Uniting group-transfer and ring-opening polymerization – block copolymers from functional Michael-type monomers and lactones

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1. GENERAL EXPERIMENTAL

All reactions and polymerizations with moisture and air-sensitive reactants were carried out in a MBraun LabMaster120 glovebox filled with argon 4.6 from Westfalen or using standard Schlenk techniques. All glassware was heat-dried prior to use. All chemicals were purchased from Sigma-Aldrich, ABCR, or TCI Europe and used without further purification unless otherwise stated. Dichloromethane, tetrahydrofuran, toluene, and pentane were dried using an MBraun SPS-800 solvent purification system and stored over 3 Å molecular sieve. 2-Vinylpyridine and ε-caprolactone were dried over CaH_2 for several days and distilled prior to use. (-)-Menthide was crystallized from a concentrated solution in dried toluene and was purified via two-fold sublimation for drying and purification. The symmetric 2-methoxyethylaminobisphenol ligand[1], catalyst precursors $Y(CH_2TMS)_3(thf)_2$[2] and $[(ONOO)^{tBu}Y(CH_2TMS)(thf)]$[3], catalysts $[(ONOO)^{tBu}Y(sym\text{-}col)(thf)]$[4] and $[((ONOO)^{tBu}Y(thf))_2(TMPy)]$[5] as well as (-)-menthide[6,7] were prepared according to literature procedures.

NMR spectra were recorded on a Bruker AV-400HD spectrometer. ^1H (400 MHz), ^{13}C (125 MHz) and ^{31}P (162 MHz). NMR spectroscopical shifts δ were reported in ppm relative to the residual proton or carbon signal of the deuterated solvent. Deuterated solvents ($CDCl_3$, benzene-d_6) were purchased from Sigma-Aldrich or Deutero and dried over 3 Å molecular sieves prior to use. DOSY NMR spectra (RT, 16 scans) were transformed with MestreNova software using the Bayesian DOSY Transform with a resolution factor of 5.00 and 5 repetitions, adapting the minimum and maximum according to the sample and with 128 points in diffusion dimension. Molecular weights and polydispersity of the polymers were determined by triple detection using two-angle light scattering at 15 ° and 90 ° coupled with a viscometer and a refractive index detector in N,N-dimethylformamide with 25 mmol/L LiBr as eluent at 30 °C on a Agilent GPC50 equipped

with two Agilent PolarGel-M columns; for absolute molecular weight (triple detection) determination of pure P2VP aliquots and homopolymers, the refractive index increment of P2VP $(dn/dc = 0.149 \text{ mL/g})$[8] was used. For relative molecular weight (single detection) determination, poly(methyl methacrylate) calibration standards were used. Lyophilization was performed on a VaCO 5-II-D at a pressure of 2 mbar and -90 °C condenser temperature from either 1,4-dioxane or benzene. Elemental analysis was performed by the Laboratory of Microanalytics at the Institute of Inorganic Chemistry at the Technical University of Munich, Department of Chemistry, Catalysis Research Center. Dynamic light scattering was performed using a Malvern Zetasizer Nano ZS in Millipore water with adjusted pH values (prepared by addition of 0.1 M HCl) and a polymer concentration of 0.5 mg/mL, each sample is filtered using a 0.45 µm PTFE syringe filter. Each sample was measured three times with 12 measurement points and the micelle diameter was averaged. Dynamic scanning calorimetry (DSC) was performed on a DSC Q2000 from TA instruments in exo-down mode with a heat rate of 10 K/min in a temperature range of -150 – 240 °C with 2 – 10 mg sample. Three cycles were recorded and the transition temperatures were determined from the third cycle (heating, cooling, heating) using TA Universal Analysis. Powder X-Ray diffraction measurements were performed on a *PANalytical Empyrean* diffractometer in Bragg-Brentano geometry equipped with a *PANalytical PIXcel 1D* detector. For the measurements, Cu K_α radiation with a voltage of 45 kV and an intensity of 40 mA is used with $\lambda_1 = 1.5406$ Å and $\lambda_1 = 1.5444$ Å $(I_1/I_2 = 0.5)$ in the range of 5 ° to 60 ° (2Θ). Obtained data was processed using *TopSpin* Software by *Malvern Panalytical*, stripping Cu K_α using *Rachingers* method and background determination was done using the *Sonneveld* and *Visser* method. The data is normalized for comparison reasons. Electrospray Ionization Mass Spectrometry (ESI-MS) was

measured using a Thermo Fisher Scientific Exactive Plus Orbitrap in positive mode in HPLC acetonitrile straight from the reaction mixture without quenching.

2. GENERAL COPOLYMERIZATION PROCEDURE

For the copolymerization of 2VP and CL, 13.5 µmol catalyst **2** or **3** were dissolved in 4 mL dichloromethane. 2VP was added and the polymerization was stirred at room temperature for 60 – 90 min. 0.1 mL as aliquot was removed from the mixture and quenched by addition of 0.3 mL wet CDCl$_3$. The respective amount of CL relative to 2VP was added immediately and the polymerization was stirred for additional 60 min. Afterwards, another 0.1 mL aliquot was withdrawn and quenched with wet CDCl$_3$ before adding 0.5 mL ethanol to the polymerization mixture quenching the reaction. The polymer was precipitated from 50 mL pentane, centrifuged, the solution was decanted off and the residual polymer was freeze-dried from 1,4-dioxane or benzene. The aliquots were subjected to ^{1}H-NMR spectroscopy to determine the conversions of 2VP and CL and SEC analysis to determine the absolute molecular weight and polydispersity of the P2VP block as well as the relative molecular weight and the polydispersity of the copolymer.

For the copolymerization of 2VP and M, 6.75 µmol catalyst **2** or **3** were dissolved in 2 mL toluene. 2VP was added and the polymerization was stirred at room temperature for 90 – 120 min. 0.1 mL as aliquot was removed from the mixture and quenched by addition of 0.3 mL wet CDCl$_3$. The respective amount of M relative to 2VP was added immediately and the polymerization was stirred for additional 48 hours. Afterwards, another 0.1 mL aliquot was withdrawn and quenched with wet CDCl$_3$ before adding 0.5 mL ethanol to the polymerization mixture quenching the reaction. The polymer was precipitated from 50 mL pentane, centrifuged, the solution was decanted off and the residual polymer is dried at 60 °C under vacuum overnight. The aliquots were subject to ^{1}H-NMR spectroscopy to determine the conversions of 2VP and M and SEC analysis to determine the

absolute molecular weight and polydispersity of the P2VP block as well as the relative molecular weight and the polydispersity of the copolymer.

Slight variation from the given general procedure and exact reaction parameters can be found in Table S1 and S2.

3. ACTIVITY MEASUREMENTS

20.5 µmol of catalyst **2** was dissolved in 6 mL toluene and the polymerization was started by addition of 4.07 mmol 2VP while stirring at room temperature. In regular intervals, aliquots of 0.1 mL were removed, quenched by addition of wet $CDCl_3$ and subject to ^{1}H-NMR and SEC analysis revealing the corresponding conversion, molecular weight, and polydispersity. After the polymerization of 2VP was completed, remaining amount of reaction solution was determined by weighing. The polymerization mixture was heated to 70 °C and an equimolar amount of (-)-menthide (2.53 mmol) was added. Again, in regular intervals 0.1 mL aliquots were withdrawn and subjected to ^{1}H-NMR and SEC analysis. Turnover frequencies TOF [h^{-1}] for both polymerizations were determined as steepest slope of conversion over time. The normalized turnover frequency for the P2VP block was determined using TOF* = TOF/I.E. with initiator efficiency I.E. = $M_{n,theo}/M_{n,abs}$ and $M_{n,abs}$ from the last P2VP aliquot. For the PM block, the calculated theoretical molecular weight using the initiator efficiency from block A and assuming 100% initiation efficiency of the P2VP macroinitiator in the (-)-menthide copolymerization is in good correspondence to the actual number of repeating units observed via NMR spectroscopy. In this case the normalized turnover frequency for M copolymerization corresponds to TOF* = TOF.

4. BLOCK COPOLYMERIZATION OF 2VP WITH CL

Table S1: Block copolymerization conditions for 2VP-CL copolymerization synthesized with the monometallic yttrium catalyst **2** (diblock copolymers AB^X) and the bimetallic yttrium catalyst **3** (triblock copolymers BAB^X).

Entry [a]	Feed [Y]/[2VP]/[CL]	Solvent	V_R [b] [mL]	$t_{R,2VP}$ [min]	X_{2VP} [c] [%]	$M_{n,theo,2VP}$ [d] [kg/mol]	I.E. [e] [%]	$t_{R,CL}$ [min]	X_{CL} [f] [%]
AB^1	1/100/100	CH_2Cl_2	3	60	96	7.7	63	60	98
AB^2	1/200/200	CH_2Cl_2	3.5	60	96	21.2	74	60	98
AB^3	1/400/400	CH_2Cl_2	7	120	87	78.8	48	60	97
AB^4	1/300/100	CH_2Cl_2	4	60	85	27.7	47	60	96
AB^5	1/100/300	CH_2Cl_2	4	60	84	7.5	55	90	98
AB^6	1/200/200	thf	4	90	19	3.8	21	60	96
AB^7	1/200/200	toluene	4	75	83	20.6	57	60	99
A^1	1/200/0	CH_2Cl_2	4	60	95	21.2	60	-	-
B^1	1/0/200	CH_2Cl_2	4	-	-	-	-	20	98
BAB^1	2/100/100	CH_2Cl_2	4	60	99	11.8	98	60	97
BAB^2	2/200/200	CH_2Cl_2	4	60	99	20.3	84	60	98
BAB^3	2/400/400	CH_2Cl_2	7	75	93	39.3	69	60	98
BAB^4	2/300/100	CH_2Cl_2	4	120	99	45.9	59	60	97
BAB^5	2/100/300	CH_2Cl_2	4	75	99	9.3	66	60	98

[a] AB^X polymers using monometallic catalyst **2,** BAB^X polymers using bimetallic catalyst **3**, catalyst-monomer ratios, 13.5 µmol catalyst, RT, [b] reaction volume for copolymerization, [c] conversion of 2-vinylpyridine determined via aliquot-^{1}H-NMR [d] theoretical molecular weight $M_{n,theo} = (M_{2VP}$ x $[2VP]/[Y]$ x $X_{2VP})$, [e] initiator efficiency determined via I.E. $= M_{n,theo,2VP}/M_{n,abs,2VP}$, [f] caprolactone conversion determined via aliquot-^{1}H-NMR integration of the CH_2-group in α-position of the ester.
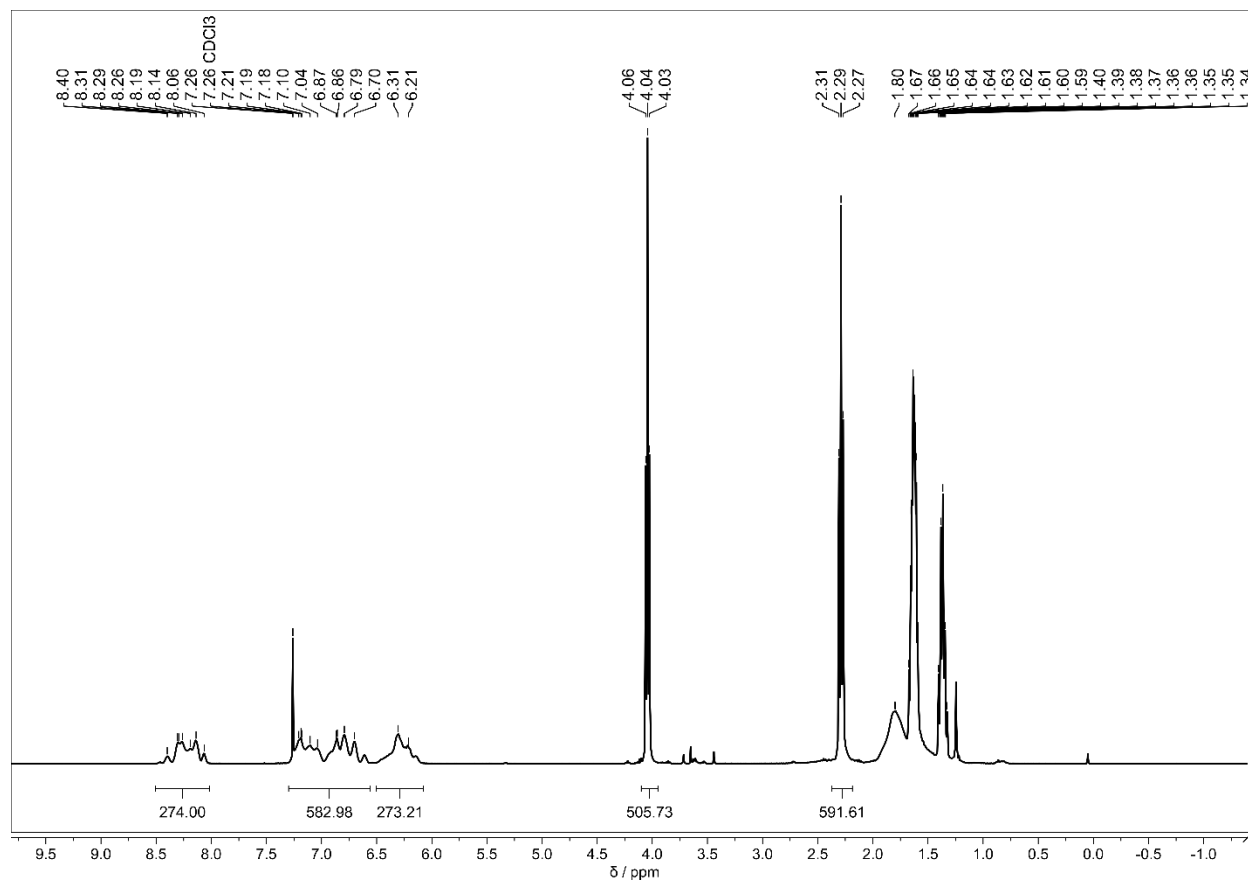
Figure S1: Exemplary ^{1}H-NMR spectrum in CDCl$_3$ from P2VP-*b*-PCL (AB^1, M$_{n,NMR,AB}$ = 57.7 kg/mol, 2VP:CL = 50:50, Đ = 1.46, Table 1, entry 1).

For the calculation of the molecular ratios of 2VP to CL in the copolymer, the integral I$_{2VP}$ (δ = 8.06 – 8.40 ppm) of the proton signal in α-position of the nitrogen atom in the 2VP ring and the integral of the CH$_2$-group signal adjacent to the ester unit I$_{CL}$ (δ = 4.04 ppm) were determined. The ratio of 2VP to CL was then calculated as %$_{2VP}$ = I$_{2VP}$/(I$_{2VP}$+0.5·I$_{CL}$), this method is applicable for both AB and BAB type copolymers. Accordingly, the ratio of CL to 2VP is calculated as %$_{CL}$ = 0.5·I$_{CL}$/(I$_{2VP}$+0.5·I$_{CL}$). The absolute molecular weight of the copolymer is calculated from absolute SEC of the P2VP aliquot and the P2VP:PCL ratio derived from the ^{1}H-NMR spectrum.
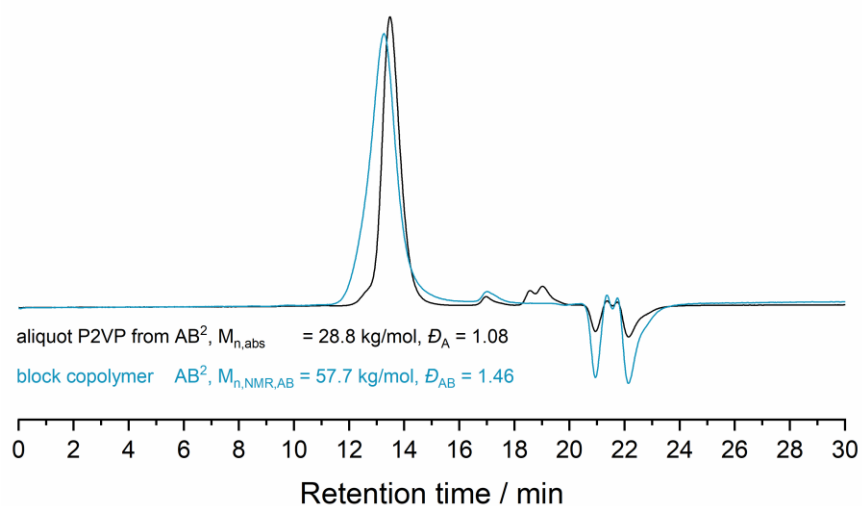
Figure S2: SEC traces from P2VP aliquot (black) and isolated P2VP-*b*-PCL AB diblock copolymer (blue) for AB^2 (Table 1, entry 2).
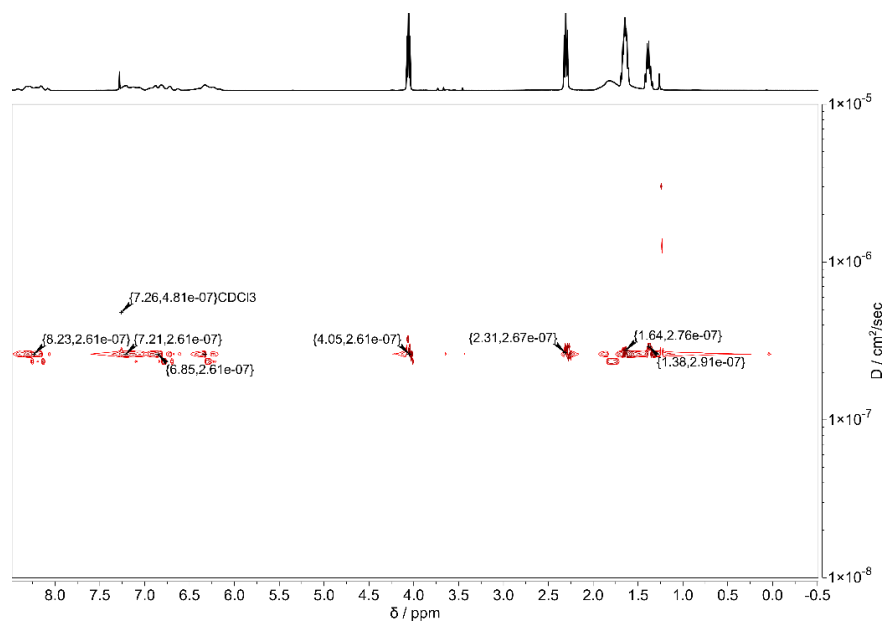

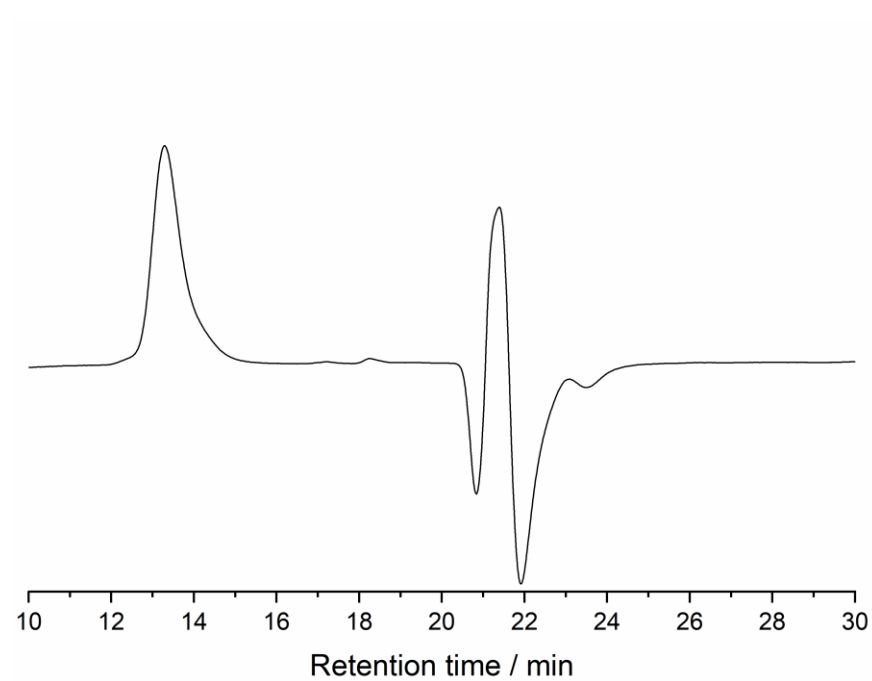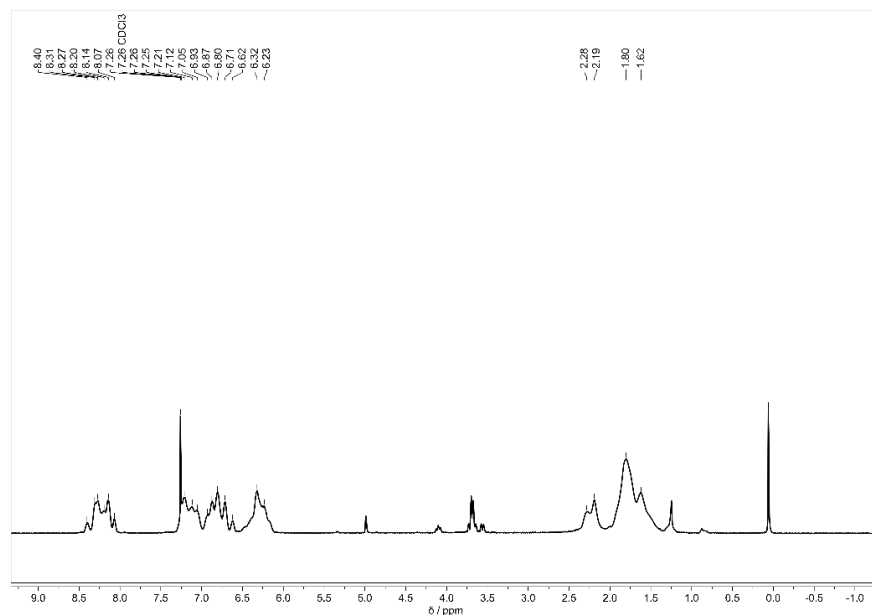Figure S3: DOSY-NMR in CDCl₃ (bottom) for AB^2 (Table 1, entry 2).

Figure S4: ^{1}H-NMR spectrum in CDCl$_3$ of P2VP homopolymer A^1 (Table 1, entry 8).

Figure S5: SEC trace of P2VP homopolymer A^1 (Table 1, entry 8).
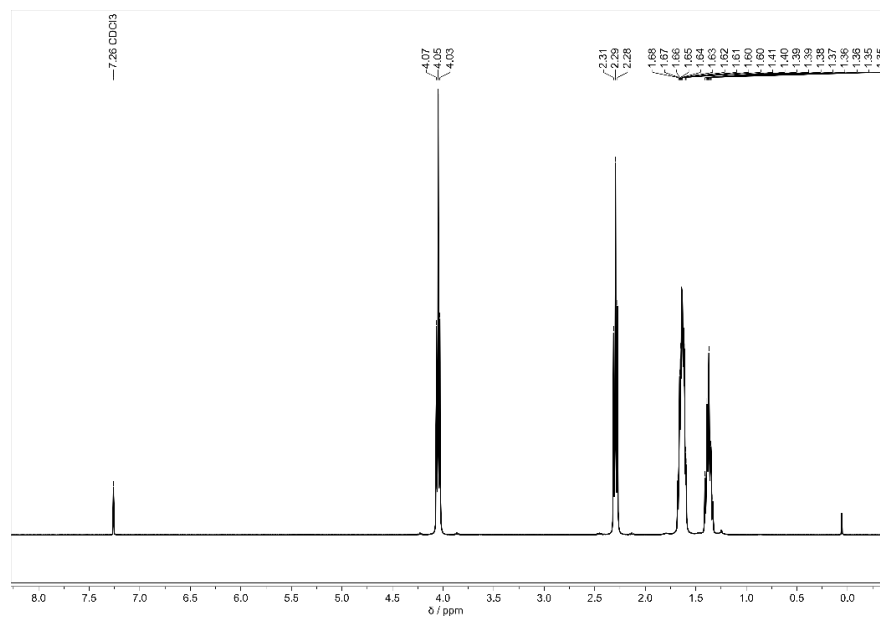
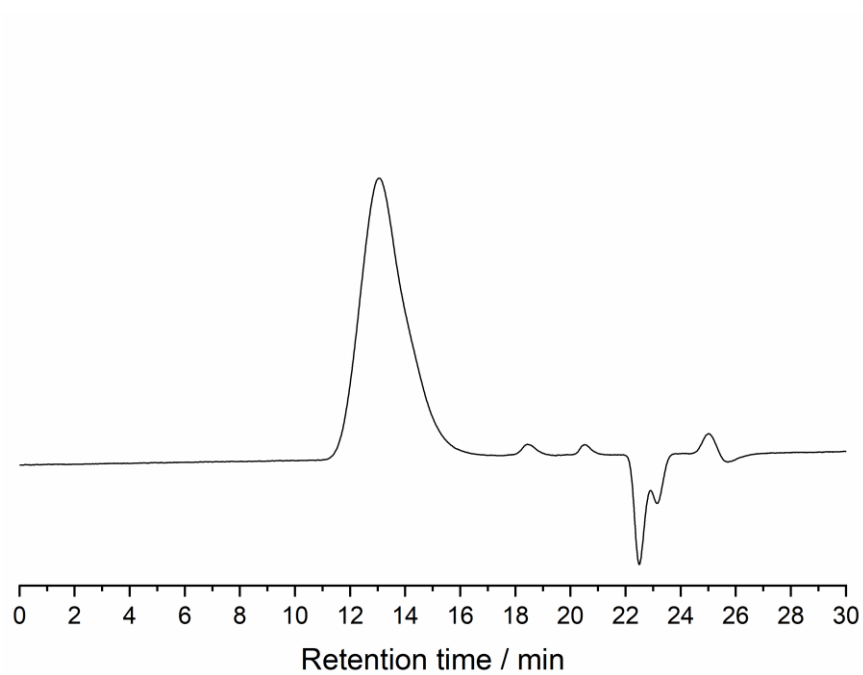Figure S6: ^{1}H-NMR spectrum in CDCl$_3$ of PCL homopolymer B^1 (Table 1, entry 9).

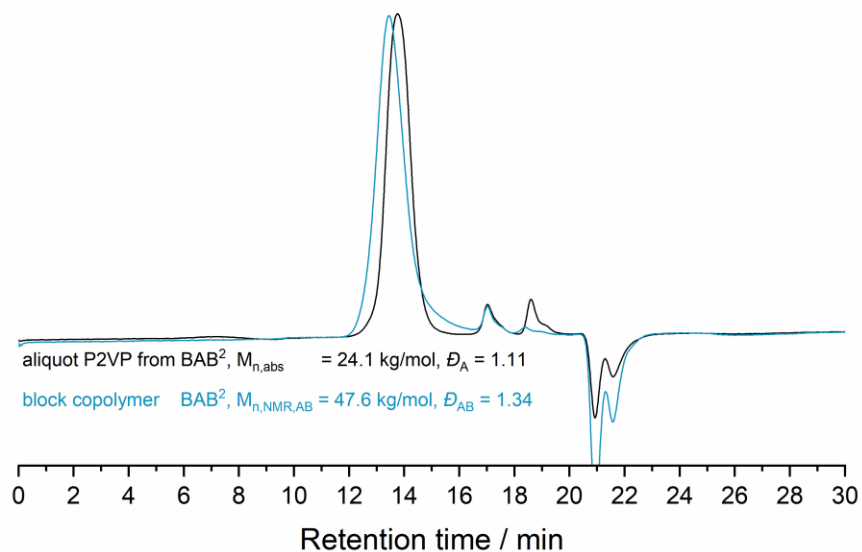Figure S7: SEC trace of PCL homopolymer B^1 (Table 1, entry 9).

Figure S8: SEC traces of P2VP aliquot (black) and isolated P2VP-*b*-PCL triblock copolymer BAB^2 (blue) (Table 1, entry 10).
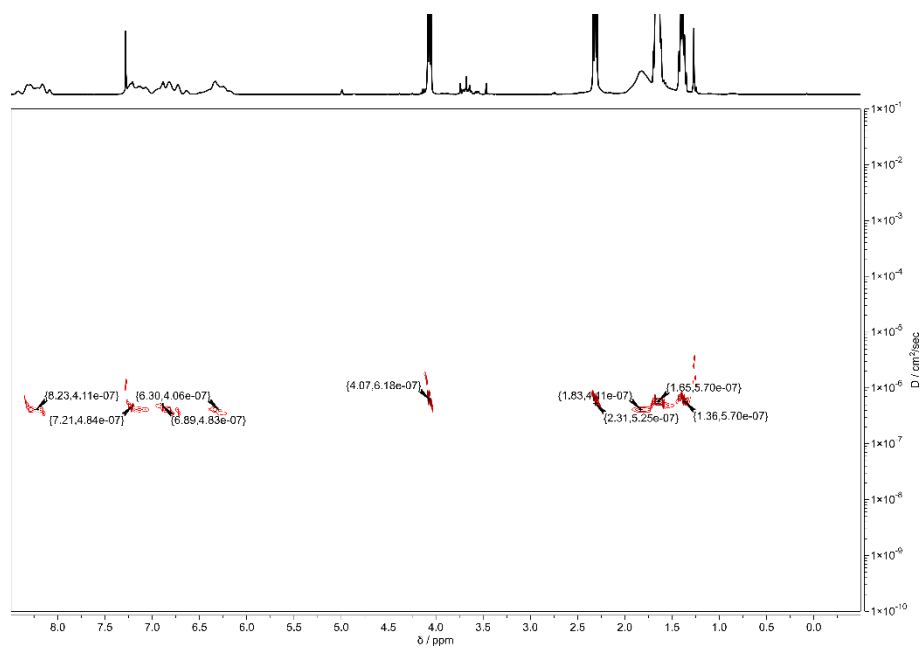

Figure S9: DOSY-NMR spectrum in CDCl$_3$ (bottom) of BAB^2 (Table 1, entry 10).
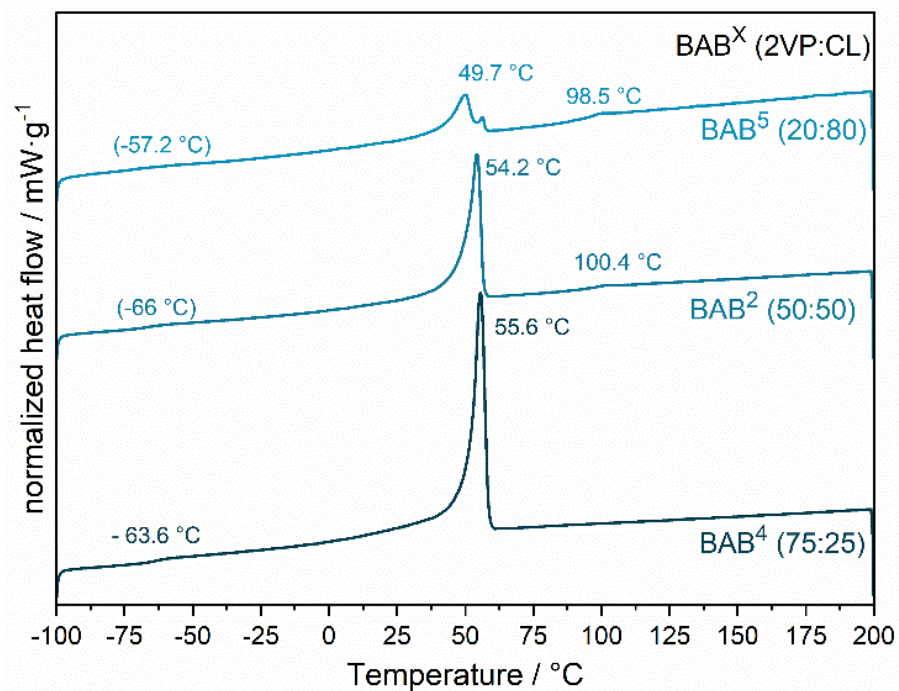
Figure S10: DSC measurements for triblock copolymers BAB[2], BAB[4] and BAB[5] (Table 1, entries 10, 13, 14).
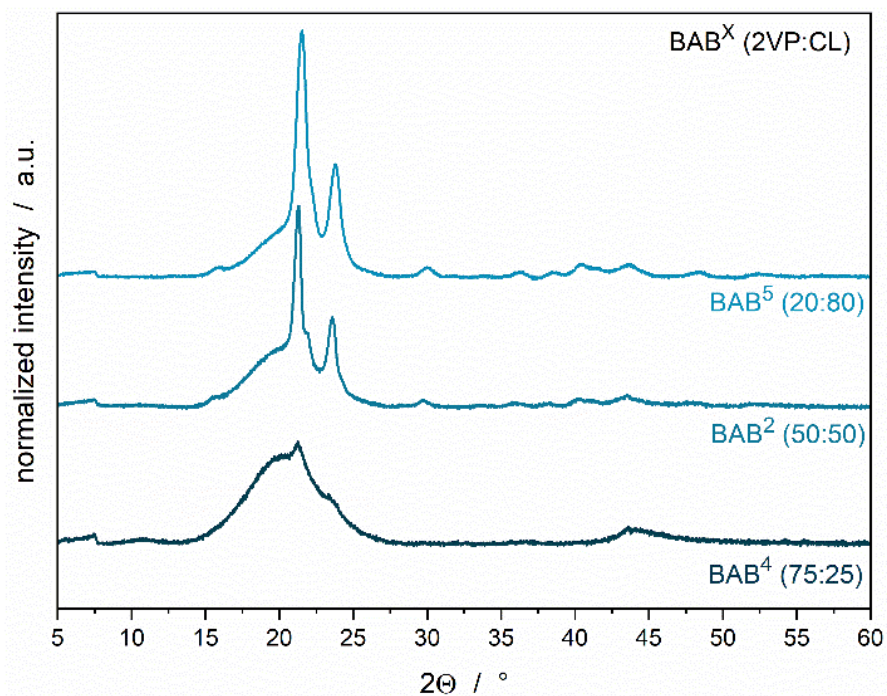

Figure S11: pXRD measurements for triblock copolymers BAB[2], BAB[4] and BAB[5] (Table 1, entries 10, 13, 14).

5. BLOCK COPOLYMERIZATION OF 2VP WITH M

Table S2: Block copolymerization conditions for 2VP-M copolymerization synthesized with the monometallic yttrium catalyst **2** (diblock copolymers AB^X) and the bimetallic yttrium catalyst **3** (triblock copolymers BAB^X).

Entry [a]	Feed [Y]/[2VP]/[CL]	Solvent	V_R [b] [mL]	$t_{R,2VP}$ [min]	X_{2VP} [c] [%]	$M_{n,theo,2VP}$ [d] [kg/mol]	I.E. [e] [%]	$t_{R,M}$ [h]	X_M [f] [%]
AB^8	1/100/100	toluene	2	90	93	9.8	51	48	62
AB^9	1/200/200	toluene	2	90	95	17.0	58	48	65
AB^{10}	1/400/400	toluene	1.5 [g]	120	94	46.1	50	48	4
AB^{11}	1/100/300	toluene	2	90	95	14.2	70	48	30
AB^{12}	1/300/100	toluene	2	90	91	31.5	57	48	65
BAB^6	2/100/100	toluene	2	90	99	13.1	76	48	78
BAB^7	2/200/200	toluene	2	90	99	24.0	82	48	83
BAB^8	2/400/400	toluene	1.5 [g]	90	99	42.3	71	48	80
BAB^9	2/100/300	toluene	2	90	98	13.1	73	48	80
BAB^{10}	1/300/100	toluene	2	90	99	33.8	71	48	70

[a] AB^X polymers using monometallic catalyst **2,** BAB^X polymers using bimetallic catalyst **3**, catalyst-monomer ratios, 6.75 µmol catalyst, [b] reaction volume for copolymerization, [c] conversion of 2-vinylpyridine determined via aliquot-^{1}H-NMR [d] theoretical molecular weight $M_{n,theo} = (M_{2VP} \times [2VP]/[Y] \times X_{2VP})$, [e] initiator efficiency determined via I.E. $= M_{n,theo,2VP}/M_{n,abs,2VP}$, [f] menthide conversion determined via aliquot-^{1}H-NMR integration of the methine protons, [g] 0.75-fold experiment.
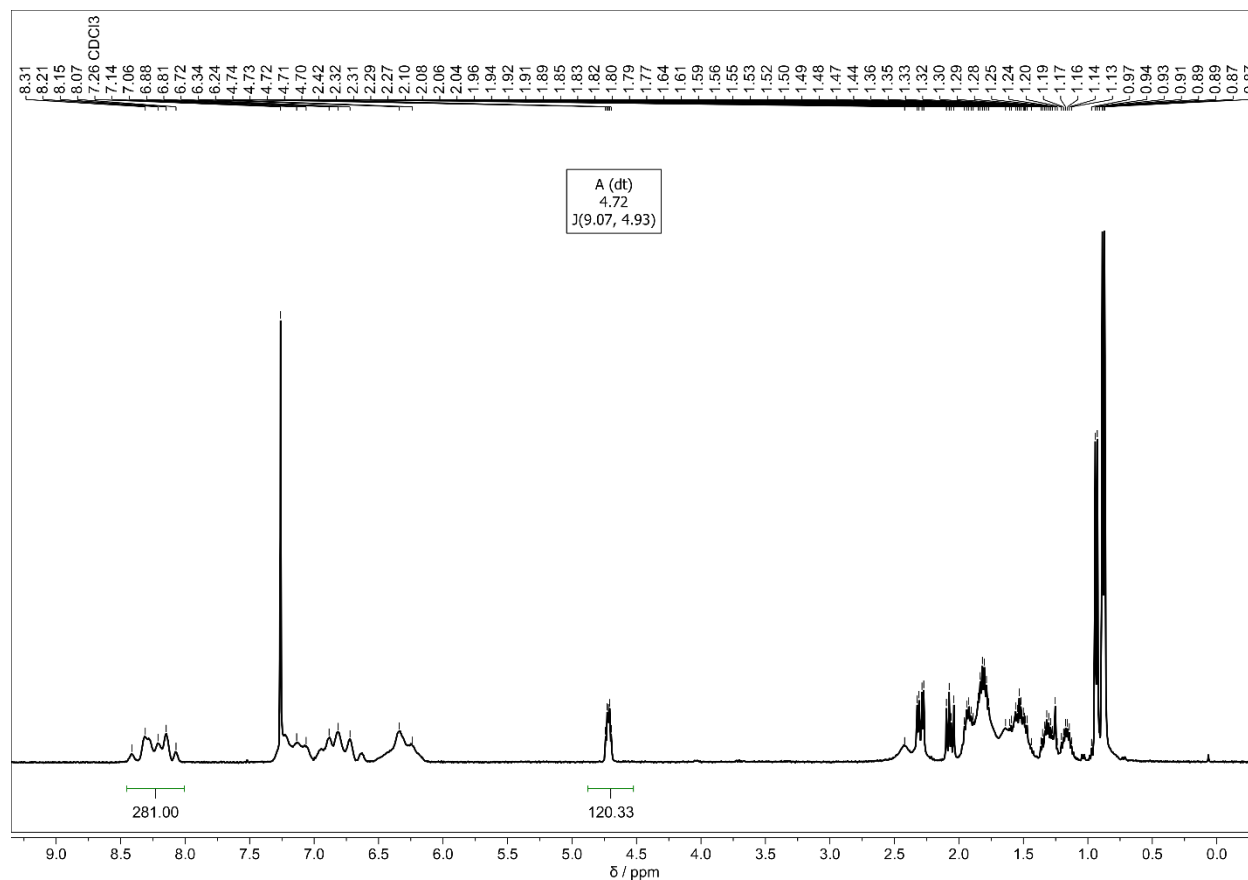
Figure S12: Exemplary ¹H-NMR spectrum in CDCl₃ from P2VP-*b*-PM AB[9] ($M_{n,NMR,AB}$ = 50.0 kg/mol, $Đ_{AB}$ = 1.14, 2VP:M = 75:25, Table 2, entry 2).

For the calculation of the molecular ratios of 2VP to M in the copolymer, the integral I_{2VP} (δ = 8.06 – 8.40 ppm) of the proton signal in α-position of the nitrogen atom in the 2VP ring and the integral of the CH-group signal adjacent to the ester unit I_M (δ = 4.04 ppm) were determined. The ratio of 2VP to M is then calculated as $\%_{2VP} = I_{2VP}/(I_{2VP}+I_M)$, this method is applicable for both AB and BAB type copolymers. Accordingly, the ratio of M to 2VP is calculated as $\%_M = I_M/(I_{2VP}+I_M)$ The absolute molecular weight of the copolymer is calculated from absolute SEC of the P2VP aliquot and the P2VP:PM ratio derived from the ¹H-NMR spectrum.
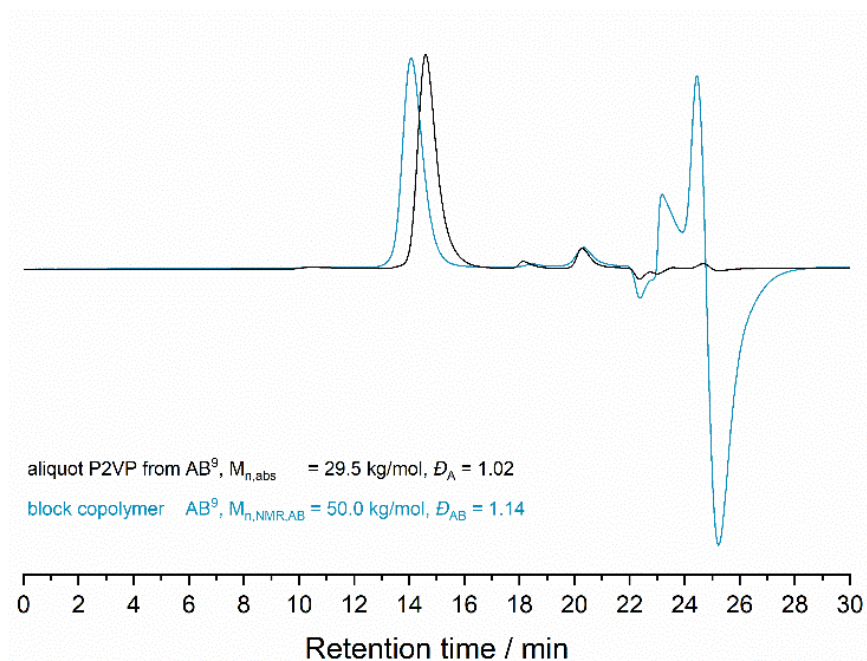
Figure S13: SEC traces of from P2VP aliquot (black) and isolated P2VP-*b*-PM diblock copolymer
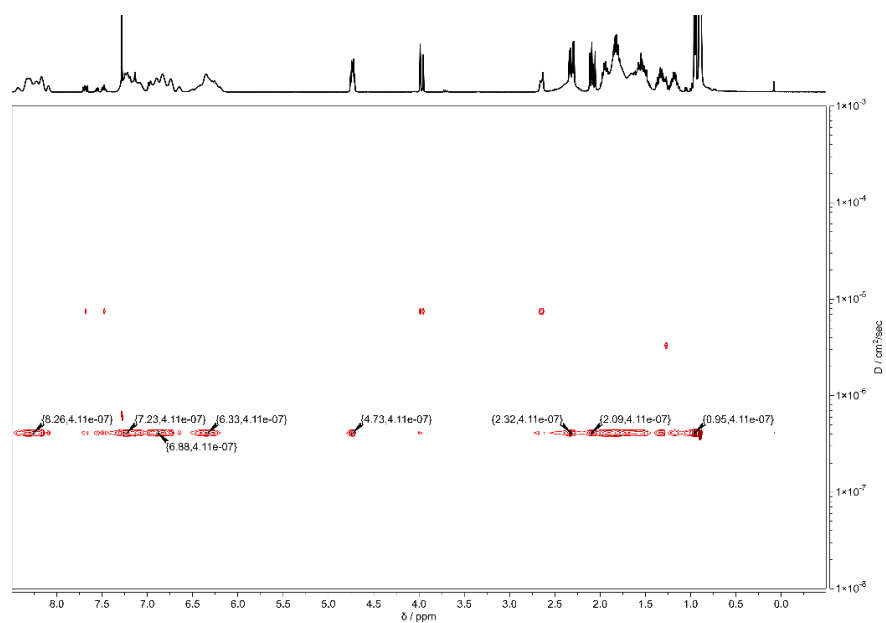
AB[9] (blue) (Table 2, entry 2).

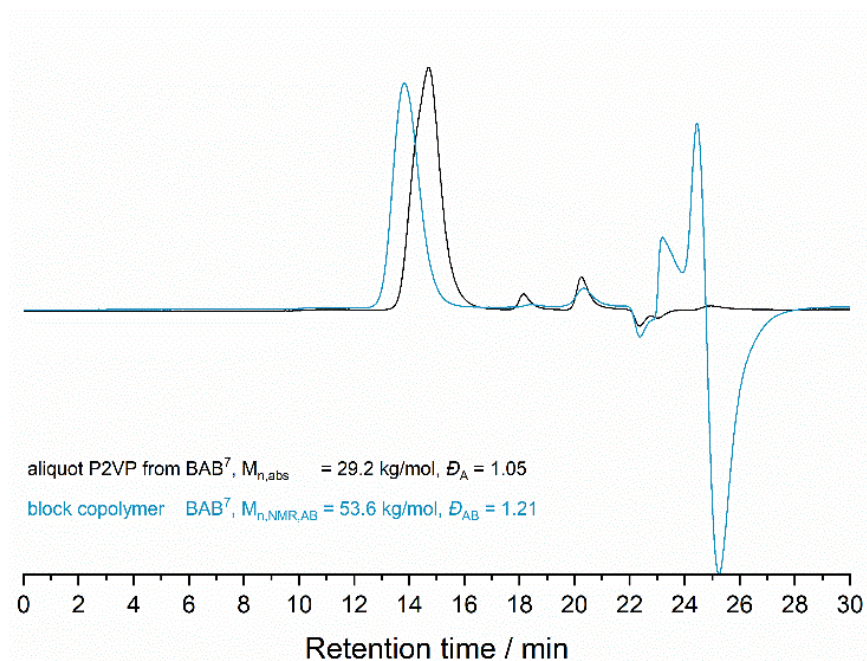Figure S14: DOSY-NMR spectrum in CDCl$_3$ (bottom) of AB[9] (Table 2, entry 2).

Figure S15: SEC traces of from P2VP aliquot (black) and isolated P2VP-*b*-PM triblock copolymer BAB[7] (blue) (Table 2, entry 7).
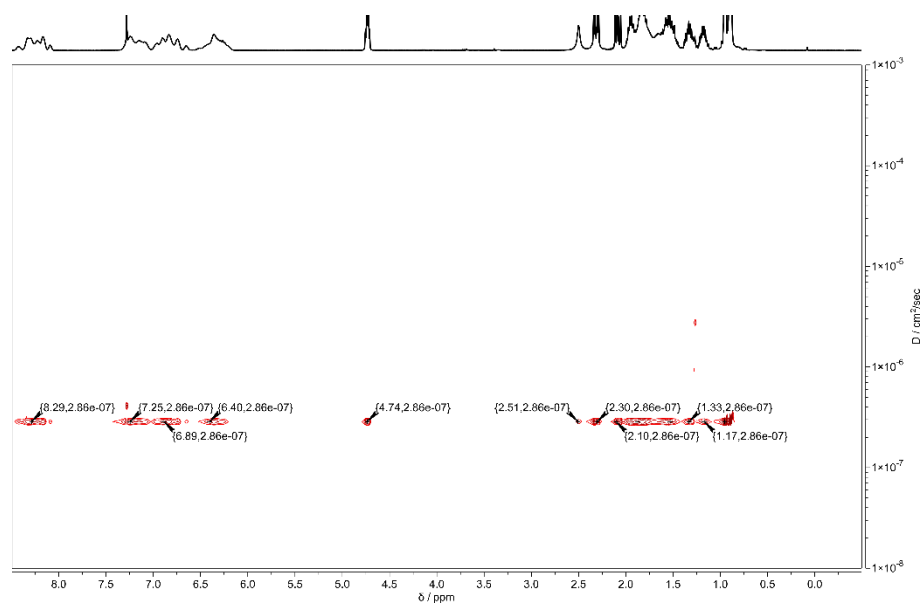

Figure S16: DOSY-NMR spectrum in CDCl$_3$ (bottom) of BAB[7] (Table 2, entry 7).
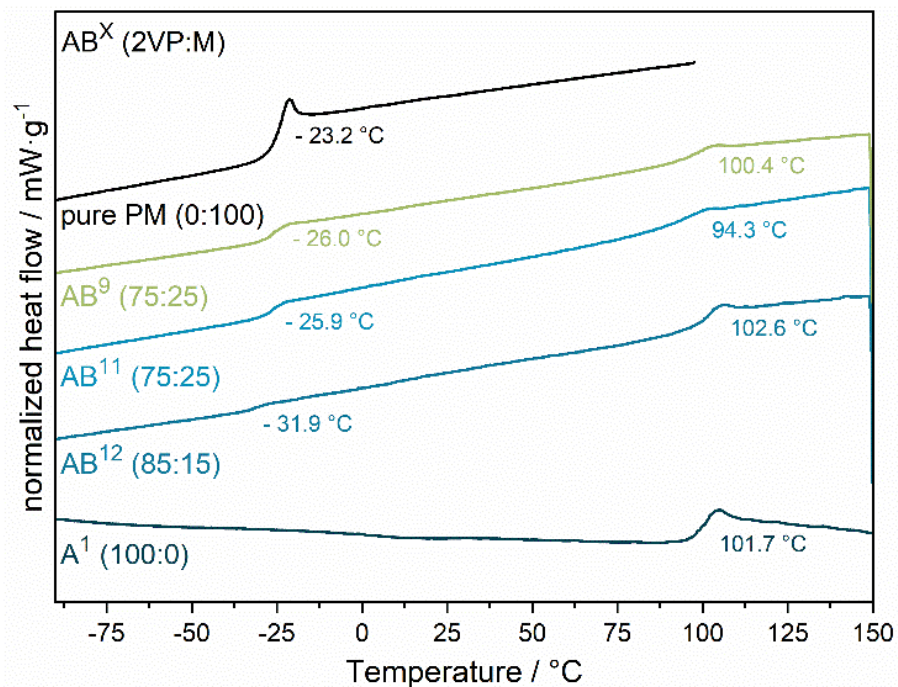
Figure S17: DSC measurements of AB block copolymers AB[9], AB[11], AB[12] and A[1] (Table 2, entries 2, 4 and 5; Table 1, entry 1).
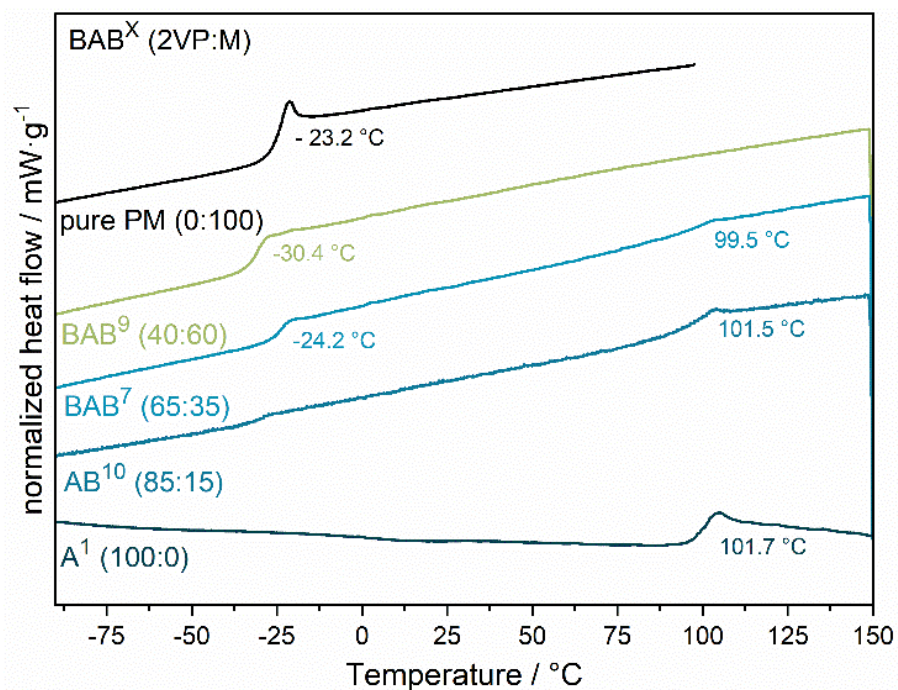

Figure S18: DSC measurements of BAB block copolymers BAB[7], BAB[9] and BAB[10] and A[1] (Table 2, entries 7, 9 and 10; Table 1, entry 1).

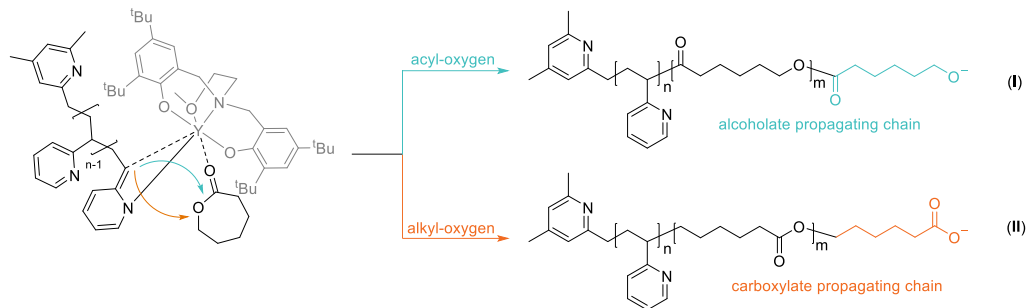## 6. ADDITIONAL MECHANISTIC DETAILS

Figure S19: Initiation pathways of lactone ring-opening by a stabilized aza enolate as active initiator of the P2VP chain coordinated to complex **2** via (I) acyl-oxygen cleavage with alkoxide chain-end or (II) alkyl-oxygen cleavage with a carboxylate chain-end.[9–11]

7. ³¹P-NMR END-CAPPING

For the phosphorus end-capping experiment, 7.4 µmol of catalyst **2** were dissolved in 1 mL C_6D_6 and 20-40 eq. of 2VP were added. The reaction mixture was stirred for 40 min before an equimolar amount of the respective lactone was added. For CL, the reaction mixture was stirred for an additional minute before an excess of chlorodiphenylphosphine oxide was added and the mixture was stirred over night at 70 °C. For M, the reaction mixture was stirred for additional 180 min at 70 °C before an excess of chlorodiphenylphosphine oxide was added and the mixture was stirred over night at 70 °C. From each experiment, ³¹P-NMR was measured, and the chemical shifts were assigned to the formed corresponding phosphorus species.
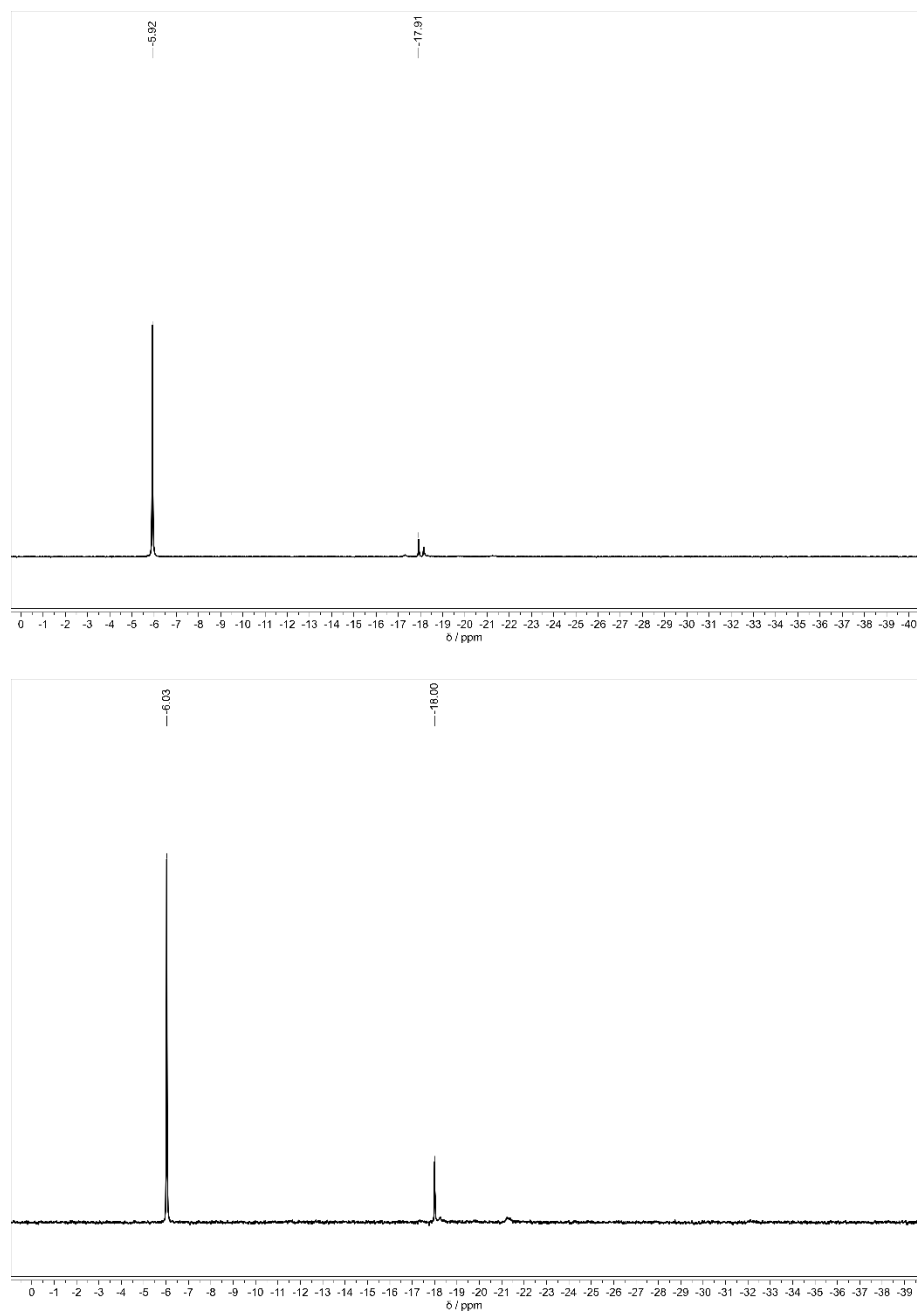
Figure S20: ^{31}P-NMR spectra in C_6D_6 from phosphorus end-capping experiments of P2VP-*b*-PCL (top) and P2VP-*b*-PM (bottom).

8. ESI-MS MEASUREMENTS OF COPOLYMERS

For obtaining oligomers for ESI-MS analysis, 27.0 µmol of catalyst **2** were dissolved in 0.6 mL dichloromethane and 135 µmol (5 eq.) 2VP in 0.5 mL dichloromethane were added. The reaction mixture was stirred for 30 min before 54 µmol (2 eq.) CL in 0.5 mL dichloromethane were added. After additional 10 min of reaction time, the resulting solution was diluted in acetonitrile (concentration of 100 µg analyte per 1 mL solvent) and ESI-MS (positive ionization) was measured.
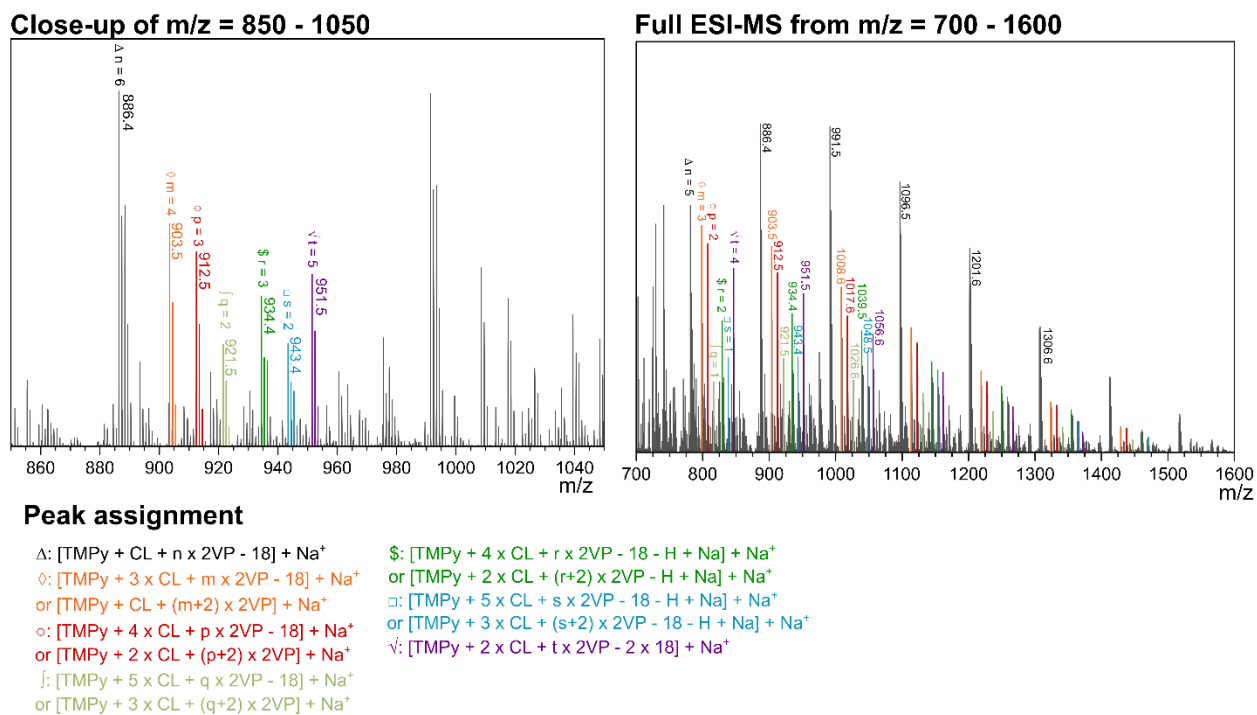

Peak assignment

Δ: [TMPy + CL + n x 2VP - 18] + Na⁺

◊: [TMPy + 3 x CL + m x 2VP - 18] + Na⁺
or [TMPy + CL + (m+2) x 2VP] + Na⁺

○: [TMPy + 4 x CL + p x 2VP - 18] + Na⁺
or [TMPy + 2 x CL + (p+2) x 2VP] + Na⁺

∫: [TMPy + 5 x CL + q x 2VP - 18] + Na⁺
or [TMPy + 3 x CL + (q+2) x 2VP] + Na⁺

$: [TMPy + 4 x CL + r x 2VP - 18 - H + Na] + Na⁺
or [TMPy + 2 x CL + (r+2) x 2VP - H + Na] + Na⁺

□: [TMPy + 5 x CL + s x 2VP - 18 - H + Na] + Na⁺
or [TMPy + 3 x CL + (s+2) x 2VP - 18 - H + Na] + Na⁺

√: [TMPy + 2 x CL + t x 2VP - 2 x 18] + Na⁺

Figure S21: ESI-MS analysis and peak assignment for P2VP-*b*-PCL oligomers prepared with catalyst **3**.

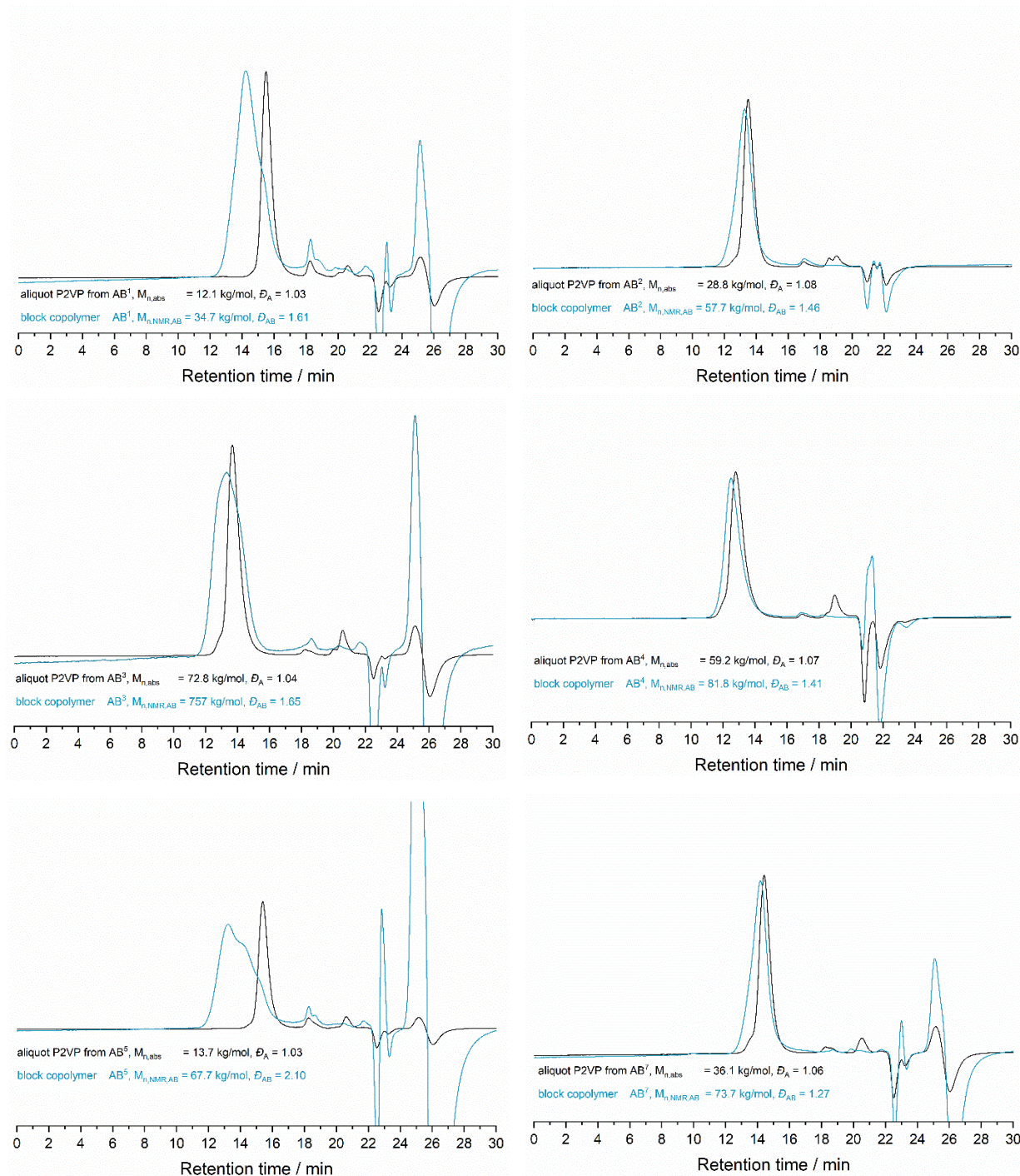## 9. FULL SEC-CHARACTERIZATION OF P2VP-*B*-PCL AB-BLOCK COPOLYMERS

Figure S22: Additional stacked SEC traces of P2VP aliquot (black) and isolated P2VP-*b*-PCL diblock copolymers (blue) AB[1], AB[2], AB[3], AB[4], AB[5] and AB[7] (Table 1, entries 1-5, 7).
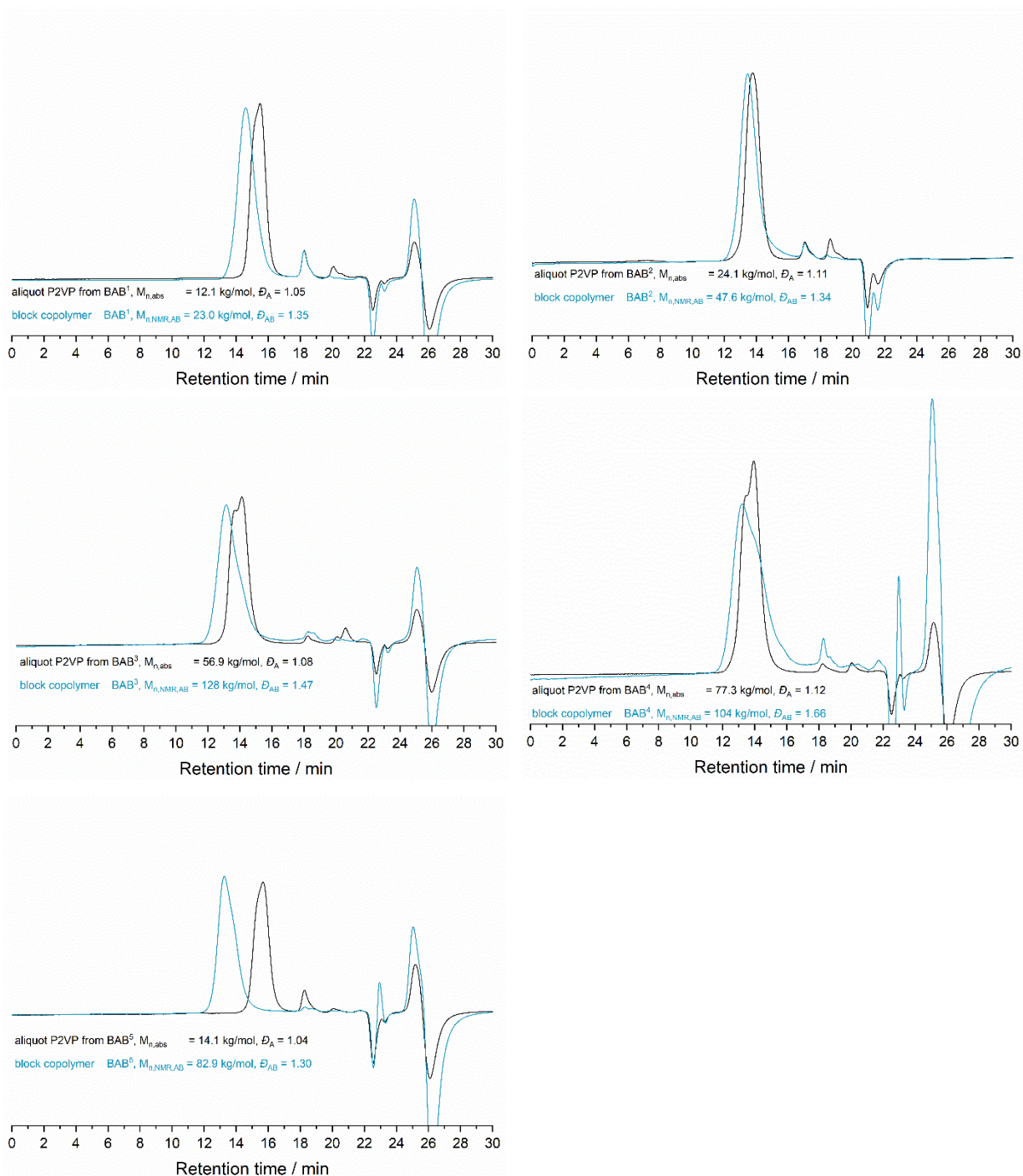
Figure S23: Additional stacked SEC traces of P2VP aliquot (black) and isolated P2VP-*b*-PCL triblock copolymers (blue) BAB[1], BAB[2], BAB[3], BAB[4] and BAB[5] (Table 1, entries 10-14).

11. FULL SEC-CHARACTERIZATION OF P2VP-*B*-PM AB-BLOCK COPOLYMERS

Figure S24: Additional stacked SEC traces of P2VP aliquot (black) and isolated P2VP-*b*-PM diblock copolymers (blue) AB^8, AB^9, AB^{10}, AB^{11} and AB^{12} (Table 2, entries 1-5).

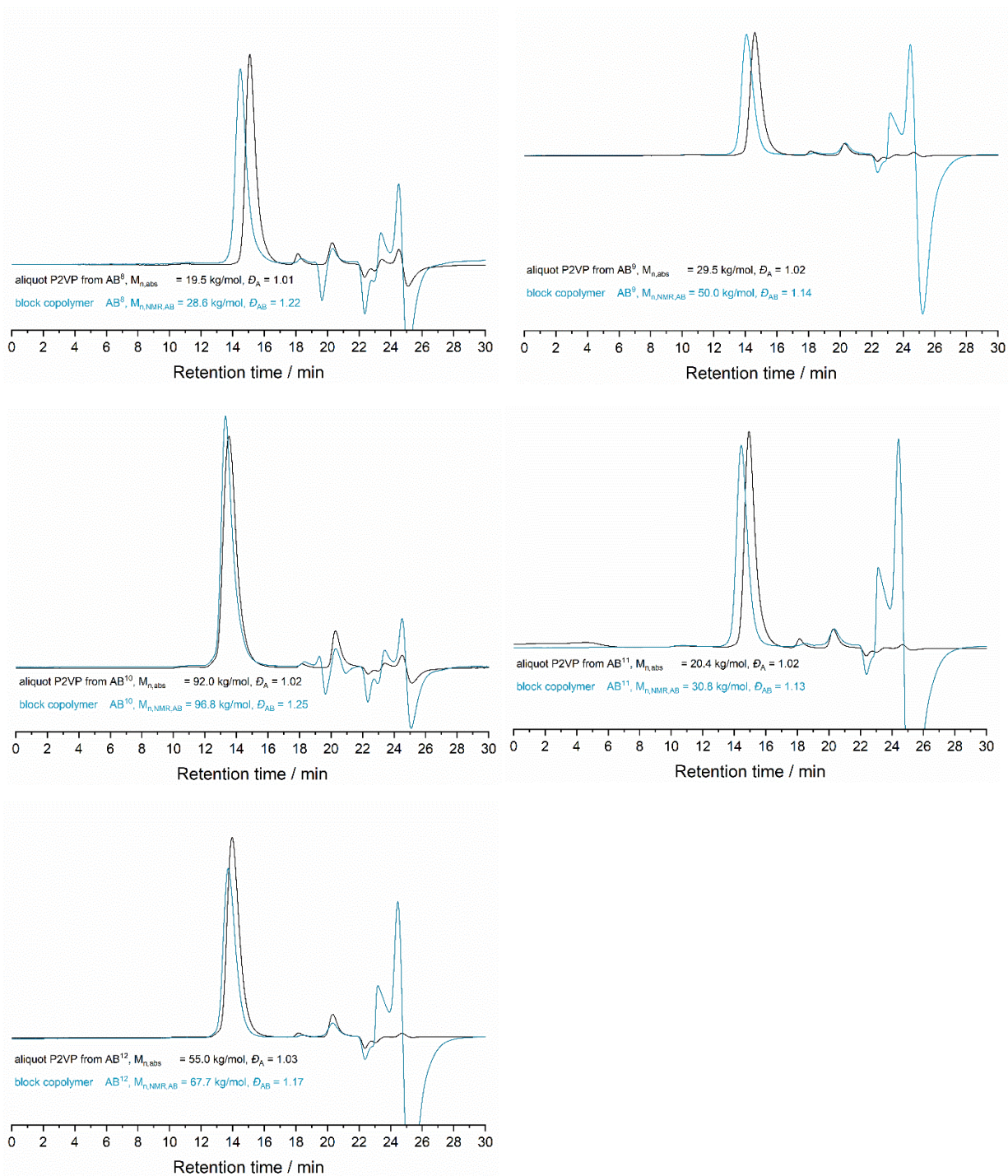## 12. FULL SEC-CHARACTERIZATION OF P2VP-*B*-PM BAB-BLOCK COPOLYMERS

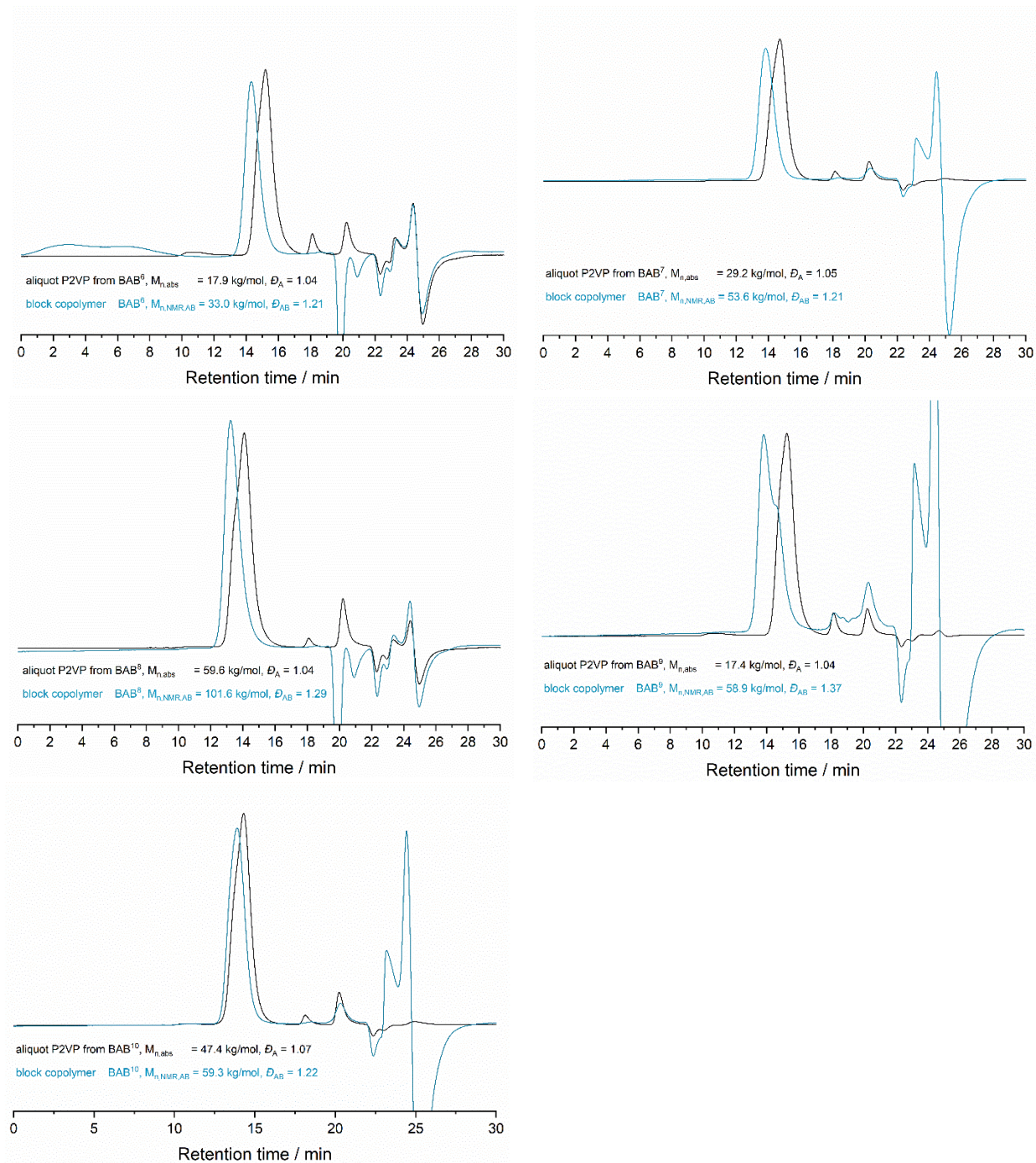

Figure S25: Additional stacked SEC traces of P2VP aliquot (black) and isolated P2VP-*b*-PM triblock copolymers (blue) BAB[6], BAB[7], BAB[8], BAB[9] and BAB[10] (Table 2, entries 6-10).

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