equations (4) and (5), where *Q* describes the reactivity of the monomer (resonance stabilization) and *e* the polarity, which varies for each monomer due to the effect of the functional groups on the vinyl group. This allows the new monomer to be classified and compared with other monomers.

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{P_1 Q_1 exp(-e_1 e_1)}{P_1 Q_2 exp(-e_1 e_2)} = \frac{Q_1}{Q_2} exp(-e_1(e_1 - e_2))$$

(4)

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$$r_2 = \frac{Q_1}{Q_2} exp(- e_1(e_1 - e_2))$$

(5)

$Q = 0.45$

$e = -2.0$
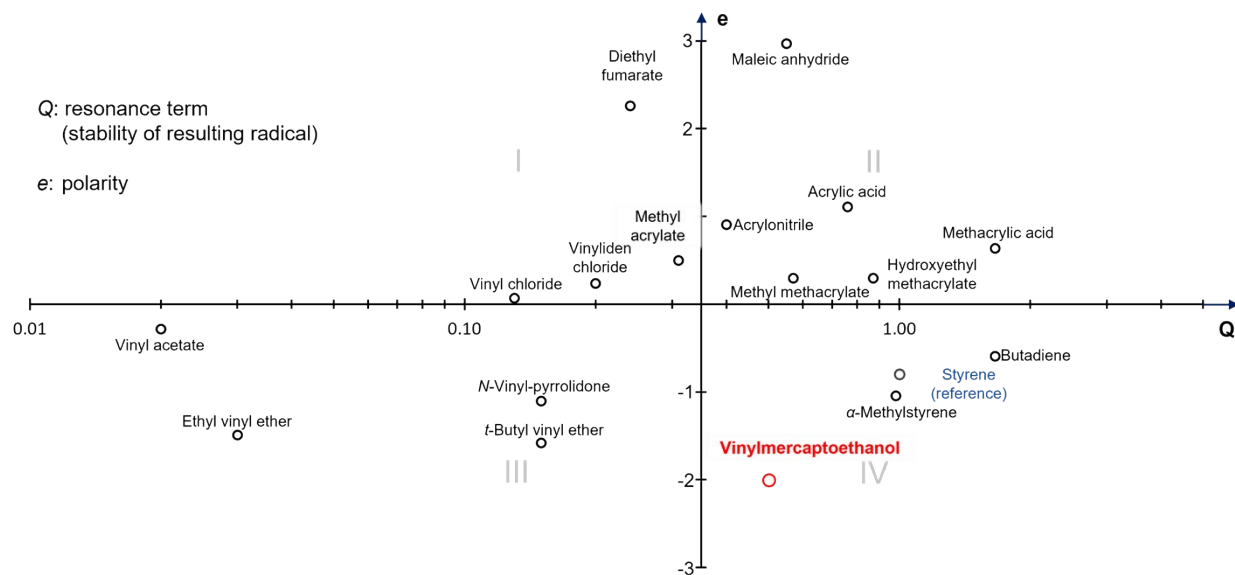
Figure S8: Q-e Scheme with different monomers.[1]
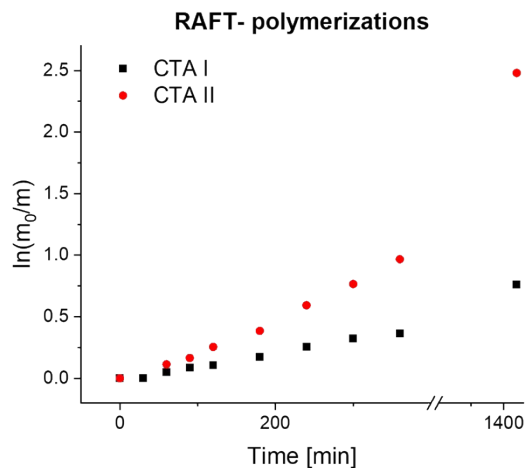
RAFT-homopolymerization

Figure S9: Ln (m$_0$/m) vs. reaction time for different RAFT-polymerizations with CTA I and CTA II at 65 °C.
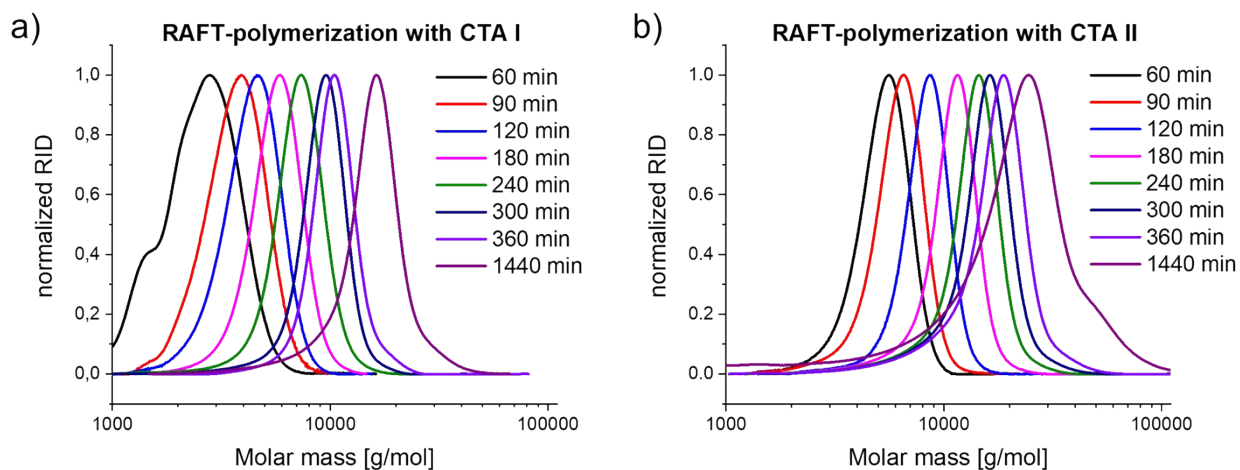

Figure S10: SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) traces of the kinetic samples taken after 60 min, 90 min, 120 min, 240 min, 300 min, 360 min and 1440 min from the RAFT-polymerization with a) CTA I, b) CTA II at 65 °C.
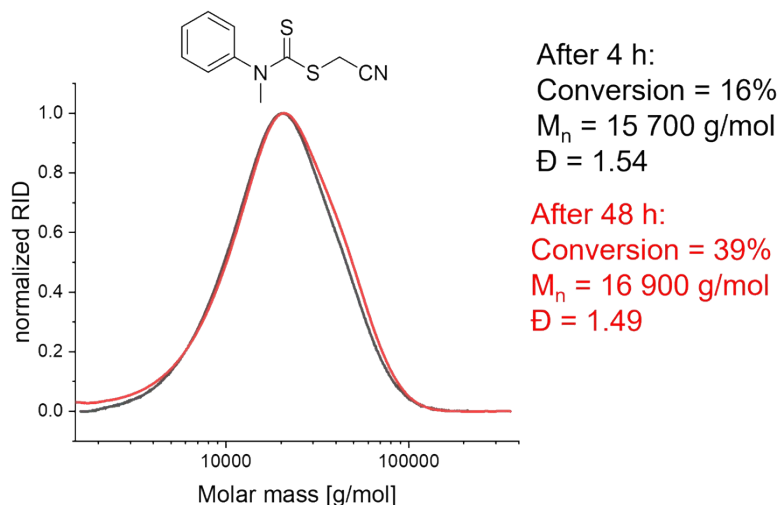
Figure S11: SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) traces of the kinetic samples taken after 4 h and 48 h from the polymerization with a carbamate-RAFT agent.
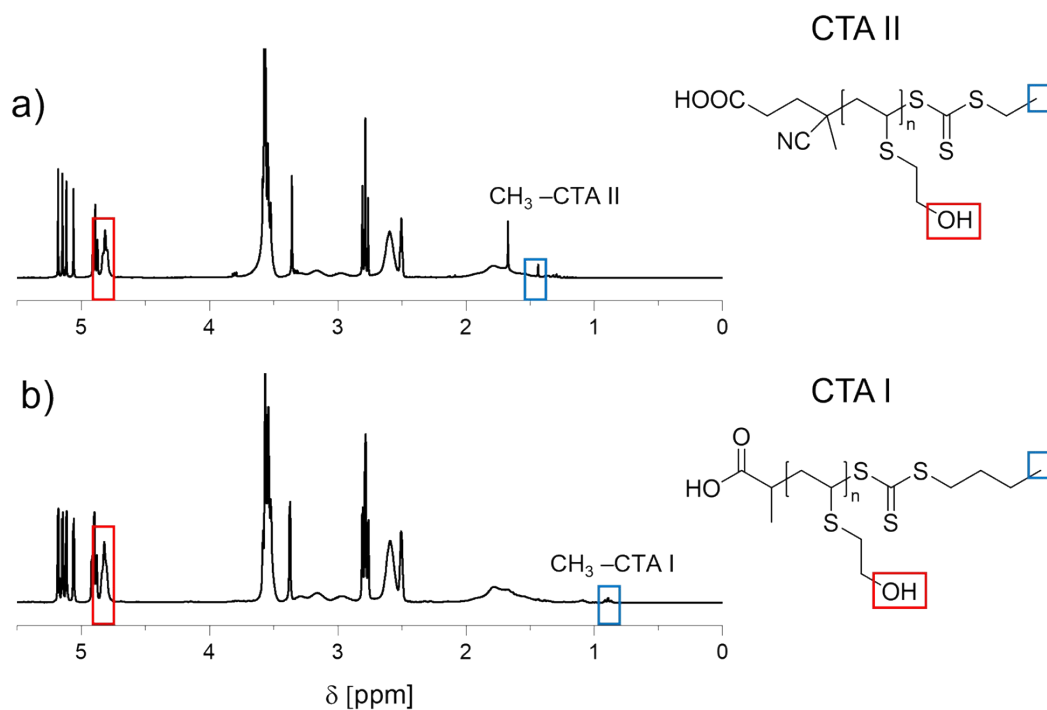
Determination of M_n with ^{1}H-NMR spectrocopy:

Figure S12: ^{1}H-NMR spectra (300 MHz, DMSO-d$_6$) of the kinetic samples of the RAFT polymerization with a) CTA II after 6 h and b) CTA I after 24 h.

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Table S7: Determination of M_n *via* the integrals of the protons in the NMR spectra.

RAFT polymerization	Integral CTA group	Integral OH-group	Repeating units	M_n [g/mol]
CTA I	3	55.63	56	6000
CTA II	3	65.56	66	7100

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RAFT-copolymerizations
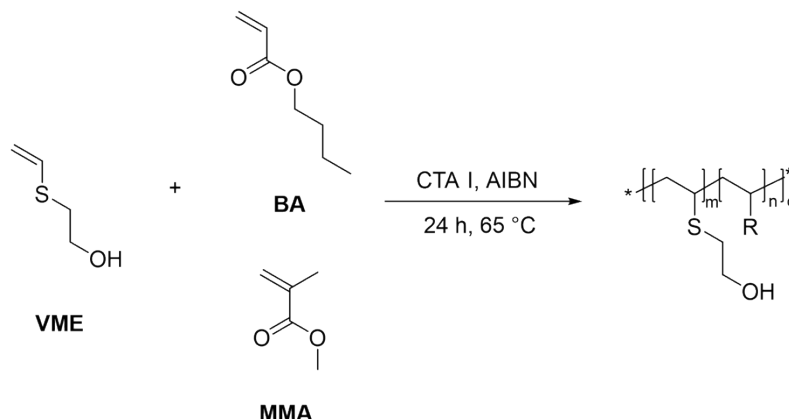
Scheme S1: Synthesis of random copolymers using RAFT.

Table S8: Conversions, molar masses (M_n) and dispersities (Đ) of the copolymers obtained from RAFT copolymerizations with different ratios of the monomers.

	Ratio VME: BA pre-weight	Conversion VME[a]	Conversion BA[a]	M_n [g mol^{-1}][b]	Đ[b]	Degree of polymerization (DP$_{calc}$)[c]
R1	3:1	47	100	15 800	1.10	74
R2	2:1	54	100	17 700	1.10	77
R3	1:1	76	88	18 300	1.12	82
R4	0.5:1	93	82	17 500	1.14	88

[a] ^{1}H-NMR (300 MHz, CDCl$_3$) after 24 h, determination *via* standard mesitylene [b] SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) after 24 h, [c] Determination from conversion of the monomers.

Table S9: Conversions, molar masses and dispersities of the copolymers obtained from RAFT copolymerizations with different ratios of CTA I and the monomers.

	Targeted DP	Conversion VME[a]	Conversion *n*-BA[a]	M_n [g mol^{-1}][b]	Đ[b]	DP$_{calc}$[c]
R5	50	76	85	10 400	1.12	40
R3	100	76	88	18 300	1.12	82
R6	200	88	99	36 700	1.12	187

[a] ^{1}H-NMR (300 MHz, CDCl$_3$) after 24 h, determination *via* standard mesitylene [b] SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) after 24 h [c] Determination from conversion of the monomers..
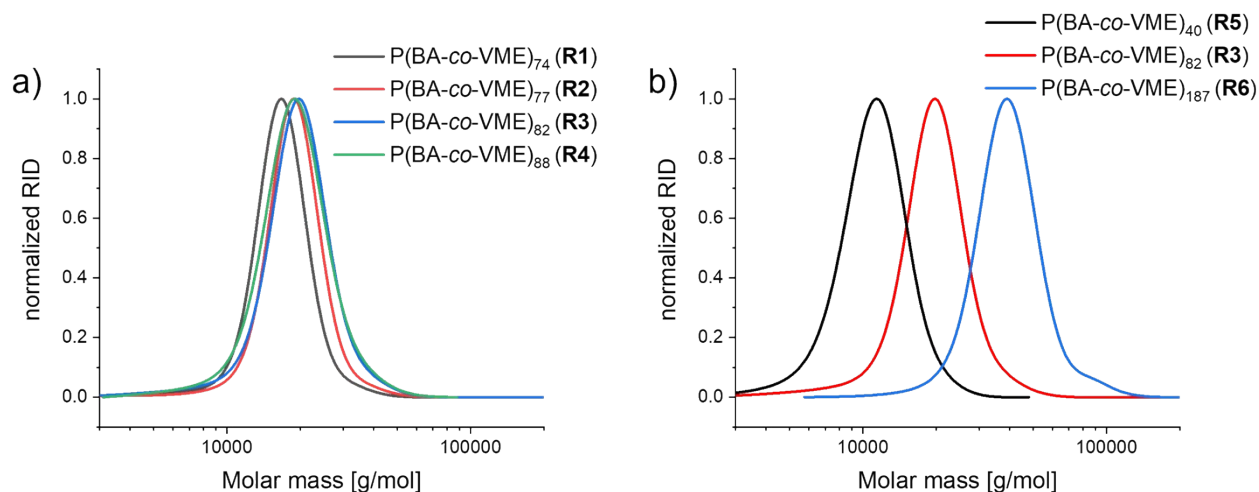
21

Figure S13: SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) traces of the RAFT-polymers R1-R6 after 24 h.

Table S10: Conversions, molar masses and dispersities of the copolymers obtained from the RAFT copolymerizations (CTA I) with different ratios of the monomers.

	Ratio VME: MMA pre-weight	Conversion VME[a]	Conversion MMA[a]	M_n [g mol^{-1}][b]	Đ[b]	DP_{calc}[c]
R7	3:1	61	100	14 900	1.11	81
R8	2:1	58	100	14 200	1.13	79
R9	1:1	63	98	16 500	1.14	81
R10	0.5:1	88	98	16 700	1.14	93

[a] ^{1}H-NMR (300 MHz, DMSO-d$_6$) after 24 h, determination *via* standard mesitylene [b] SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) after 24 h [c] Determination from conversion of the monomers.

Table S11: Conversions, molar masses and dispersities of the copolymers obtained from RAFT copolymerizations with different ratios of CTA I and the monomers.

	Targeted DP	Conversion VME[a]	Conversion MMA[a]	M_n [g mol^{-1}][b]	Đ[b]	DP_{calc}[c]
R11	50	94	99	10 500	1.15	48
R9	100	63	98	16 500	1.14	81
R12	200	61	93	26 700	1.16	154

[a] ^{1}H-NMR (300 MHz, DMSO-d$_6$) after 24 h, determination *via* standard mesitylene [b] SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) after 24 h [c] Determination from conversion of the monomers.
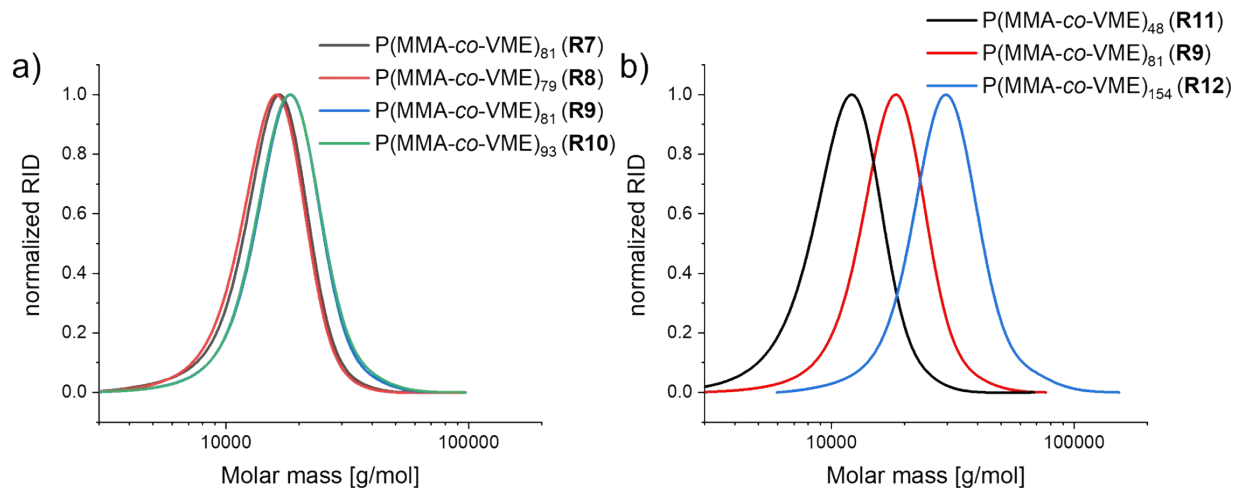
22

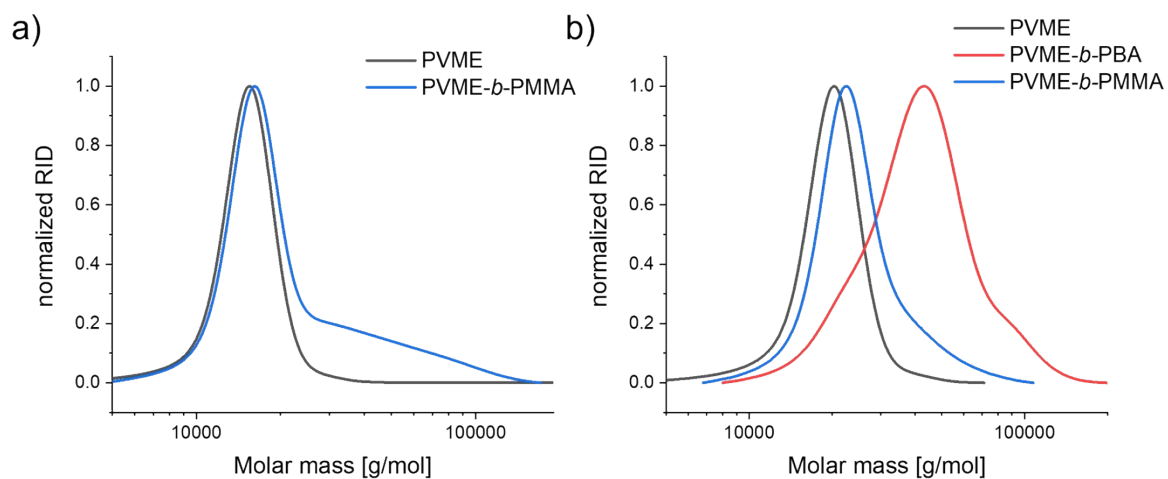**Figure S14: SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) traces of the RAFT-polymers R7-R12 after 24 h.**

Figure S15: SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) traces of a) PVME$_{62}$ and PVME$_{62}$-*b*-PMMA with a reaction time of 4 h and b) of the different *block*-copolymers with a reaction time of 24 h.
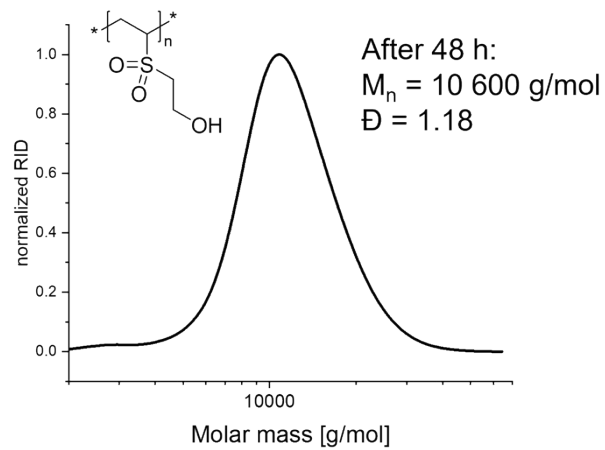
23

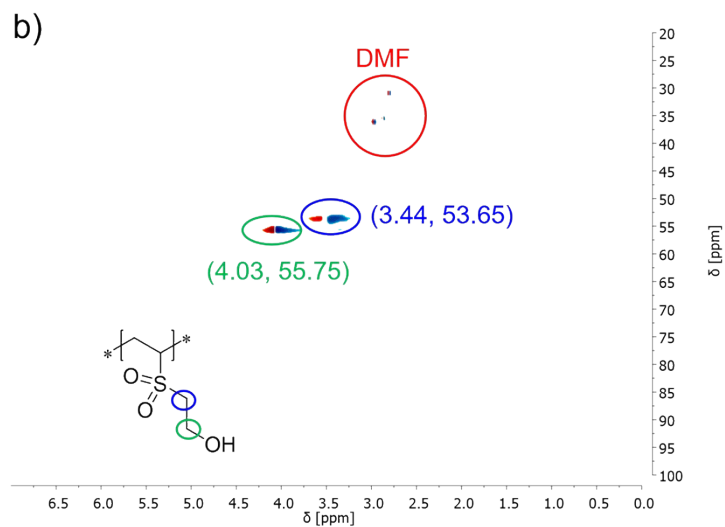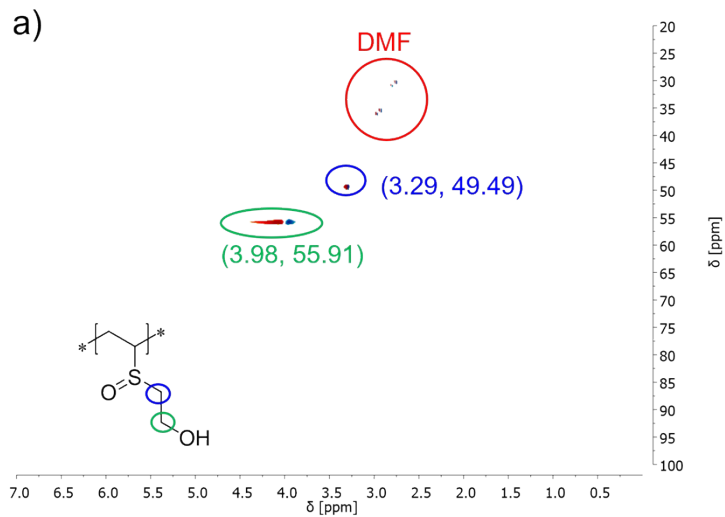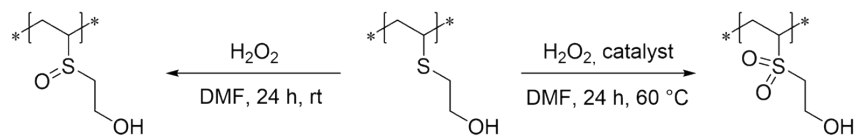**Figure S16: SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) traces of PVSE.**

Figure S17: Zoomed HSQC-NMR-spectra (400 MHz, DMF-d$_7$, 298 K) of the oxidized species prepared a) without any catalyst and b) with the catalyst sodium tungstate.
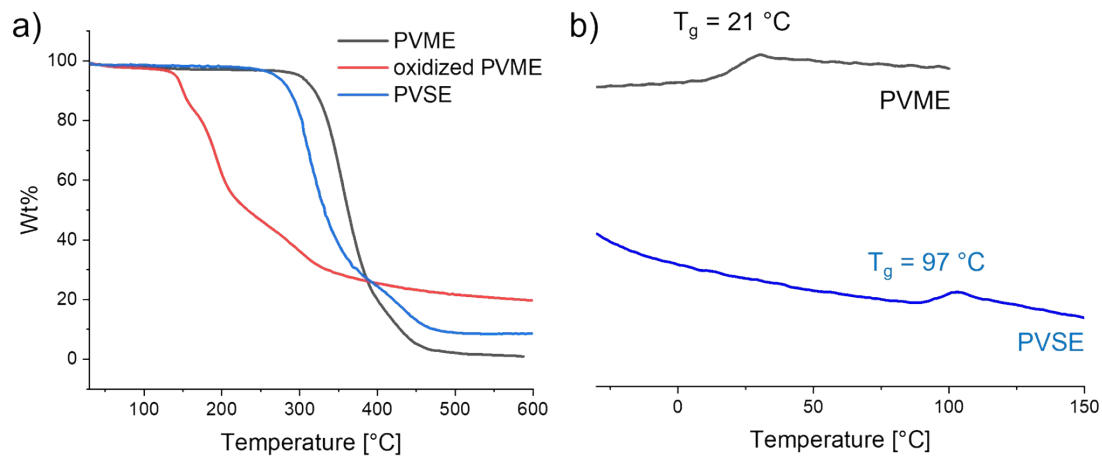
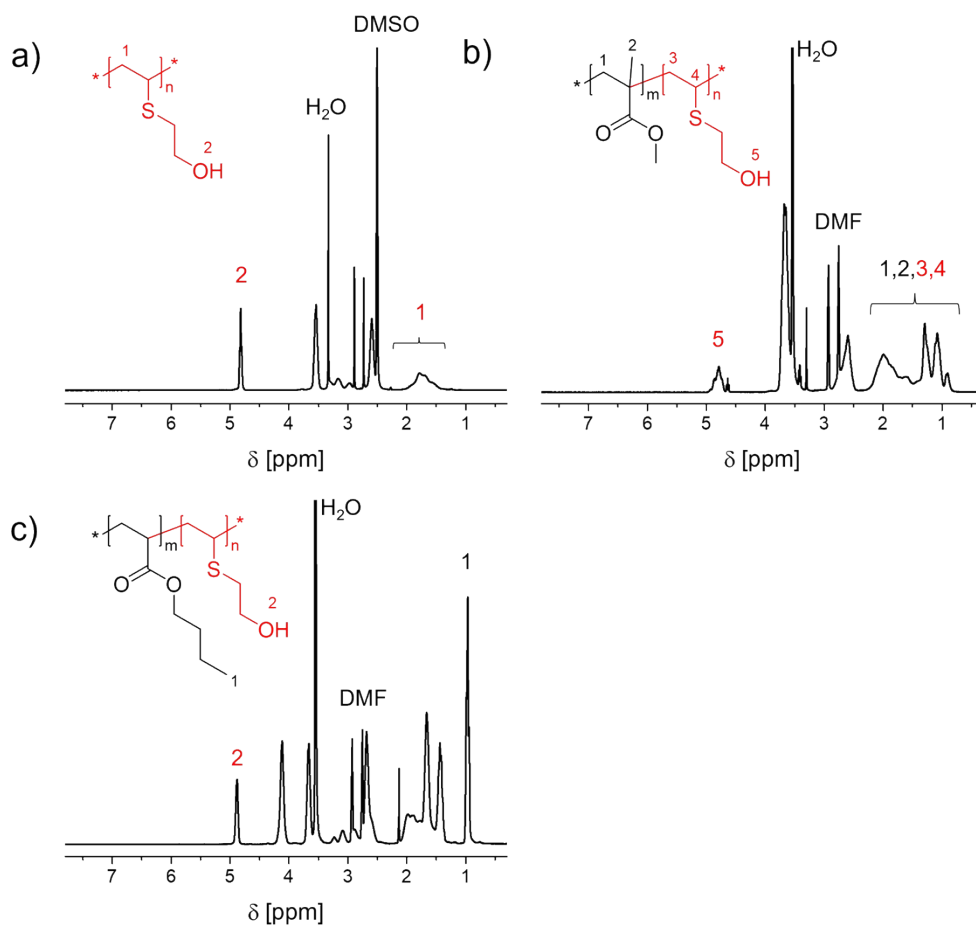**Figure S18: a) TGA-data and b) DSC-data of PVME, the oxidized species of PVME and PVSE.**

Figure S19: a) ^{1}H-NMR (300 MHz, DMSO-d$_6$) spectrum of the homopolymer P1, b) ^{1}H-NMR (300 MHz, DMF-d$_7$) spectrum of the copolymer P3, c) ^{1}H-NMR (300 MHz, DMF-d$_7$) spectrum of the copolymer P4.

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Table S12: Composition, number average molar mass and thermal data of homo and copolymers synthesized *via* free radical polymerizatuion.

Polymer	VME content [%] [a]	M_n [kg mol^{-1}] [b]	Đ [b]	T_g [°C] [c]
PVME **(P1)**	100	146 100	2.3	21
P(VME-*co*-MMA) **(P2)**	19	272 700	2.0	96
P(VME-*co*-MMA) **(P3)**	40	304 800	1.6	69
P(VME-*co*-BA) **(P4)**	45	408 700	2.4	- 17

[a] Determination via ^{1}H-NMR (300 MHz)-spectroscopy after precipitation and purification [b] SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) [c] Determination from DSC measurements.

Table S13: Composition, number average molar mass and thermal data of random copolymers synthesized *via* RAFT polymerization.

Polymer	VME content [%] [a]	M_n [kg mol^{-1}] [b]	Đ [b]	T_g [°C] [c]
P(BA-*co*-VME)$_{40}$ **(R5)**	47	10 100	1.1	- 23
P(BA-*co*-VME)$_{82}$ **(R3)**	44	19 300	1.1	- 25
P(BA-*co*-VME)$_{187}$ **(R6)**	47	38 100	1.1	- 19
P(MMA-*co*-VME)$_{48}$ **(R11)**	57	14 600	1.1	57
P(MMA-*co*-VME)$_{81}$ **(R9)**	44	17 000	1.1	56
P(MMA-*co*-VME)$_{154}$ **(R12)**	44	26 800	1.2	55

[a] Determination via ^{1}H-NMR (300 MHz)-spectroscopy after precipitation and purification [b] SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) [c] Determination from DSC measurements.

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Table S14: Composition, number average molar mass and thermal data of block-copolymers synthesized *via* RAFT polymerization.

Polymer	VME content [%] [a]	M_n [kg mol^{-1}] [b]	Đ [b]	T_g [°C] [c]
PVME$_{62}$ **(R13)**	100	14 600	1.1	12
PVME$_{62}$-*b*-PBA$_{83}$ **(R14)**	43	22 100	1.1	- 48
				7
PBA$_{92}$ **(R15)**	0	13 100	1.1	- 53
PBA$_{92}$-*b*-PVME$_{21}$ **(R16)**	19	30 700	1.1	- 52
				13
PMMA$_{96}$ **(R17)**	0	11 800	1.1	95
PMMA$_{96}$-*b*-PVME$_{32}$ **(R18)**	25	18 200	1.1	109

[a] Determination via ^{1}H-NMR (300 MHz)-spectroscopy after precipitation and purification [b] SEC (DMAc (+ 0.21 wt.% LiCl), PMMA standards) [c] Determination from DSC measurements.
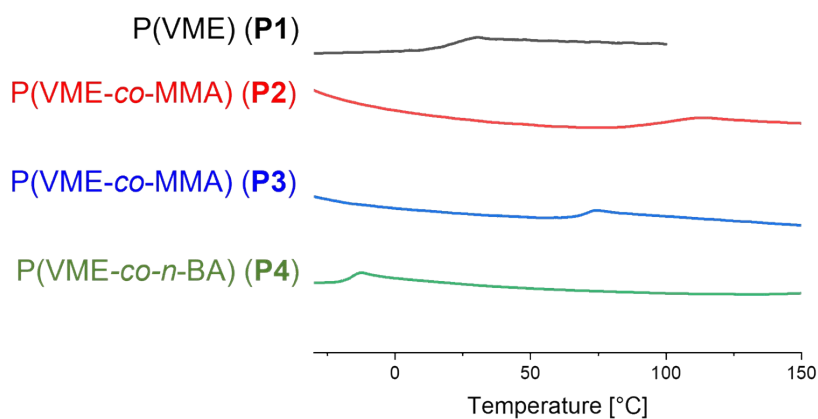
29

P(VME) (**P1**)

P(VME-*co*-MMA) (**P2**)

P(VME-*co*-MMA) (**P3**)

P(VME-*co*-*n*-BA) (**P4**)

Temperature [°C]

Figure S20: DSC-data of homo- and copolymers P1-P4 synthesized *via* free radical polymerization.

a)

P(BA-*co*-VME)$_{40}$ (**R5**)

P(BA-*co*-VME)$_{82}$ (**R3**)

P(BA-*co*-VME)$_{187}$ (**R6**)

Temperatur [°C]

b)

P(MMA-*co*-VME)$_{48}$ (**R11**)

P(MMA-*co*-VME)$_{81}$ (**R9**)
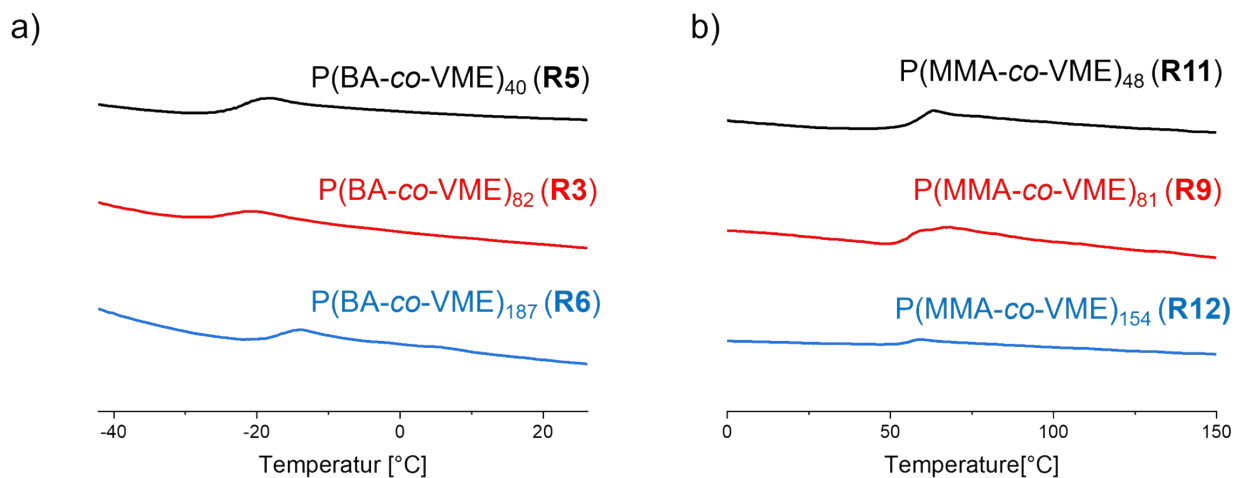
P(MMA-*co*-VME)$_{154}$ (**R12**)

Temperature[°C]

Figure S21: DSC-data of the a) P*(*BA-*co*-VME) copolymers R3/5/6 and the b) P(MMA-*co*-VME) copolymers R9/11/12 synthesized *via* RAFT polymerization.
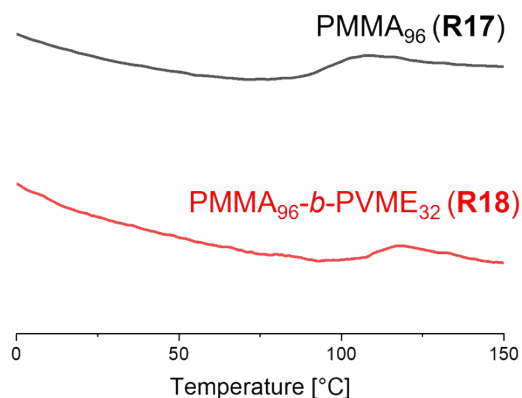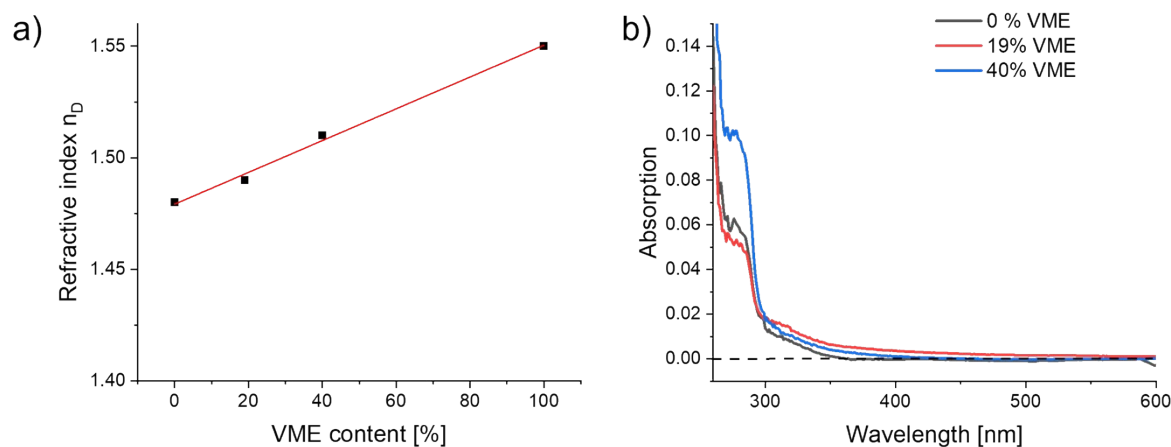
30

Figure S22: DSC-data of the copolymers R17 and R18.

Figure S23: a) Plot of the refractive index *vs.* the VME content in the polymer b) UV-Vis spectra of the polymer with different amount of VME.

Table S15: Optical and mechanical properties of the different homo-and copolymers.

Copolymer	n_D (632.8 nm)[a]	E- modulus [MPa]	Hardness [MPa]	Creep [nm]
PMMA	1.48	3136 ± 125[b]	115 ± 2.6[b]	65 ± 2[b]
P(VME-*co*-MMA) **(P2)**	1.49	2678 ± 93[b]	100 ± 2.8[cb]	72 ± 1[b]
P(VME-*co*-MMA) **(P3)**	1.51	3209 ± 78[b]	99 ± 1.1[b]	65 ± 2[b]
P(VME-*co*-BA) **(P4)**	1.52	2.5 ± 0.3[c]	0.1 ± 0.01[c]	378 ± 14[c]

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PVME **(P1)**	1.55	4.4 ± 0.3^{c}	0.09 ± 0.003^{c}	977 ± 16^{c}

[a] Determination *via* ellipsometry measurements [b] Determination *via* nano-indenter measurements with a load of 1 mN [c] Determination nano-indenter measurements with a load of 0.3 mN

1.   J. Brandrup, E. H. Immergut and W. A. Grulke, *Polymer Handbook*, John Wiley & Sons, Inc., Hoboken, New Jersey, 1999.
2.   G. Beadie, M. Brindza, R. A. Flynn, A. Rosenberg and J. S. Shirk, *Appl. Opt.*, 2015, **54**, F139-F143.

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