Supporting Information

Exhaustive Baeyer–Villiger Oxidation: A Tailor-made Post-polymerization Modification to Access Challenging Poly(vinyl acetate) Copolymers

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1. Materials and Methods

Materials. Unless otherwise noted, commercial reagents and solvents were used as received. Dry *m*-chloroperoxybenzoic acid (*m*CPBA, containing ~17% *m*-chlorobenzoic acid, ~83% purity) was prepared by the following procedure: commercial *m*CPBA (≤ 77% (~69%) purity, Sigma-Aldrich) was dissolved in dichloromethane (0.2 $g \cdot mL^{-1}$), dried with anhydrous sodium sulfate, filtered, and dried by air flow overnight. Methyl vinyl ketone (MVK) was distilled to remove inhibitors and acidic impurities, and stored at –20 °C prior to polymerization. Styrene (St), methyl acrylate (MA), ethyl acrylate (EA), methyl methacrylate (MMA), and acrylonitrile (AN) were passed through a column of basic alumina to remove inhibitors and stored at –20 °C prior to polymerization. Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol and stored at –20 °C. Tetrahydrofuran was distilled from sodium/benzophenone under an atmosphere of nitrogen immediately before use. The reversible addition-fragmentation chain transfer (RAFT) agents 2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoic acid (DDMAT) and 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) were synthesized following literature methods.[1,2]

Characterization Methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer at 298 K and referenced to residual protium in the NMR solvent ($CDCl_3$ δ 7.26, CD_2Cl_2 δ 5.30 in ^1H NMR) and the carbon resonances of the solvent ($CDCl_3$ δ 77.16, CD_2Cl_2 δ 53.52 in ^{13}C NMR). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. NMR peaks are described as singlet (s), doublet (d), triplet (t), multiplet (m), approximate (app), and broad (br).

Size exclusion chromatography (SEC) was conducted using an Agilent Technologies 1260 Infinity equipped with a differential refractometer and serially connected PLgel columns (10 μm MIXED-BLS, 5 μm MIXED-C, and 5 μm MIXED-D). The system was equilibrated at 40 °C in anhydrous THF as the eluent with a flow rate of 1.0 $mL \cdot min^{-1}$. The weight-average molar mass (M_w) and the number-average molar mass (M_n) of the polymers were determined relative to the linear polystyrene standards and used to estimate the dispersity ($Đ = M_w/M_n$).

Differential scanning calorimetry (DSC) was performed with a NETZSCH DSC 214 Polyma instrument under an atmosphere of nitrogen at a heating rate of 10 $°C \cdot min^{-1}$. The glass transition temperatures (T_g) were obtained from the second heating run.

Thermogravimetric Analysis (TGA) was performed with a NETZSCH STA449F3 Jupiter instrument at a heating rate of 10 $°C \cdot min^{-1}$ from room temperature to 800 °C under an atmosphere of nitrogen.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI–TOF MS) was carried out using a Bruker ultrafleXtreme spectrometer in the linear positive mode. Indole-3-acetic acid (IAA) or *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) were used as the matrices. Silver trifluoroacetate (AgTFA) was used as the cationic reagent in specified cases.

Fourier transform infrared (FT–IR) spectra were recorded using a Thermo Nicolet Nexus 6700 FT–IR spectrometer. Polymer samples were dissolved in dichloromethane and drop-cast onto a polished KBr window.

High-resolution mass spectra (HRMS) were conducted with a Bruker tims-TOF spectrometer using atmospheric pressure chemical ionization (APCI) in positive mode or in negative mode.

2. The Correlation between the Ratio of “Ideal” Functionalized Polymers (IFPs) and the Degree of Chain Scission or Degree of Polymerization (DP)

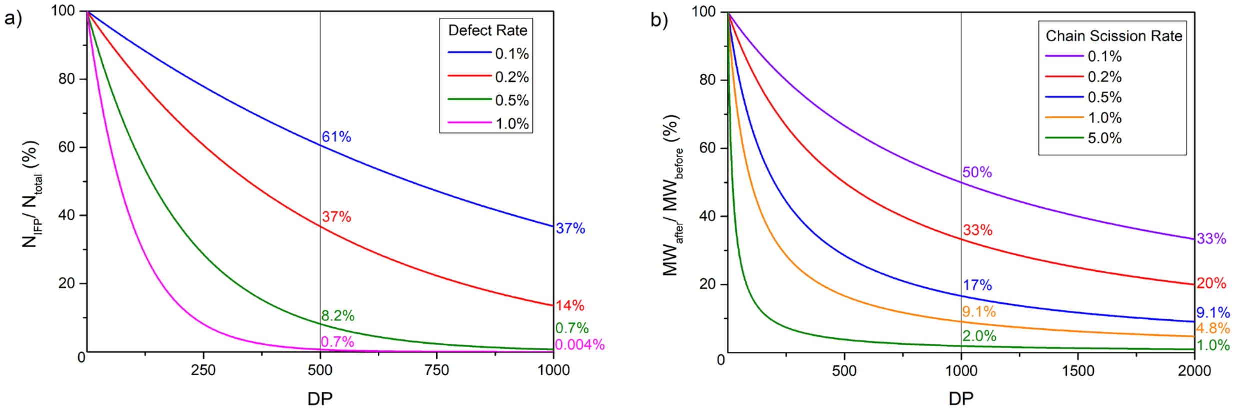


Figure S1. a) The correlation between the ratio of IFPs and the DP; b) The correlation between the ratio of the molar mass of functionalized polymers and the DP.

$$X=\frac{\overline{N}_{\text{IFP}}}{\overline{N}_{\text{total}}}=\left([1-Y]^\wedge\overline{DP}_{\text{before}}\right)\times 100\% \tag{1}$$

The ratio of “ideal” functionalized polymers (*X*) was estimated with the following equation (1) where *Y* represents the ratio of defect to functionalization, and DP_{before} represents the degree of polymerization before post-polymerization modification.

If DP_{before} = 500, after post-polymerization modification with a defect rate of 0.1%, *X* will be 61%; after post-polymerization modification with a defect rate of 0.2%, *X* will be 37%; after post-polymerization modification with a defect rate of 0.5%, *X* will be 8.2%; after post-polymerization modification with a defect rate of 1.0%, *X* will be 0.7%.

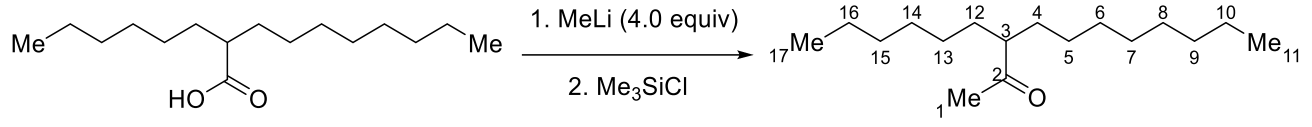
$$X=1-\frac{\overline{M}_{n,\text{after}}}{\overline{M}_{n,\text{before}}}=1-\frac{\overline{DP}_{\text{after}}}{\overline{DP}_{\text{before}}}=\left(1-\frac{1}{[\overline{DP}_{\text{before}}\times Y]+1}\right)\times 100\% \tag{2}$$

The degree of polymer degradation (*X*) was estimated with the following equation (1) where *Y* represents the ratio of chain-scission to functionalization, and DP_{before} and DP_{after} represents the degree of polymerization before and after post-polymerization modification.

If DP_{before} = 1000, after post-polymerization modification with a chain scission rate of 0.1%, *X* will be 50%; after post-polymerization modification with a chain scission rate of 0.2%, *X* will be 67%; after post-polymerization modification with a chain scission rate of 0.5%, *X* will be 83%; after post-polymerization modification with a chain scission rate of 1.0%, *X* will be 91%; after post-polymerization modification with a chain scission rate of 5.0%, *X* will be 98%.

3. Synthesis of Small-molecule Compounds

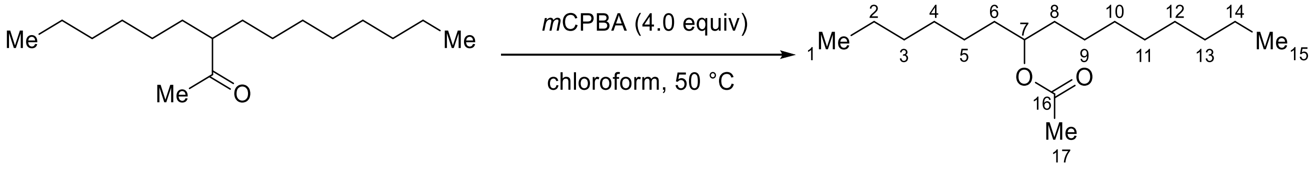
*3-Hexylundecan-2-one (**1**)*



1

The title compound **1** was prepared according to a modification of literature procedure.[3] Under an N_2 atmosphere, a solution of 2-hexyldecanoic acid (2.56 g, 10.0 mmol) in anhydrous tetrahydrofuran (75 mL) was cooled to 0 °C. To the stirred solution was added (ca. 15 s) a solution of methyllithium in diethyl ether (1.6 M, 25.0 mL, 40.0 mmol, 4.0 equiv). The mixture was stirred at 0 °C for 2 h followed by the addition of chlorotrimethylsilane (25.4 mL, 200.0 mmol, 20.0 equiv) (ca. 15 s). The reaction mixture was then allowed to warm to room temperature and aqueous HCl (1 M, 75 mL) was added. The resulting biphasic mixture was stirred for 0.5 h and then transferred into a separatory funnel and extracted with diethyl ether (3 × 125 mL). The combined organic layers were washed with half-saturated brine (100 mL), dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (eluent: petroleum ether/ethyl acetate, 20:1 v/v) to afford the title compound **1** as a colorless liquid (2.32 g, 91%). R_f = 0.30 (petroleum ether/ethyl acetate, 40:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (tt, *J* = 8.2, 5.6 Hz, 1H, H_3), 2.11 (s, 3H, H_1), 1.65–1.34 (m, 4H, $H_{4,12}$), 1.35–1.13 (m, 20H, $H_{5,6,7,8,9,10,13,14,15,16}$), 0.96–0.80 (m, 6H, $H_{11,17}$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 213.2, 53.4, 31.8, 31.7 (2C), 31.7, 29.7, 29.4 (2C), 29.2, 28.6, 27.4, 27.4, 22.6, 22.6, 14.1, 14.0. LC-HRMS (APCI) m/z: $[M + H]^+$ calcd for $C_{17}H_{35}O$ 255.2682; found 255.2682.

*Pentadecan-7-yl acetate (**2**)*



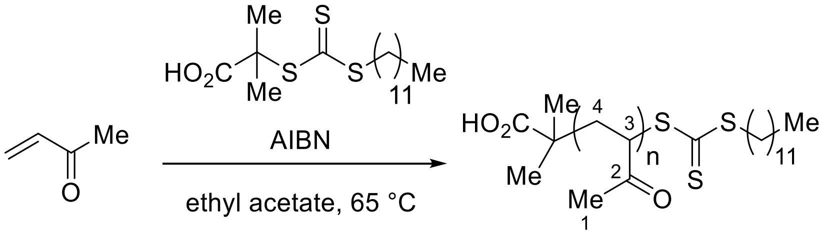
1 **2**

The title compound **2** was prepared according to a modification of the literature procedure.[4] Compound **1** (152.4 mg, 0.6 mmol), *m*CPBA (600.0 mg, 2.40 mmol, ~69% purity), and chloroform (2.00 mL) were added successively into a reaction bottle with a magnetic stir bar. The mixture was stirred at 50 °C in an aluminum heating block for 16 h. The reaction mixture was cooled to room temperature, then diluted with dichloromethane (10 mL) and quenched with an excess of half-saturated $Na_2S_2O_3$ solution (20 mL). The resulting mixture was then extracted with dichloromethane (20 mL), and washed with a half-saturated $NaHCO_3$ solution (20 mL) and half-saturated brine (20 mL) successively. The organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The conversion was measured by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. The crude product was purified by flash column chromatography over silica gel (eluent: petroleum ether/dichloromethane, 40:1 v/v) to afford the title compound **2** as a colorless liquid (153.5 mg, 95%). R_f = 0.63 (petroleum ether/ethyl acetate, 40:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00–4.72 (m, 1H, H_7), 2.06 (s, 3H, H_{17}), 1.59–1.45 (m, 4H, $H_{6,8}$), 1.38–1.21 (m, 20H, $H_{2,3,4,5,9,10,11,12,13,14}$), 0.99–0.81 (m, 6H, $H_{1,15}$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 74.5, 34.1 (2C), 31.9, 31.7, 29.5, 29.5, 29.2, 29.2, 25.3, 25.3, 22.6, 22.6, 21.3, 14.1, 14.0.

4. Preparation of Poly(Methyl Vinyl Ketone)s (PMVKs) for Reaction Optimization

Commercially available PMVK **3a** (average M_w ~ 500,000 by SEC, Sigma-Aldrich) was used for reaction optimization without purification. The molar mass of **3a** was established by size exclusion chromatography (SEC) in our laboratory. SEC (DMF, PS calibration) M_n: 143.7 to 212.4 kDa, M_w: 384.2 to 493.7 kDa, *Đ*: 2.21 to 2.68; SEC (THF, PS calibration) M_n: 51.4 to 69.0 kDa, M_w: 127.5 to 167.0 kDa, *Đ*: 2.42 to 2.54.

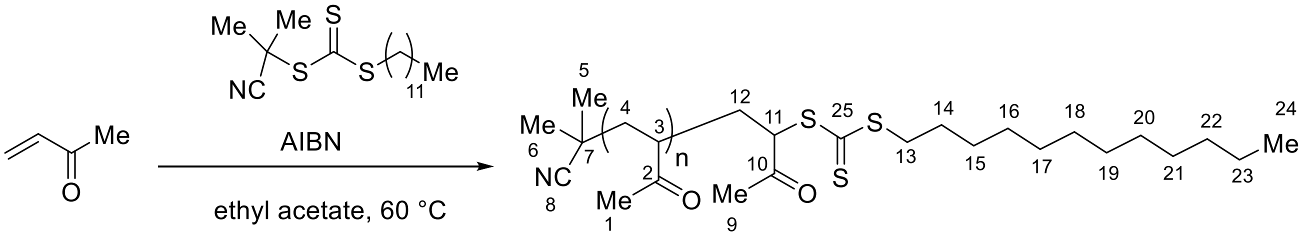
*PMVK (RAFT) (**3b**)*



3b

The title polymer **3b** was prepared according to a modification of the literature procedure.[5] A 10-mL Schlenk flask was charged with MVK (2.03 mL, 25.0 mmol), DDMAT (36.5 mg, 0.10 mmol), AIBN (3.3 mg, 0.02 mmol), and ethyl acetate (2.03 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 65 °C for 18 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Aliquots were taken and diluted for SEC (THF, PS calibration) and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 36 h at 40 °C to afford the title polymer **3b** as a yellow solid (1.21 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.78–2.00 (m, $H_{1,3}$), 2.00–0.97 (m, H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 210.6 (C_2), 48.1 (C_3), 34.7–30.4 (C_4), 29.5 (C_1). FT–IR (KBr): ν (cm^{-1}) 2927, 1712, 1426, 1356, 1241, 1164, 1108, 959, 803, 735, 595, 494. SEC (THF, PS calibration): M_n: 12.6 kDa, M_w: 13.5 kDa, *Đ*: 1.07.

*PMVK (RAFT) (**3c**)*



3c

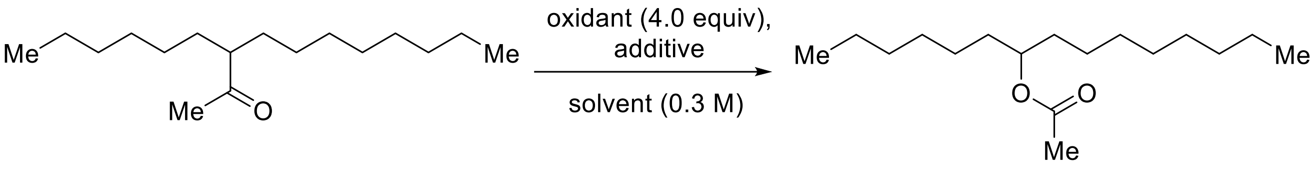
The title polymer **3c** was prepared according to a modification of the literature procedure.[5] A 10-mL Schlenk flask was charged with MVK (1.01 mL, 12.4 mmol), CPDT (43.0 mg, 0.12 mmol), AIBN (2.0 mg, 0.01 mmol), and ethyl acetate (1.00 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 60 °C for 7 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Aliquots were taken and diluted for SEC (THF, PS calibration) and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 36 h at 40 °C to afford title polymer **3c** as a yellow solid (280.0 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.65–5.08 (m, H_{11}), 3.42–3.13 (m, H_{13}), 2.78–2.00 (m, $H_{1,3,9}$), 2.00–0.97 (m, $H_{4,5,6,12,14,15,16,17,18,19,20,21,22,23}$), 0.86–0.67 (m, H_{24}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 221.8 (C_{25}), 210.5 (C_2), 202.9 (C_{10}), 124.4 (C_8), 55.7 (C_{11}), 47.9 (C_3), 41.1 (C_7), 37.9 (C_{13}), 34.7–30.4 ($C_{4,12,22}$), 30.1–28.4 ($C_{1,9}$), 28.4–25.7 ($C_{5,6,14,15,16,17,18,19,20,21}$), 22.5 ($C_{23}$), 14.0 ($C_{24}$). FT–IR (KBr): ν (cm$^-$

^{1}) 2926, 2855, 1712, 1427, 1356, 1242, 1163, 1069, 958, 735. SEC (THF, PS calibration): M_n: 2.4 kDa, M_w: 2.5 kDa, $Đ$: 1.05.

5. Reaction Optimizations

5.1 Optimizations of the Baeyer−Villiger (BV) Oxidation of Model Compound 1

Table S1. Evaluation of literature methods using a small-molecule model.[a]



1

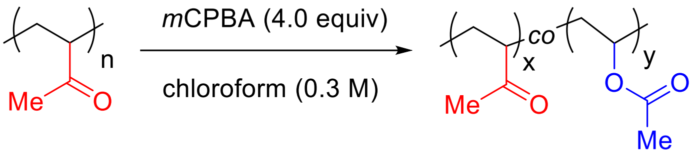
2

Entry	Solvent	Oxidant	Additive	Temperature (°C)	Time (h)	Yield[b] (%)
1[6]	$CHCl_3$	*m*CPBA	none	50	8	96
2[6]	$CHCl_3$	*m*CPBA	CF_3CO_2H	50	8	98
3[6]	$CHCl_3$	*m*CPBA	TsOH	50	8	98
4[6]	$CHCl_3$	*m*CPBA	H_2SO_4	50	8	98
5[6]	$CHCl_3$	*m*CPBA	$BF_3{\cdot}Et_2O$	50	8	>99
6[6]	$CHCl_3/H_2O$[c]	*m*CPBA	Na_2HPO_4[d]	50	8	92
7[6]	$CHCl_3/H_2O$[c]	*m*CPBA	NaOAc[d]	50	8	94
8[6,7]	$CHCl_3$	MMPP	H_2SO_4[d]	50	8	94
9[6,7]	AcOH	MMPP	none	50	8	99
10[6,8]	CH_2Cl_2	TFPAA[e]	none	rt	8	97
11[6,8]	$CHCl_3$	TFPAA[e]	none	50	8	96
12[6,9]	AcOH	PAA[e]	H_2SO_4[d]	50	24	87

[a]Standard conditions: 3-hexylundecanone-2-one **1** (50.6 mg, 0.20 mmol), oxidant (0.80 mmol), and additive (0.02 mmol) were stirred in solvent (0.70 mL). MMPP: magnesium monoperoxyphthalate hexahydrate, TFPAA: Peroxytrifluoroacetic acid, PAA: peracetic acid, TsOH: *p*-toluenesulfonic acid. [b]Determined by ^{1}H NMR of the crude products using 1,1,1,3-tetrachloropropane as an internal standard. [c]$CHCl_3/H_2O$ (1.40 mL, 1:1 v/v). [d]0.80 mmol of additive. [e]TFPAA and PAA were prepared prior to use by adding the corresponding anhydrides to a suspension of urea hydrogen peroxide adduct at 0 °C.

5.2 Optimizations of the BV Oxidation of Polymer 3a

Table S2. The influence of temperature and reaction time on the BV oxidation of PMVK **3a** in chloroform.

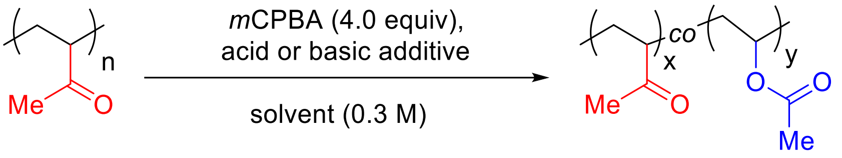


3a **4a**

Entry	Temperature (°C)	Time (h)	Conversion[b] (%)	$M_{n,SEC}$[c] (kDa)	$Đ$[c]
1	40	8	37	65.5	2.58
2	40	24	73	32.2	2.01
3	40	48	79	28.9	2.06
4	50	8	52	28.3	2.00
5	50	24	77	23.1	1.99
6	50	48	80	18.8	1.90
7	60	8	71	38.2	2.21
8	60	24	85	23.6	2.07
9	60	48	92	14.1	1.80

[a] Standard conditions: commercial PMVK **3a** (41.7 mg, containing 0.60 mmol repeating units) and *m*CPBA (600.0 mg, 2.40 mmol, ~69% purity) were stirred in chloroform (2.00 mL). The M_n and $Đ$ of **3a** were 69.0 kDa/2.42. [b] Determined by ^{1}H NMR of the crude products using 1,1,1,3-tetrachloropropane as an internal standard. [c] Determined by SEC (THF) analysis relative to polystyrene standards.

Table S3. Evaluation of the selected conditions in **Table S1** for the BV oxidation of PMVK **3a**.[a]

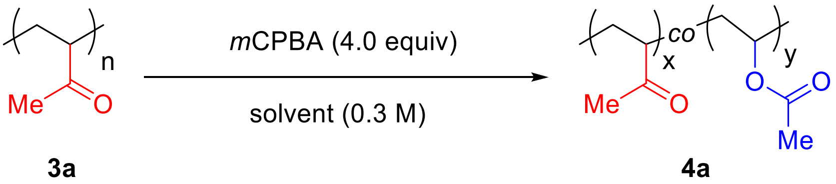


3a **4a**

Entry	Solvent	Oxidant	Additive	Conversion[b] (%)	$M_{n,SEC}$[c] (kDa)	$Đ$[c]
1	$CHCl_3$	*m*CPBA	none	46	19.6	1.94
2	$CHCl_3$	*m*CPBA	CF_3CO_2H	58	37.3	2.23
3	$CHCl_3$	*m*CPBA	TsOH	80	13.7	1.82
4	$CHCl_3$	*m*CPBA	H_2SO_4	53	30.4–59.4[i]	2.16–2.64[i]
5	$CHCl_3$	*m*CPBA	$BF_3·Et_2O$	53	53.0	2.50
6	$CHCl_3/H_2O$[d]	*m*CPBA	Na_2HPO_4[e]	29	35.2	2.22
7	$CHCl_3/H_2O$[d]	*m*CPBA	NaOAc[e]	54	10.3	1.68
8	$CHCl_3$	MMPP	H_2SO_4[e]	39	15.0	1.93
9	AcOH	MMPP	none	n.a.[j]	1.9	1.16
10[g]	CH_2Cl_2	TFPAA[f]	none	90	7.7	1.62
11	$CHCl_3$	TFPAA[f]	none	n.a.[j]	3.8	1.58
12[h]	AcOH	PAA[e]	H_2SO_4[e]	n.a.[j]	4.5	1.38

[a] Standard conditions: commercial PMVK **3a** (41.7 mg, containing 0.60 mmol repeating units), oxidant (2.40 mmol), and additive (0.06 mmol) were stirred in solvent (2.00 mL) at 50 °C for 8 h. The M_n and $Đ$ of **3a** were 63.8 kDa/2.42. MMPP: magnesium monoperoxyphthalate hexahydrate, TFPAA: Peroxytrifluoroacetic acid, PAA: peracetic acid, TsOH: *p*-toluenesulfonic acid. [b] Determined by ^1H NMR of the crude products using 1,1,1,3-tetrachloropropane as an internal standard. [c] Determined by SEC (THF) analysis relative to polystyrene standards. [d] $CHCl_3/H_2O$ (4.00 mL, 1:1 v/v). [e] 2.40 mmol of additive. [f] TFPAA and PAA were prepared prior to use by adding the corresponding anhydrides to a suspension of urea hydrogen peroxide adduct at 0 °C. [g] Reaction was run at room temperature for 8 h. [h] Reaction was run at 50 °C for 24 h. [i] Ranges of $M_{n,SEC}$ and $Đ$ values in three experiments. [j] Conversion data from NMR were not applicable due to serious degradation of the polymers.

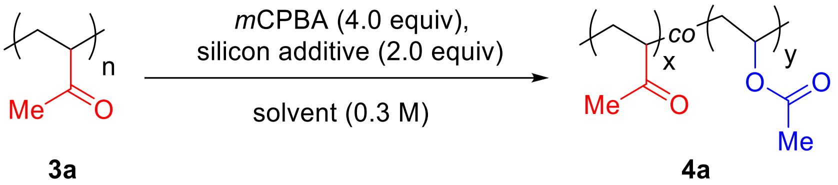
Table S4. Evaluation of solvents for the BV oxidation of PMVK **3a**.[a]



Entry	Solvent	Temperature (°C)	Time (h)	Conversion[b] (%)	$M_{n,SEC}$[c] (kDa)	$Đ$[c]
1	$CHCl_3$	50	8	55	36.1	2.18
2	CH_2Cl_2	30	24	44	41.9	2.27
3	1,2-dichloroethane	50	8	52	61.9	2.50
4	EtOAc	50	8	23	63.9	2.45
5	THF	50	8	14	60.8	2.58
6	Et_2O	30	24	26	63.3	2.55
7	dioxane	50	8	12	62.1	2.56
8	EtOH	50	8	22	60.8	2.53
9	$(CF_3)_2CHOH$	50	8	16	55.2	2.49
10	MeCN	50	8	16	54.1	2.43
11	*N*-methylpyrrolidone	50	8	12	59.6	2.58
12	DMF	50	8	11	60.8	2.53
13	*n*-hexane	50	8	86	64.0	2.43
14	toluene	50	8	34	63.6	2.61
15	(trifluoromethyl)benzene	50	8	80	63.7	2.44
16	fluorobenzene	50	8	71	69.8	2.61
17	chlorobenzene	50	8	75	71.3	2.57
18	*m*-dichlorobenzene	50	8	79	67.7	2.49
19	*o*-dichlorobenzene	50	8	81	65.4	2.46
20	1,2,4-trichlorobenzene	50	8	85	68.5	2.38

[a] Standard conditions: commercial PMVK **3a** (41.7 mg, containing 0.60 mmol repeating units) and *m*CPBA (600.0 mg, 2.40 mmol, ~69% purity) were stirred in chloroform (2.00 mL). The M_n and $Đ$ of **3a** were 66.0 kDa/2.54. [b] Determined by ^1H NMR of the crude products using 1,1,1,3-tetrachloropropane as an internal standard. [c] Determined by SEC (THF) analysis relative to polystyrene standards.

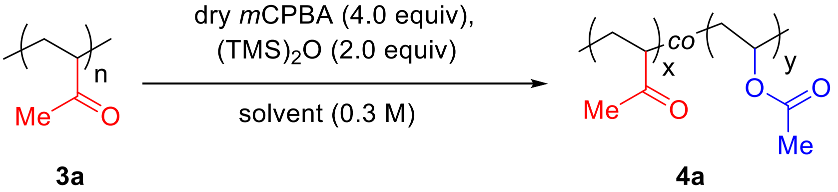
Table S5. Evaluation of silicon additives for the BV oxidation of PMVK **3a**.[a]



Entry	Silicon additive[b]	Conversion[c] (%)	$M_{n,SEC}$[d] (kDa)	$Đ$[d]
1	HMDS[e]	n.a.[f]	-	-
2	BSU[e]	n.a.[f]	21.4	1.66
3	BSTFA[e]	n.a.[f]	1.3	1.13
4	ethoxytrimethylsilane	97	52.2	2.41
5	hexamethyldisiloxane	>99	55.8	2.29
6	hexamethyl-cyclotrisiloxane	>99	51.8	2.59

[a] Standard conditions: commercial PMVK **3a** (41.7 mg, containing 0.60 mmol repeating units), *m*CPBA (600.0 mg, 2.40 mmol, ~69% purity), and silicon additive (1.20 mmol) were stirred in 1,2,4-trichlorobenzene (2.00 mL) at 50 °C for 24 h. The M_n and $Đ$ of **3a** were 51.4 kDa/2.48. [b] HMDS: 1,1,1,3,3,3-hexamethyldisilazane, BSU: 1,3-bis(trimethylsilyl) urea, BSTFA: bis(trimethylsilyl) trifluoroacetamide. [c] Determined by ^1H NMR of the crude products using 1,1,1,3-tetrachloropropane as an internal standard. [d] Determined by SEC (THF) analysis relative to polystyrene standards. [e] The addition of the silicon additive triggers a highly exothermic reaction which must be handled with caution. [f] n.a. = not applicable.

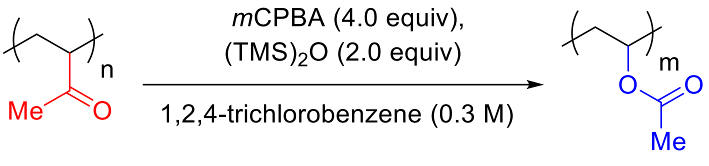
Table S6. Optimizations of the exhaustive BV protocol of PMVK **3a** with selected solvents.[a]



Entry	Solvent	Silicon reagent	Temperature (°C)	Conversion[b] (%)	$M_{n,SEC}$[c] (kDa)	$Đ$[c]
1	fluorobenzene	none	50	95	50.0	2.41
2	chlorobenzene	none	50	97	63.2	2.51
3	1,2,4-trichlorobenzene	none	50	>99	49.4	2.29
4	fluorobenzene	$(TMS)_2O$	50	96	59.5	2.43
5	chlorobenzene	$(TMS)_2O$	50	98	70.0	2.38
6	1,2,4-trichlorobenzene	$(TMS)_2O$	50	>99	66.4	2.42
7	fluorobenzene	$(TMS)_2O$	45	93	65.3	2.49
8	chlorobenzene	$(TMS)_2O$	45	96	70.7	2.49
9	1,2,4-trichlorobenzene	$(TMS)_2O$	45	98	70.3	2.47

[a]Standard conditions: commercial PMVK **3a** (41.7 mg, containing 0.60 mmol repeating units), dry *m*CPBA (500.0 mg, 2.40 mmol, ~83% purity), and silicon additive (1.20 mmol) were stirred in solvent (2.00 mL) for 24 h. The M_n and $Đ$ of **3a** were 61.4 kDa/2.54. $(TMS)_2O$: hexamethyldisiloxane. [b]Determined by ^1H NMR of the crude products using 1,1,1,3-tetrachloropropane as an internal standard. [c]Determined by SEC (THF) analysis relative to polystyrene standards.

Table S7. Optimizations of the exhaustive BV protocol of PMVK **3a** with H_2O and $(TMS)_2O$.[a]



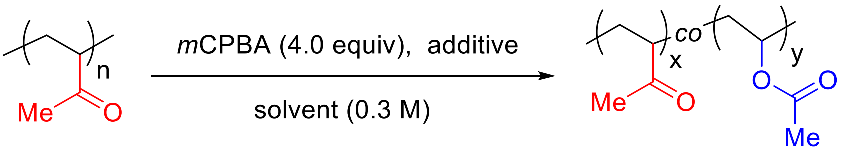
3a **5a**

Entry	Oxidant	Silicon reagent	Conversion[b] (%)	$M_{n,SEC}$[c] (kDa)	$Đ$[c]
1	*m*CPBA	none	>99	50.6	2.51
2	dry *m*CPBA	none	>99	53.8	2.37
3	*m*CPBA	$(TMS)_2O$	>99	57.4	2.46
4	dry *m*CPBA	$(TMS)_2O$	>99	60.9	2.49

[a]Standard conditions: commercial PMVK **3a** (41.7 mg, containing 0.60 mmol repeating units), *m*CPBA (600.0 mg, 2.40 mmol, ~69% purity) or dry *m*CPBA (600.0 mg, 2.40 mmol, ~83% purity), and $(TMS)_2O$ (254 µL, 1.19 mmol) were stirred in 1,2,4-trichlorobenzene (2.00 mL) at 50 °C for 24 h. The M_n and $Đ$ of **3a** were 60.1 kDa/2.51. $(TMS)_2O$: hexamethyldisiloxane. [b]Determined by ^1H NMR of the crude products using 1,1,1,3-tetrachloropropane as an internal standard. [c]Determined by SEC (THF) analysis relative to polystyrene standards.

5.3 Optimizations of the BV Oxidation of Polymer 3b

Table S8. Evaluation of the BV oxidation of PMVK (RAFT) **3b** using the established protocol for PMVK **3a**.[a]

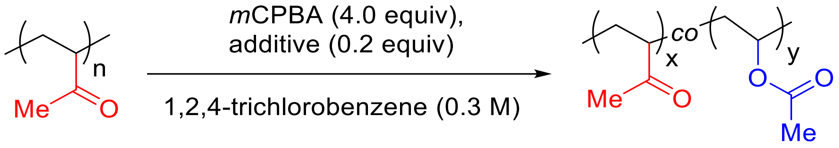


3b (RAFT polymer) **4b**

Entry	Solvent	Additive	Oxidant	Conversion[b] (%)	$M_{n,SEC}$[c] (kDa)	$Đ$[b]
1	1,2,4-trichlorobenzene	$(TMS)_2O$	dry *m*CPBA	n.a.	2.1	1.63
2	1,2,4-trichlorobenzene	none	*m*CPBA	99	4.4	1.43
3[d]	1,2,4-trichlorobenzene	none	*m*CPBA	97	13.6	1.18
4[d]	1,2,4-trichlorobenzene	DDMAT[e]	*m*CPBA	n.a.	4.0	1.34

[a]Standard conditions: PMVK (RAFT) **3b** (41.7 mg, containing 0.60 mmol repeating units), *m*CPBA (600.0 mg, 2.40 mmol, ~69% purity) or dry *m*CPBA (500.0 mg, 2.40 mmol, ~83% purity), and $(TMS)_2O$ (254 µL, 1.19 mmol) were stirred in solvent (2.00 mL) at 50 °C for 24 h. The M_n and $Đ$ of **3b** were 12.6 kDa/1.07. $(TMS)_2O$: hexamethyldisiloxane, DDMAT: RAFT agent 2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoic acid. [b]Determined by ^1H NMR of the crude products using 1,1,1,3-tetrachloropropane as an internal standard. [c]Determined by SEC (THF) analysis relative to polystyrene standards. [d]The sulfur-based end group of PMVK (RAFT) **3b** was removed by following the literature procedure[10] prior to the post-modification. The M_n and $Đ$ of the PMVK homopolymer after end-group removal were 12.7 kDa/1.10. Reaction was run for 14 h instead of 24 h. [e]3.00 µmol of DDMAT.

Table S9. Evaluation of additives for the BV oxidation of PMVK (RAFT) **3b**.



3b (RAFT polymer) **4b**

Entry	Additive	Conversion[b] (%)	$M_{n,SEC}$[c] (kDa)	$Đ$[c]
1	Et_3N	90	10.7	1.30
2	DABCO	81	11.6	1.24
3	*N*,*N*-diisopropylethylamine	88	10.0	1.32
4	2,6-lutidine	61	13.1	1.18
5	NH_4HCO_3	96	9.4	1.29
6	NH_4OAc	83	6.9	1.34
7	$(NH_4)_2SO_4$	>99	13.8	1.15
8	acetamide	>99	12.2	1.21
9	benzamide	99	10.7	1.25
10	phenylacetamide	>99	11.9	1.21
11	trimethyl acetamide	99	12.5	1.19
12	trifluoroacetamide	>99	11.3	1.23
13	*p*-toluenesulfonamide	98	3.3	1.35
14	diphenylphosphinamide	>99	13.0	1.17
15	1,3-dimethylurea	98	13.9	1.15
16	1,3-diphenylurea	69	4.3	1.39
17	glutarimide	96	4.3	1.43
18	2-imidazolidinone	98	13.3	1.16
19	2-pyrrolidone	99	12.7	1.19
20	1,3-propyleneurea	98	13.6	1.15
21	biuret	>99	9.1	1.31
22	urea	>99	13.5	1.15
23	thiourea	98	11.8	1.21
24	ammonium carbamate	87	6.9	1.37
25	methyl carbamate	98	3.6	1.38
26	*t*-butyl carbamate	>99	13.0	1.16

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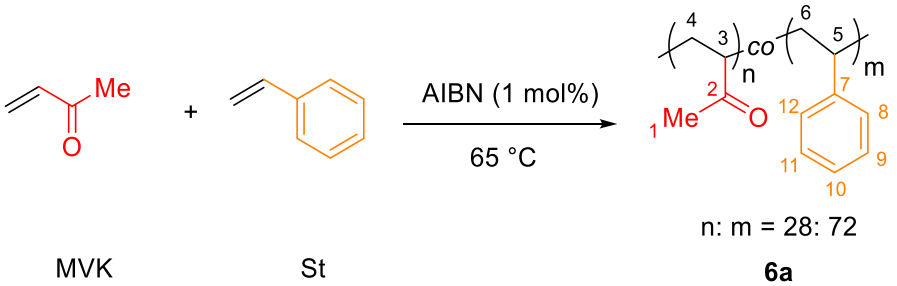
[a] Standard conditions: PMVK (RAFT) **3b** (41.7 mg, containing 0.60 mmol repeating units), *m*CPBA (600.0 mg, 2.40 mmol, ~69% purity), and additive (0.12 mmol) were stirred in solvent (2.00 mL) at 50 °C for 24 h. The M_n and $Đ$ of **3b** were 12.5 kDa/1.07. DABCO: 1,4-diazabicyclo[2.2.2]octane. [b] Determined by ^{1}H NMR of the crude products using 1,1,1,3-tetrachloropropane as an internal standard. [c] Determined by SEC (THF) analysis relative to polystyrene standards.

6. Copolymerization of MVK and Other More Activated Monomers (MAMs)

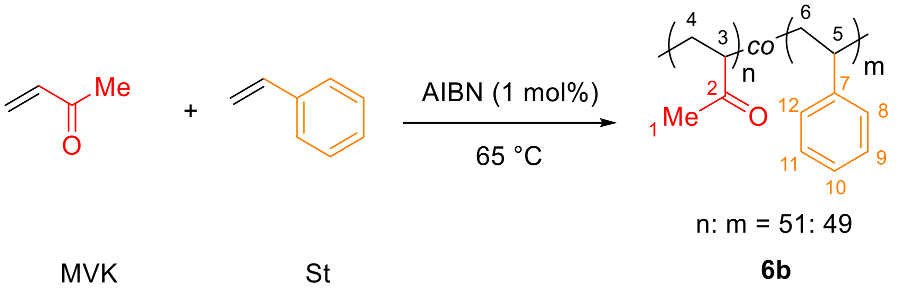
*PMVK-co-PS (28/72) (**6a**)*



6a

A 10-mL Schlenk flask was charged with MVK (325 µL, 4.00 mmol), styrene (1.83 mL, 16.0 mmol), AIBN (32.8 mg, 0.20 mmol), and ethyl acetate (2.00 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 65 °C for 8 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Then, 1,1,1,3-tetrachloropropane was added as an internal standard. Aliquots were taken and diluted for SEC and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 36 h at 40 °C to afford the title polymer **6a** as a white solid (1.08 g, 45%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.61–6.31 (m, $H_{8,9,10,11,12}$), 2.63–0.70 (m, $H_{1,3,4,5,6}$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 211.1 (C_2), 147.1–142.2 (C_7), 129.1–126.9 ($C_{8,9,11,12}$), 125.9 (C_{10}), 48.9–46.9 (C_3), 46.9–42.3 (C_6), 42.3–39.7 (C_5), 39.7–35.5 (C_4), 28.0 (C_1). FT–IR (KBr): ν (cm^{-1}) 3082, 3060, 3026, 3001, 2925, 2852, 1711, 1601, 1583, 1493, 1452, 1353, 1266, 1160, 1071, 1029, 967, 909, 759, 700, 544. SEC (THF, PS calibration): M_n: 23.9 kDa, M_w: 42.8 kDa, $Đ$: 1.79. TGA: 396 °C (50% weight loss). DSC: T_g: 86.8 °C.

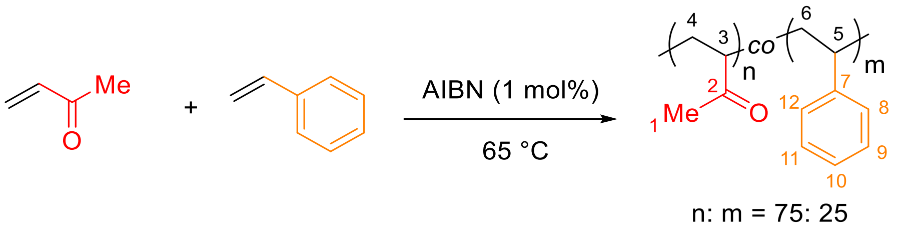
*PMVK-co-PS (51/49) (**6b**)*



6b

A 10-mL Schlenk flask was charged with MVK (610 µL, 7.50 mmol), styrene (860 µL, 7.50 mmol), AIBN (24.6 mg, 0.15 mmol), and ethyl acetate (1.50 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 65 °C for 7 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Then, 1,1,1,3-tetrachloropropane was added as an internal standard. Aliquots were taken and diluted for SEC and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 36 h at 40 °C to afford the title polymer **6b** as a white solid (943.3 mg, 57%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.79–6.27 (m, $H_{8,9,10,11,12}$), 2.73–0.56 (m, $H_{1,3,4,5,6}$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 210.6 (C_2), 146.4–141.9 (C_7), 129.7–127.1 ($C_{8,9,11,12}$), 126.4 (C_{10}), 49.0–47.0 (C_3), 46.6–30.2 ($C_{4,5,6}$), 29.9–27.1 (C_1). FT–IR (KBr): ν (cm^{-1}) 3083, 3060, 3026, 3001, 2925, 2853, 1712, 1601, 1583, 1493, 1453, 1354, 1267, 1239, 1162, 1073, 1029, 970, 912, 761, 737, 702, 553. SEC (THF, PS calibration): M_n: 34.4 kDa, M_w: 65.2 kDa, $Đ$: 1.90. TGA: 380 °C (50% weight loss). DSC: T_g: 75.0 °C.

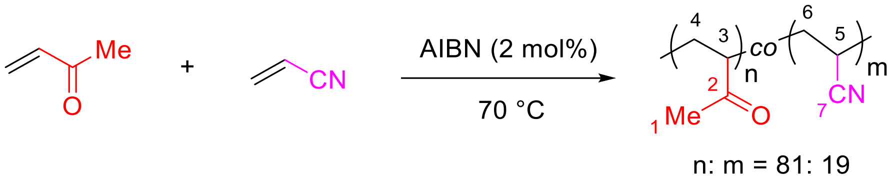
PMVK-co-PS (75/25) ***(6c)***



MVK St **6c**

A 10-mL Schlenk flask was charged with MVK (975 µL, 12.0 mmol), styrene (345 µL, 3.00 mmol), AIBN (24.6 mg, 0.15 mmol), and ethyl acetate (1.50 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N$_2$ atmosphere and then stirred at 65 °C for 6 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Then, 1,1,1,3-tetrachloropropane was added as an internal standard. Aliquots were taken and diluted for SEC and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 36 h at 40 °C to afford the title polymer **6c** as a white solid (940.6 mg, 62%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.70–6.41 (m, H$_{8,9,10,11,12}$), 2.96–0.51 (m, H$_{1,3,4,5,6}$). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$): δ 210.4 (C$_2$), 145.2–141.5 (C$_7$), 129.6–127.3 (C$_{8,9,11,12}$), 127.3–125.6 (C$_{10}$), 49.3–46.7 (C$_3$), 41.7 (C$_5$), 40.4–30.6 (C$_{4,6}$), 30.2–27.4 (C$_1$). FT-IR (KBr): ν (cm^{-1}) 3060, 3026, 3001, 2930, 2856, 1713, 1602, 1494, 1453, 1355, 1240, 1162, 1073, 1030, 958, 764, 736, 704, 597. SEC (THF, PS calibration): M_n: 37.2 kDa, M_w: 76.5 kDa, *Đ*: 2.06. TGA: 376 °C (50% weight loss). DSC: T_g: 55.2 °C.

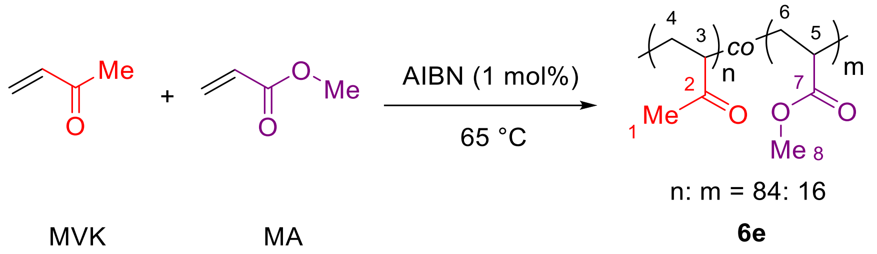
PMVK-co-PAN (81/19) ***(6d)***



MVK AN **6d**

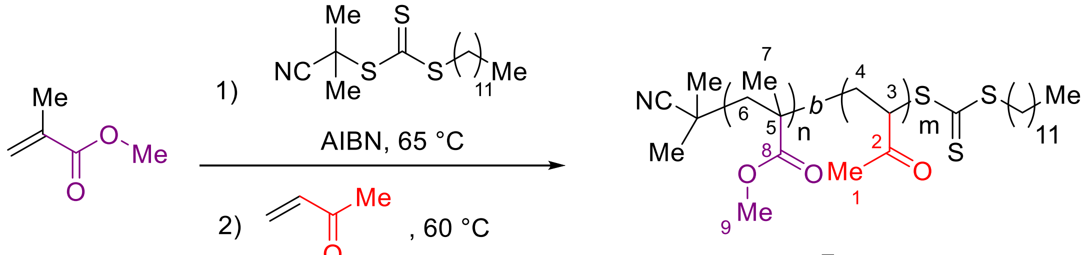
A 10-mL Schlenk flask was charged with MVK (975 µL, 12.0 mmol), acrylonitrile (195 µL, 3.00 mmol), AIBN (49.2 mg, 0.30 mmol), and ethyl acetate (1.50 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N$_2$ atmosphere and then stirred at 70 °C for 5 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Then, 1,1,1,3-tetrachloropropane was added as an internal standard. Aliquots were taken and diluted for SEC and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 36 h at 40 °C to afford the title polymer **6d** as a white solid (967.7 mg, 71%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.43–0.72 (m, H$_{1,3,4,5,6}$). ^{13}C NMR (101 MHz, CDCl$_3$): δ 212.3–207.9 (C$_2$), 122.2–118.5 (C$_7$), 48.8–46.5 (C$_3$), 36.1–30.6 (C$_{4,6}$), 30.6–28.6 (C$_1$), 28.6–25.7 (C$_5$). FT–IR (KBr): ν (cm^{-1}) 3060, 3001, 2925, 2853, 2238, 1712, 1633, 1427, 1357, 1270, 1241, 1164, 1108, 960, 736, 702, 595. SEC (THF, PS calibration): M_n: 12.6 kDa, M_w: 29.2 kDa, *Đ*: 2.33. TGA: 401 °C (50% weight loss). DSC: T_g: 41.7 °C.

PMVK-co-PMA (84/16) ***(6e)***



A 10-mL Schlenk flask was charged with MVK (650 μL, 8.00 mmol), MA (180 μL, 2.00 mmol), AIBN (16.4 mg, 0.10 mmol), and ethyl acetate (1.50 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 65 °C for 5 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Then, 1,1,1,3-tetrachloropropane was added as an internal standard. Aliquots were taken and diluted for SEC and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 36 h at 40 °C to afford the title polymer **6e** as a white solid (620.0 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (s, H_8), 2.77–2.00 (m, $H_{1,3,5}$), 2.00–0.95 (m, $H_{4,6}$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 210.3 (C_2), 174.4 (C_7), 51.7 (C_8), 49.3–46.8 (C_3), 41.4 (C_5), 36.5–30.6 ($C_{4,6}$), 30.6–28.4 (C_1). FT–IR (KBr): ν (cm^{-1}) 3000, 2950, 1739, 1713, 1435, 1357, 1240, 1164, 1110, 959, 735, 702, 595. SEC (THF, PS calibration): M_n: 39.2 kDa, M_w: 90.7 kDa, $Đ$: 2.31. TGA: 394 °C (50% weight loss). DSC: T_g: 29.1 °C.

*PMMA-b-PMVK diblock copolymer (**7a**)*



7a

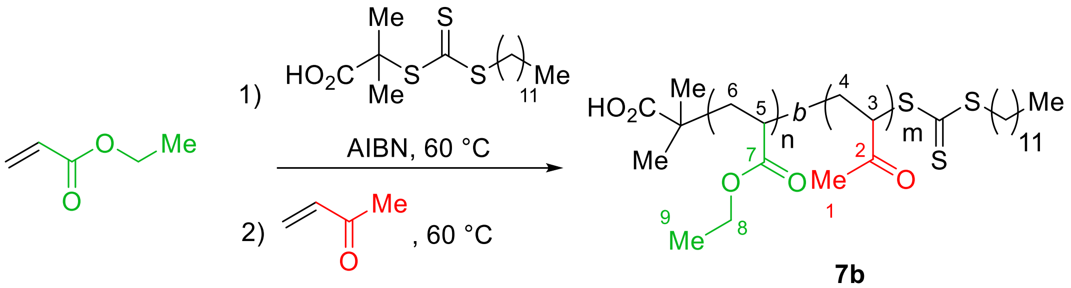
The title polymer **7a** was prepared according to a modification of the literature procedure.[11,12]

A 10-mL Schlenk flask was charged with MMA (1.55 mL, 14.6 mmol), CPDT (25.3 mg, 73.2 μmol), AIBN (0.012 M in ethyl acetate, 600 μL, 7.32 μmol), and ethyl acetate (950 μL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 65 °C for 12 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Aliquots were taken and diluted for SEC (THF, PS calibration) and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in methanol three times. The precipitate was collected and dried in a vacuum oven for 12 h at 40 °C to afford the PMMA macro-CTA as a yellow solid (559.4 mg, 34%; M_n = 7.7 kDa, $Đ$ = 1.28).

To obtain the diblock copolymer **7a**, a 10-mL Schlenk flask was charged with MVK (440 μL, 5.40 mmol), RAFT-terminated PMMA (230.1 mg, 30.0 μmol), AIBN (0.012 M in ethyl acetate, 310 μL, 3.75 μmol), and ethyl acetate (290 μL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 60 °C for 14 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Aliquots were taken and diluted for SEC and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 36 h at 40 °C to afford the title polymer **7a** as a yellow solid (343.7 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.58 (s, H_9), 2.73–2.01 (m, $H_{1,3}$), 2.01–1.06 (m, $H_{4,6}$), 1.06–0.50 (m, H_7). ^{13}C NMR (101 MHz, $CDCl_3$): δ 210.6 (C_2), 178.5–176.6 (C_8), 54.9–52.3 (C_6), 51.8 (C_9), 48.1 (C_3), 45.2–44.0

(C$_5$), 34.5–30.7 (C$_4$), 30.5–28.1 (C$_1$), 19.5–15.8 (C$_7$). FT–IR (KBr): ν (cm^{-1}) 2997, 2950, 2856, 1738, 1712, 1485, 1435, 1357, 1273, 1242, 1193, 1150, 1064, 986, 966, 764, 756. SEC (THF, PS calibration): M_n: 14.0 kDa, M_w: 16.4 kDa, $Đ$: 1.18. TGA: 394 °C (50% weight loss). DSC: T_g: 38.2 and 99.6 °C.

*PEA-b-PMVK diblock copolymer (**7b**)*



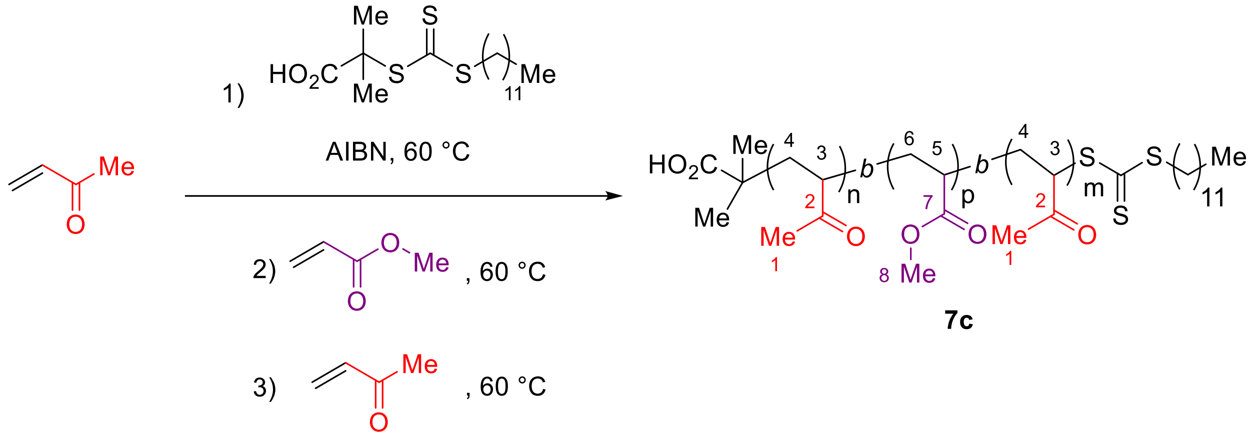
7b

The title polymer **7b** was prepared according to a modification of the literature procedure.[12,13]

A 10-mL Schlenk flask was charged with EA (1.21 mL, 11.3 mmol), DDMAT (19.7 mg, 56.9 µmol), AIBN (0.012 M in ethyl acetate, 465 µL, 5.69 µmol), and ethyl acetate (745 µL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N$_2$ atmosphere and then stirred at 60 °C for 3.5 h. The reaction mixture was cooled to room temperature and quenched by opening the flask to air. Aliquots were taken and diluted for SEC (THF, PS calibration) and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 12 h at 40 °C to afford the PEA macro-CTA as a yellow solid (478.8 mg, 37%; M_n = 8.6 kDa, $Đ$ = 1.06).

To obtain the diblock copolymer **7b**, a 10-mL Schlenk flask was charged with MVK (880 µL, 10.8 mmol), RAFT-terminated PEA (467.0 mg, 54.1 µmol), AIBN (0.012 M in ethyl acetate, 310 µL, 3.75 µmol), and ethyl acetate (290 µL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N$_2$ atmosphere and then stirred at 60 °C for 14 h. The reaction mixture was cooled to room temperature and quenched by opening the flask to air. Aliquots were taken and diluted for SEC and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 36 h at 40 °C to afford the title polymer **7b** as a yellow solid (667.1 mg, 45%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.39–3.82 (m, H$_8$), 2.69–2.01 (m, H$_{1,3,5}$), 2.01–1.33 (m, H$_{4,6}$), 1.34–0.93 (m, H$_9$). ^{13}C NMR (101 MHz, CDCl$_3$): δ 210.3 (C$_2$), 174.5 (C$_7$), 60.2 (C$_8$), 47.8 (C$_3$), 41.9–40.8 (C$_5$), 37.1–33.9 (C$_6$), 33.9–30.4 (C$_4$), 29.5 (C$_1$), 14.1 (C$_9$). FT–IR (KBr): ν (cm^{-1}) 2981, 2934, 2856, 1732, 1712, 1446, 1357, 1243, 1162, 1097, 1025, 959, 853, 736, 595. SEC (THF, PS calibration): M_n: 13.9 kDa, M_w: 15.3 kDa, $Đ$: 1.10. TGA: 397 °C (50% weight loss). DSC: T_g: –17.8 and 30.9 °C.

*PMVK-b-PMA-b-PMVK triblock copolymer (**7c**)*



The title polymer **7c** was prepared according to a modification of the literature procedure. [12,13]

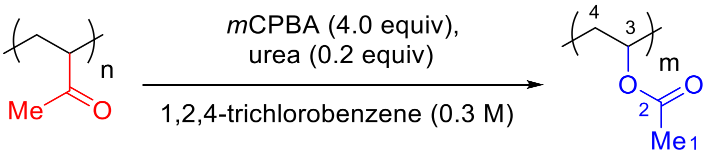
A 10-mL Schlenk flask was charged with MVK (730 µL, 9.00 mmol), DDMAT (21.9 mg, 0.06 mmol), AIBN (0.012 M in ethyl acetate, 500 µL, 6.00 µmol), and ethyl acetate (100 µL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 60 °C for 8 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Aliquots were taken and diluted for SEC (THF, PS calibration) and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 12 h at 40 °C to afford the PMVK macro-CTA as a yellow solid (313.4 mg, 37%; M_n = 5.2 kDa, $Đ$ = 1.05).

To obtain the PMVK-*b*-PMA, a 10-mL Schlenk flask was charged with MA (1.29 mL, 14.2 mmol), RAFT-terminated PMVK (298.1 mg, 0.057 mmol), AIBN (0.012 M in ethyl acetate, 465 µL, 5.69 µmol), and ethyl acetate (825 µL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 60 °C for 3 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Aliquots were taken and diluted for SEC (THF, PS calibration) and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 12 h at 40 °C to afford the PMVK-*b*-PMA as a yellow solid (843.4 mg, 51%; M_n = 15.5 kDa, $Đ$ = 1.11).

Finally, a 10-mL Schlenk flask was charged with MVK (850 µL, 10.5 mmol), RAFT-terminated PMVK-*b*-PMA (843.0 mg, 0.057 mmol), AIBN (0.012 M in ethyl acetate, 465 µL, 5.69 µmol), and ethyl acetate (385 µL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere, and then stirred at 60 °C for 5.5 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Aliquots were taken and diluted for SEC and ^{1}H NMR analysis. Volatiles were removed *in vacuo* and the polymer was purified via dissolution in a minimal amount of ethyl acetate and precipitated in *n*-hexane three times. The precipitate was collected and dried in a vacuum oven for 12 h at 40 °C to afford the title polymer **7c** as a yellow solid (514.5 mg, 28%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.62 (s, H$_8$), 2.77–1.98 (m, H$_{1,3,5}$), 1.98–0.89 (m, H$_{4,6}$). ^{13}C NMR (101 MHz, CDCl$_3$): δ 210.6 (C$_2$), 174.8 (C$_7$), 51.7 (C$_8$), 49.3–46.6 (C$_3$), 41.2 (C$_5$), 36.6–33.9 (C$_6$), 33.9–30.7 (C$_4$), 29.4 (C$_1$). FT–IR (KBr): ν (cm^{-1}) 3000, 2952, 2856, 1738, 1712, 1436, 1357, 1164, 1112, 972, 735, 702, 595. SEC (THF, PS calibration): M_n: 20.0 kDa, M_w: 22.8 kDa, $Đ$: 1.14. TGA: 401 °C (50% weight loss). DSC: T_g: 26.3 °C.

7. Exhaustive BV Oxidation of PMVK RAFT Homopolymers

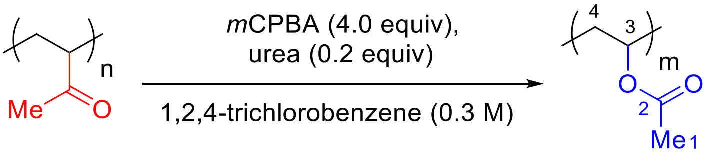
7.1 Synthesis of Narrow-Dispersed PVAc Homopolymer 5b



3b **5b**

A 50-mL Schlenk flask was charged with PMVK RAFT homopolymer **3b** (200.0 mg), urea (34.6 mg, 0.57 mmol), *m*CPBA (2.88 g, 11.52 mmol, ~69% purity), and 1,2,4-trichlorobenzene (9.60 mL). The mixture was stirred at 50 °C for 24 h. The reaction mixture was cooled to room temperature, and then diluted and dialyzed for 24 h against ethyl acetate. The solution was then concentrated and precipitated into diethyl ether/*n*-hexane (50 mL, 1:10 v/v). The collected precipitate was dried in a vacuum oven at 40 °C for 12 h and then at 120 °C for an additional 15 min. The title polymer **5b** was obtained as a white solid (214.3 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.40–4.52 (m, H_3), 2.41–1.94 (m, H_1), 1.94–1.44 (m, H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4 (C_2), 68.7–65.5 (C_3), 40.4–37.8 (C_4), 21.0 (C_1). FT–IR (KBr): ν (cm^{-1}) 2926, 1737, 1433, 1374, 1241, 1124, 1023, 947, 796, 631, 606. SEC (THF, PS calibration): M_n: 14.7 kDa, M_w: 17.0 kDa, $Đ$: 1.16. TGA: 336 °C (50% weight loss). DSC: T_g: 36.2 °C. MALDI-TOF MS (IAA) m/z: $[M + H]^+$ calcd for $C_{716}H_{1077}O_{361}S$ 15489; found 15488.

7.2 Synthesis of Narrow-Dispersed PVAc Homopolymer 5c



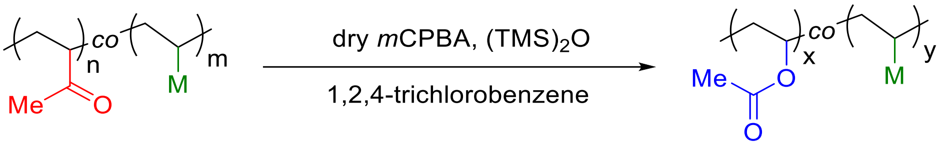
3c **5c**

A 50-mL Schlenk flask was charged with PMVK homopolymer **3c** (83.4 mg), urea (14.4 mg, 0.24 mmol), *m*CPBA (1.20 g, 4.80 mmol, ~69% purity), and 1,2,4-trichlorobenzene (4.00 mL). The mixture was stirred at 50 °C for 24 h. The reaction mixture was cooled to room temperature, then diluted and dialyzed for 24 h against ethyl acetate. The solution was then concentrated and precipitated into diethyl ether/*n*-hexane (50 mL, 1:10 v/v). The collected precipitate was dried in a vacuum oven at 40 °C for 12 h and then at 120 °C for an additional 15 min. Aliquots were taken for MALDI-TOF analysis. The title polymer **5c** was obtained as a white solid (62.2 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.53–4.43 (m, H_3), 2.36–1.95 (m, H_1), 1.95–1.48 (m, H_4). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4 (C_2), 69.4–65.7 (C_3), 40.6–37.3 (C_4), 20.9 (C_1). FT–IR (KBr): ν (cm^{-1}) 2926, 1738, 1434, 1373, 1241, 1124, 1023, 947, 796, 606. SEC (THF, PS calibration): M_n: 2.2 kDa, M_w: 2.4 kDa, $Đ$: 1.07. MALDI-TOF MS (DCTB) m/z: $[M + H]^+$ calcd for $C_{128}H_{194}O_{65}NS$ 2818.2; found 2818.6.

8. Exhaustive BV Oxidation of PMVK Copolymers

8.1 Oxidation of PMVK Statistical Copolymers

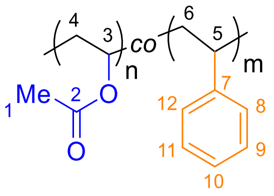
General procedures for preparation of PVAc statistical copolymers



M = Ph, CN or CO_2Me

A 50-mL Schlenk flask was charged with PMVK statistical copolymer (200.0 mg), dry *m*CPBA (2.00 g, 9.60 mmol, ~83% purity), $(TMS)_2O$ (1.02 mL, 4.80 mmol), and 1,2,4-trichlorobenzene (8.00 mL). The mixture was stirred for 24 h. The reaction mixture was cooled to room temperature, then diluted and dialyzed for 24 h against ethyl acetate. The solution was then concentrated and precipitated into diethyl ether/*n*-hexane (50 mL, 1:10 v/v). The collected precipitate was dried in a vacuum oven at 40 °C for 12 h and then at 120 °C for an additional 15 min.

PVAc-co-PS (28/72) ***(8a)***

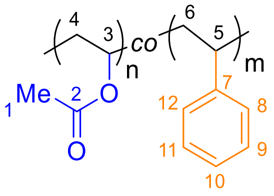


8a

n: m = 28: 72

The title polymer **8a** was prepared at 35 °C according to the general procedure and obtained as an off-white solid (198.3 mg, 95%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.30–6.34 (m, $H_{8,9,10,11,12}$), 4.79–4.00 (m, H_3), 2.93–0.74 (m, $H_{1,4,5,6}$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 169.9 (C_2), 147.3–142.3 (C_7), 129.6–126.9 ($C_{8,9,11,12}$), 125.9 (C_{10}), 71.2–69.9 (C_3), 47.5–40.8 ($C_{4,5,6}$), 21.3–20.0 (C_1). FT–IR (KBr): ν (cm^{-1}) 3083, 3060, 3026, 2926, 2852, 1735, 1601, 1583, 1493, 1453, 1371, 1241, 1181, 1028, 938, 909, 759, 700, 544. SEC (THF, PS calibration): M_n: 24.5 kDa, M_w: 46.3 kDa, $Đ$: 1.89. TGA: 374 °C (50% weight loss). DSC: T_g: 87.5 °C.

PVAc-co-PS (50/50) ***(8b)***

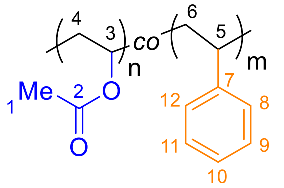


8b

n: m = 50: 50

The title polymer **8b** was prepared at 40 °C according to the general procedure and obtained as an off-white solid (209.0 mg, 96%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.42–6.15 (m, $H_{8,9,10,11,12}$), 5.08–3.82 (m, H_3), 2.82–0.78 (m, $H_{1,4,5,6}$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 169.9 (C_2), 146.5–141.1 (C_7), 129.1–126.9 ($C_{8,9,11,12}$), 126.2 (C_{10}), 72.1–67.8 (C_3), 46.4–38.8 ($C_{4,5,6}$), 20.7 (C_1). FT–IR (KBr): ν (cm^{-1}) 3061, 3027, 2926, 2854, 1736, 1602, 1494, 1453, 1372, 1241, 1180, 1025, 938, 761, 738, 701. SEC (THF, PS calibration): M_n: 36.3 kDa, M_w: 73.8 kDa, $Đ$: 2.04. TGA: 365 °C (50% weight loss). DSC: T_g: 73.0 °C.

PVAc-co-PS (75/25) ***(8c)***

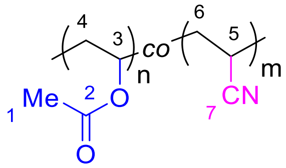


8c

n: m = 75: 25

The title polymer **8c** was prepared at 45 °C according to the general procedure and obtained as a white solid (199.6 mg, 86%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.42–6.45 (m, $H_{8,9,10,11,12}$), 5.24–3.97 (m, H_3), 2.95–0.56 (m, $H_{1,4,5,6}$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 170.2 (C_2), 145.4–141.7 (C_7), 128.9–126.9 ($C_{8,9,11,12}$), 126.3 (C_{10}), 72.1–65.2 (C_3), 43.0–36.8 ($C_{4,5,6}$), 20.7 (C_1). FT–IR (KBr): ν (cm^{-1}) 2922, 2852, 1738, 1658, 1633, 1469, 1454, 1435, 1373, 1241, 1023, 946, 737, 703. SEC (THF, PS calibration): M_n: 37.3 kDa, M_w: 95.5 kDa, $Đ$: 2.56. TGA: 354 °C (50% weight loss). DSC: T_g: 56.1 °C.

*PVAc-co-PAN (81/19) (**8d**)*

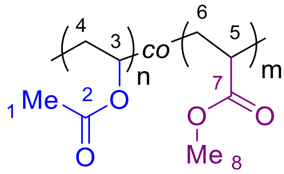


8d

n: m = 81: 19

The title polymer **8d** was prepared at 50 °C according to the general procedure and obtained as a white solid (180.2 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.50–4.55 (m, H_3), 3.23–2.46 (m, H_5), 2.46–1.05 (m, $H_{1,4,6}$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4 (C_2), 122.0–117.3 (C_7), 69.6–64.6 (C_3), 40.6–37.9 (C_4), 37.9–35.2 (C_6), 27.2–23.9 (C_5), 21.0 (C_1). FT–IR (KBr): ν (cm^{-1}) 2924, 2852, 2240, 1738, 1659, 1434, 1373, 1237, 1180, 1076, 1023, 946, 797, 736, 702, 631, 605. SEC (THF, PS calibration): M_n: 14.3 kDa, M_w: 34.6 kDa, $Đ$: 2.43. TGA: 351 °C (50% weight loss). DSC: T_g: 45.9 °C.

*PVAc-co-PMA (83/17) (**8e**)*



8e

n: m = 83: 17

The title polymer **8e** was prepared at 50 °C according to the general procedure and obtained as a white solid (209.2 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32–4.45 (m, H_3), 3.67 (s, H_8), 2.56–1.40 (m, $H_{1,4,5,6}$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 175.2 (C_7), 170.4 (C_2), 70.9–65.7 (C_3), 51.8 (C_8), 42.0–35.7 ($C_{4,5,6}$), 21.0 (C_1). FT–IR (KBr): ν (cm^{-1}) 2923, 2852, 1738, 1435, 1373, 1238, 1169, 1022, 946, 736, 606. SEC (THF, PS calibration): M_n: 40.5 kDa, M_w: 89.9 kDa, $Đ$: 2.22. TGA: 352 °C (50% weight loss). DSC: T_g: 40.1 °C.

Table S10. Molecular weight characteristics of PMVK-*co*-PS and PVAc-*co*-PS.[a]

Entry	Feed ratio[b] (MVK/St)	Before oxidation			T (°C)	After oxidation		
		Monomer ratio[c] (MVK/St)	$M_{n,SEC}$[d] (kDa)	*Đ*[d]		Monomer ratio[e] (VAc/St)	$M_{n,SEC}$[d] (kDa)	*Đ*[d]
1	20/80	28/72	23.9	1.79	35	28/72	24.5	1.89
2	50/50	51/49	34.4	1.90	40	50/50	36.3	2.04
3	80/20	75/25	37.2	2.06	45	75/25	37.3	2.56

[a] Standard conditions: PMVK-*co*-PS statistical copolymer (200.0 mg), dry *m*CPBA (2.00 g, 9.60 mmol, ~83% purity), and $(TMS)_2O$ (1.02 mL, 4.76 mmol) were stirred in 1,2,4-trichlorobenzene (8.00 mL) for 24 h. [b] The monomer feed mole ratios for the preparation of the PMVK-*co*-PS statistical copolymer. [c] The copolymerization ratio of MVK copolymer was calculated by the equation $P_{MVK/St} = \frac{N_{MVK0}-N_{MVKr}}{N_{St0}-N_{Str}}$, where N_{MVK0} and N_{St0} are the molar amounts of MVK and St respectively for the initial feed of the polymerization, N_{MVKr} and N_{Str} are the remaining molar amounts of MVK and St at the end of polymerization, which were measured by NMR with 1,1,1,3-tetrachloropropane as an internal standard. [d] Determined by SEC (THF) analysis relative to polystyrene standards. [e] The ratio of VAc units to St units after BV oxidation was obtained from the NMR spectra of the purified polymer.

Table S11. The T_g and thermal stability of PMVK-*co*-PS and PVAc-*co*-PS.

Entry	Feed ratio (MVK/St)	Before oxidation			After oxidation		
		Monomer ratio (MVK/St)	T_g[a] (°C)	Temperature[b] at 50% weight loss (°C)	Monomer ratio (VAc/St)	T_g[a] (°C)	Temperature[b] at 50% weight loss (°C)
1	20/80	28/72	86.8	396	28/72	87.5	374
2	50/50	51/49	75.0	380	50/50	73.0	365
3	80/20	75/25	55.2	376	75/25	56.1	354

[a] The midpoint of the step change of DSC curve was determined as the T_g of the polymer. [b] The temperature corresponding to the loss of half the weight of the polymer in the TGA test.

Table S12. Molecular weight characteristics of PMVK-*co*-PMA, PMVK-*co*-PAN, PVAc-*co*-PMA and PVAc-*co*-PAN.[a]

Entry	Comonomer	Feed ratio[b] (MVK/MAM)	Before oxidation			After oxidation		
			Monomer ratio[c] (MVK/MAM)	$M_{n,SEC}$[d] (kDa)	$Đ$[d]	Monomer ratio[e] (VAc/MAM)	$M_{n,SEC}$[d] (kDa)	$Đ$[d]
1	MA	80/20	84/16	39.2	2.31	83/17	40.5	2.22
2	AN	80/20	81/19	12.5	2.33	81/19	14.3	2.43

[a]Standard conditions: PMVK statistical copolymer (200.0 mg), dry *m*CPBA (2.00 g, 9.60 mmol, ~83% purity), and $(TMS)_2O$ (1.02 mL, 4.76 mmol) were stirred in 1,2,4-trichlorobenzene (8.00 mL) at 50 °C for 24 h. [b]The monomer feed mole ratios for the preparation of the PMVK statistical copolymers. [c]The copolymerization ratio of MVK copolymer was calculated by the equation $P_{MVK/MAM} = \frac{N_{MVK0}-N_{MVKr}}{N_{MAM0}-N_{MAMr}}$, where N_{MVK0} and N_{MAM0} are the molar amounts of MVK and MAM respectively for the initial feed of the polymerization, N_{MVKr} and N_{MAMr} are the remaining molar amounts of MVK and MAM at the end of polymerization, which were measured by NMR with 1,1,1,3-tetrachloropropane as an internal standard. [d]Determined by SEC (THF) analysis relative to polystyrene standards. [e]The ratio of VAc units to MAM units after BV oxidation was obtained from the NMR spectra of the purified polymer.

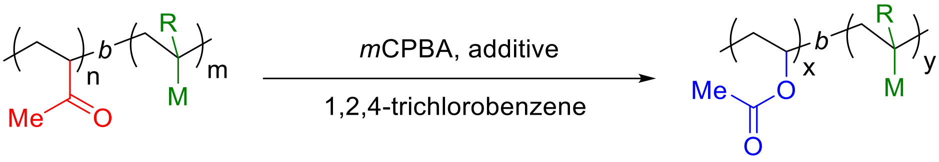
Table S13. The T_g and thermal stability of PMVK-*co*-PMA, PMVK-*co*-PAN, PVAc-*co*-PMA and PVAc-*co*-PAN.

Entry	Comonomer	Before oxidation			After oxidation		
		Monomer ratio (MVK/MAM)	T_g[a] (°C)	Temperature[b] at 50% weight loss (°C)	Monomer ratio (VAc/MAM)	T_g[a] (°C)	Temperature[b] at 50% weight loss (°C)
1	MA	84/16	29.1	394	83/17	40.1	352
2	AN	81/19	41.7	401	81/19	45.9	351

[a]The midpoint of step change of DSC curve was determined as the T_g of polymer. [b]The temperature corresponding to the loss of half the weight of the polymer in the TGA test.

8.2 Oxidation of PMVK Block Copolymers

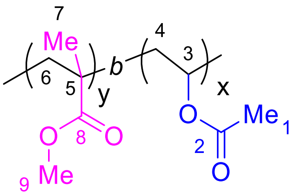
General procedures for preparation of PVAc block copolymers



M = CO_2Me or CO_2Et
R = H or Me

A 50-mL Schlenk flask was charged with PMVK block copolymer (200.0 mg), additive (0.24 mmol), *m*CPBA (2.00 g, 9.60 mmol, ~69% purity), and 1,2,4-trichlorobenzene (8.00 mL). The mixture was stirred at 50 °C for 24 h. The reaction mixture was cooled to room temperature, and then diluted and dialyzed for 24 h against ethyl acetate. The solution was then concentrated and precipitated into diethyl ether/*n*-hexane (50 mL, 1:10 v/v). The collected precipitate was dried in a vacuum oven at 40 °C for 12 h and then at 120 °C for an additional 15 min.

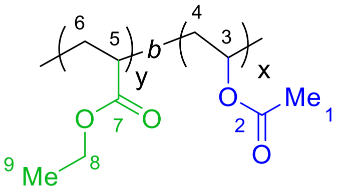
*PMMA-b-PVAc diblock copolymer (**9a**)*



9a

The title polymer **9a** was prepared according to the general procedure and obtained as a white solid (202.5 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.55–4.45 (m, H_3), 3.57 (s, H_9), 2.24–1.93 (m, H_1), 1.93–1.12 (m, $H_{4,6}$), 1.12–0.53 (m, H_7). ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.4–176.3 (C_8), 170.3 (C_2), 68.7–65.4 (C_3), 55.1–52.3 (C_6), 51.7 (C_9), 45.6–43.9 (C_5), 40.5–37.8 (C_4), 21.0 (C_1), 19.2–15.7 (C_7). FT–IR (KBr): ν (cm^{-1}) 2993, 2951, 2852, 1733, 1485, 1435, 1373, 1242, 1194, 1149, 1023, 991, 948, 736, 702, 605. SEC (THF, PS calibration): M_n: 14.4 kDa, M_w: 17.7 kDa, $Đ$: 1.23. TGA: 351 °C (50% weight loss). DSC: T_g: 58.6 °C.

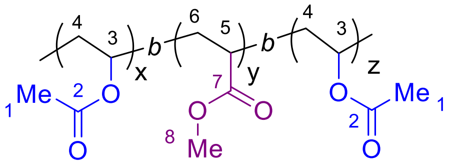
*PEA-b-PVAc diblock copolymer (**9b**)*



9b

The title polymer **9b** was prepared according to the general procedure and obtained as a white solid (210.0 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.15–4.65 (m, H_3), 4.39–3.88 (m, H_8), 2.61–2.12 (m, H_5), 2.12–1.95 (m, H_1), 1.95–1.35 (m, $H_{4,6}$), 1.35–1.05 (m, H_9). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.5 (C_7), 170.2 (C_2), 68.5–65.5 (C_3), 60.4 (C_8), 42.2–40.4 (C_5), 40.4–37.7 (C_4), 37.7–33.3 (C_6), 21.0 (C_1), 14.1 (C_9). FT–IR (KBr): ν (cm^{-1}) 2993, 2951, 1733, 1485, 1435, 1373, 1242, 1194, 1149, 1023, 991, 948, 736, 702, 605. SEC (THF, PS calibration): M_n: 14.4 kDa, M_w: 16.2 kDa, $Đ$: 1.12. TGA: 339 °C (50% weight loss). DSC: T_g: 11.4 °C.

*PVAc-b-PMA-b-PVAc triblock copolymer (**9c**)*

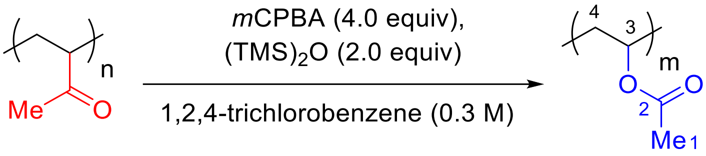


9c

The title polymer **9c** was prepared according to the general procedure and obtained as a white solid (207.1 mg, 95%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.36–4.55 (m, H$_3$), 3.64 (s, H$_8$), 2.51–2.16 (m, H$_5$), 2.16–1.95 (m, H$_1$), 1.95–1.31 (m, H$_{4,6}$). ^{13}C NMR (101 MHz, CDCl$_3$): δ 174.8 (C$_7$), 170.2 (C$_2$), 68.6–65.4 (C$_3$), 51.7 (C$_8$), 41.3 (C$_5$), 40.5–37.7 (C$_4$), 36.6–33.3 (C$_6$), 20.9 (C$_1$). FT–IR (KBr): ν (cm^{-1}) 2954, 1739, 1437, 1374, 1243, 1166, 1121, 1023, 948, 828, 736, 606. SEC (THF, PS calibration): M_n: 20.9 kDa, M_w: 23.7 kDa, $Đ$: 1.13. TGA: 386 °C (50% weight loss). DSC: T_g: 27.0 °C.

9. Gram-scale BV Oxidation of PMVK and PMVK-*co*-PS

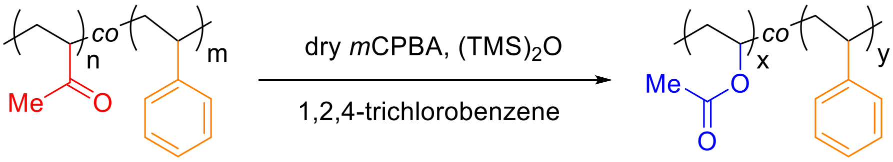
BV oxidation of commercial PMVK 3a



3a **5a**

A 250-mL round bottom flask was charged with commercial PMVK **3a** (1.25 g, containing 17.83 mmol repeating units), dry *m*CPBA (15.00 g, 72.0 mmol, ~83% purity), (TMS)$_2$O (7.60 mL, 36.0 mmol), and 1,2,4-trichlorobenzene (60 mL). The mixture was stirred at 50 °C for 24 h and then added dropwise to a solution of diethyl ether and *n*-hexane (150 mL, 1:2 v/v). After the supernatant liquid was decanted, the viscous residue was re-dissolved with ethyl acetate (20 mL). The precipitation process was repeated three times, and then the crude product was dried in a vacuum oven at 40 °C for 12 h and then at 120 °C for an additional 15 min. The polymer **5a** was obtained as a white solid (1.44 g, 94 %). ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.40–4.46 (m, H$_3$), 2.32–1.92 (m, H$_1$), 1.92–1.36 (m, H$_4$). ^{13}C NMR (101 MHz, CDCl$_3$): δ 170.4 (C$_2$), 68.6–65.2 (C$_3$), 40.7–38.1 (C$_4$), 20.9 (C$_1$). FT–IR (KBr): ν (cm^{-1}) 2926, 1739, 1434, 1373, 1240, 1022, 947, 736, 631, 606. SEC (THF, PS calibration): M_n: 60.1 kDa, M_w: 149.1 kDa, $Đ$: 2.48. TGA: 342 °C (50% weight loss). DSC: T_g: 43.4 °C.

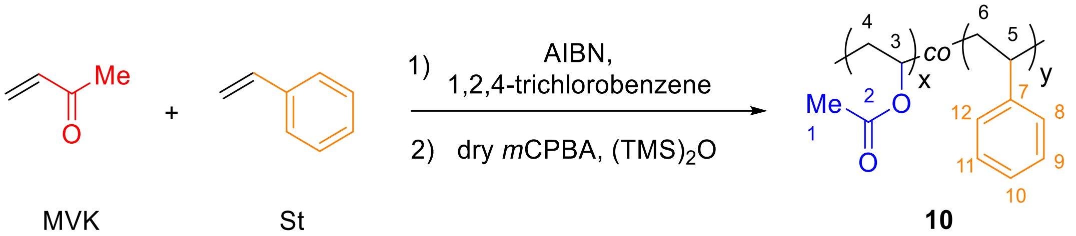
BV oxidation of PMVK-*co*-PS 6b



6b **8b**

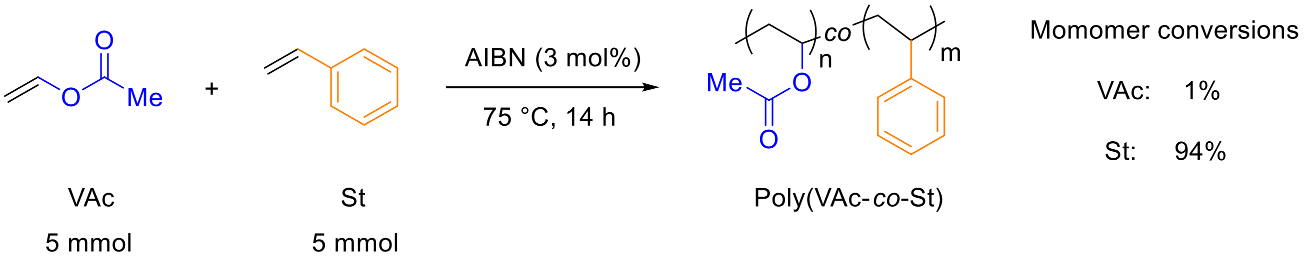
A 250-mL round bottom flask was charged with PMVK-*co*-PS (51/49) **6b** (1.50 g, containing 8.82 mmol MVK repeating units), dry *m*CPBA (15.00 g, 72.0 mmol, ~83% purity), (TMS)$_2$O (7.60 mL, 36.0 mmol), and 1,2,4-trichlorobenzene (60 mL). The mixture was stirred at 40 °C for 24 h and then added dropwise to a solution of diethyl ether and *n*-hexane (150 mL, 1:2 v/v). After the supernatant liquid was decanted, the viscous residue was re-dissolved with ethyl acetate (20 mL). The precipitation process was repeated three times, and then the crude product was dried in a vacuum oven at 40 °C for 12 h and then at 120 °C for an additional 15 min. The copolymer PVAc-*co*-PS (VAc/St = 50/50) **8b** was obtained as an off-white solid (1.38 g, 85%). NMR data were in agreement with the data of **8b** in section **8.1**.

One-Pot Synthesis of PVAc-*co*-PS 10



A 10-mL Schlenk flask was charged with MVK (605 µL, 7.50 mmol), styrene (860 µL, 7.50 mmol), AIBN (24.6 mg, 0.15 mmol), and 1,2,4-trichlorobenzene (6.00 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 70 °C for 24 h. The reaction mixture was then cooled to room temperature. To the polymer solution was added dry *m*CPBA (13.05 g, 62.6 mmol, ~83% purity), $(TMS)_2O$ (6.53 mL, 31.3 mmol), and 1,2,4-trichlorobenzene (46 mL). The mixture was stirred at 40 °C for 24 h and then added dropwise to a solution of diethyl ether and *n*-hexane (150 mL, 1:2 v/v). After the supernatant liquid was decanted, the viscous residue was re-dissolved with ethyl acetate (20 mL). The precipitation process was repeated three times, and then the crude product was dried in a vacuum oven at 40 °C for 12 h and then at 120 °C for an additional 15 min. The copolymer PVAc-*co*-PS (VAc/St = 49/51) **10** was obtained as an off-white solid (1.15 g, 81%). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.42–6.15 (m, $H_{8,9,10,11,12}$), 5.08–3.82 (m, H_3), 2.82–0.78 (m, $H_{1,4,5,6}$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 169.9 (C_2), 146.5–141.7 (C_7), 129.2–126.9 ($C_{8,9,11,12}$), 126.2 (C_{10}), 72.0–67.3 (C_3), 46.4–38.8 (m, $C_{4,5,6}$), 20.7 (C_1). SEC (THF, PS calibration): M_n: 17.3 kDa, M_w: 38.5 kDa, *Đ*: 2.23.

10. Copolymerization of VAc and St



A 10-mL Schlenk flask was charged with VAc (465 µL, 5.00 mmol), St (575 µL, 5.00 mmol), AIBN (49.2 mg, 0.30 mmol), and ethyl acetate (200 µL). The mixture was deoxygenated by three freeze-pump-thaw cycles under an N_2 atmosphere and then stirred at 75 °C for 14 h. The reaction mixture was cooled to room temperature and then quenched by opening the flask to air. Aliquots were taken and diluted for ^1H NMR analysis to determine the monomer conversions. The conversions of VAc and St were 1% and 94% respectively.

11. Supplemental Figures

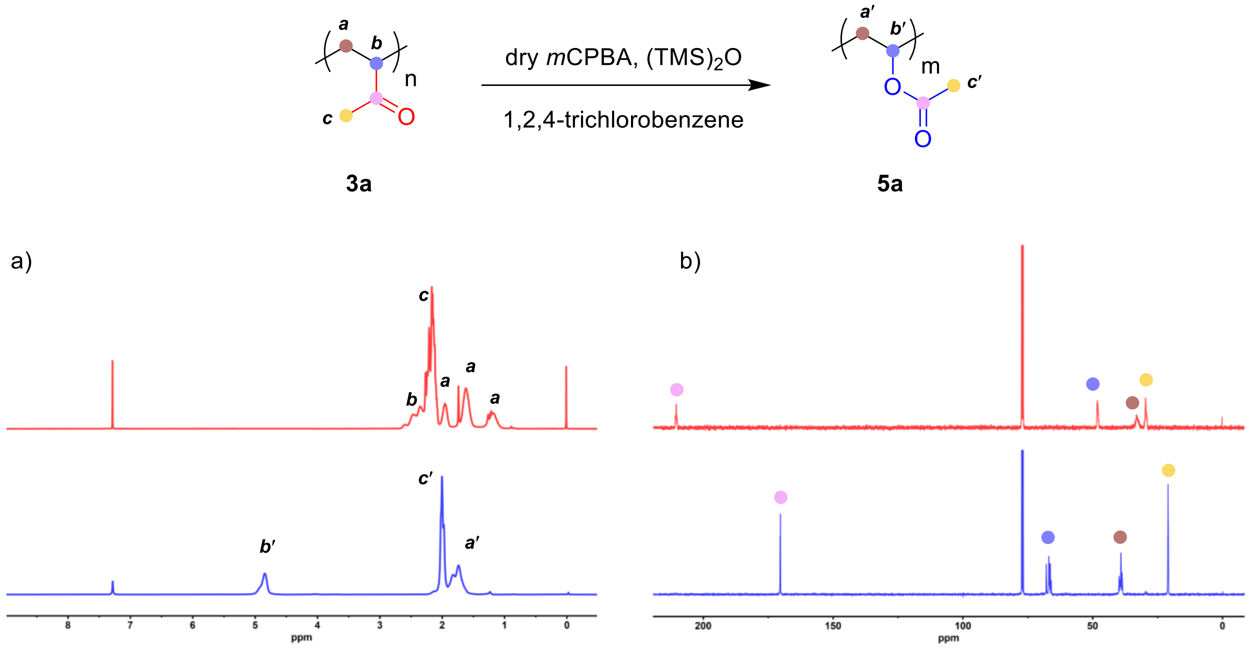


Figure S2. Exhaustive BV oxidation of commercial PMVK **3a**. Comparison of (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra before and after the exhaustive BV oxidation of **3a**. The NMR spectra were recorded using $CDCl_3$ as a solvent.

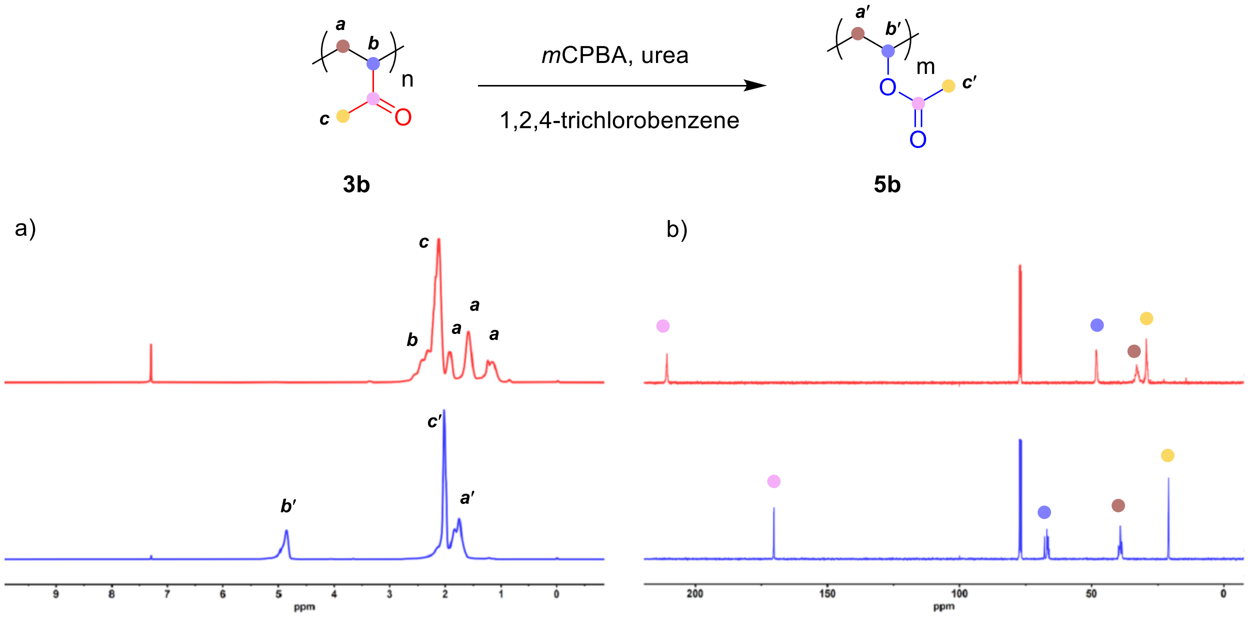


Figure S3. Exhaustive BV oxidation of PMVK (RAFT) **3b**. Comparison of (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra before and after the exhaustive BV oxidation of **3b**. The NMR spectra were recorded using $CDCl_3$ as a solvent.

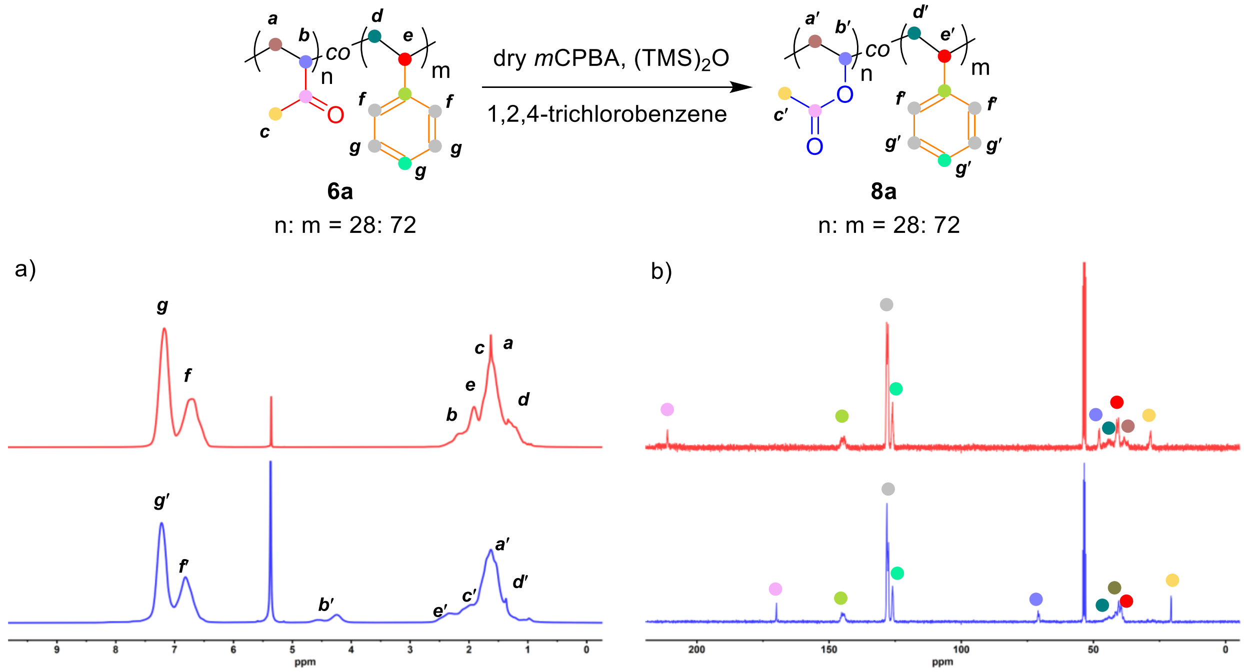


Figure S4. Exhaustive BV oxidation of PMVK-*co*-PS (28/72) statistical copolymers **6a**. Comparison of (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra before and after the exhaustive BV oxidation of **6a**. The NMR spectra were recorded using CD_2Cl_2 as a solvent.

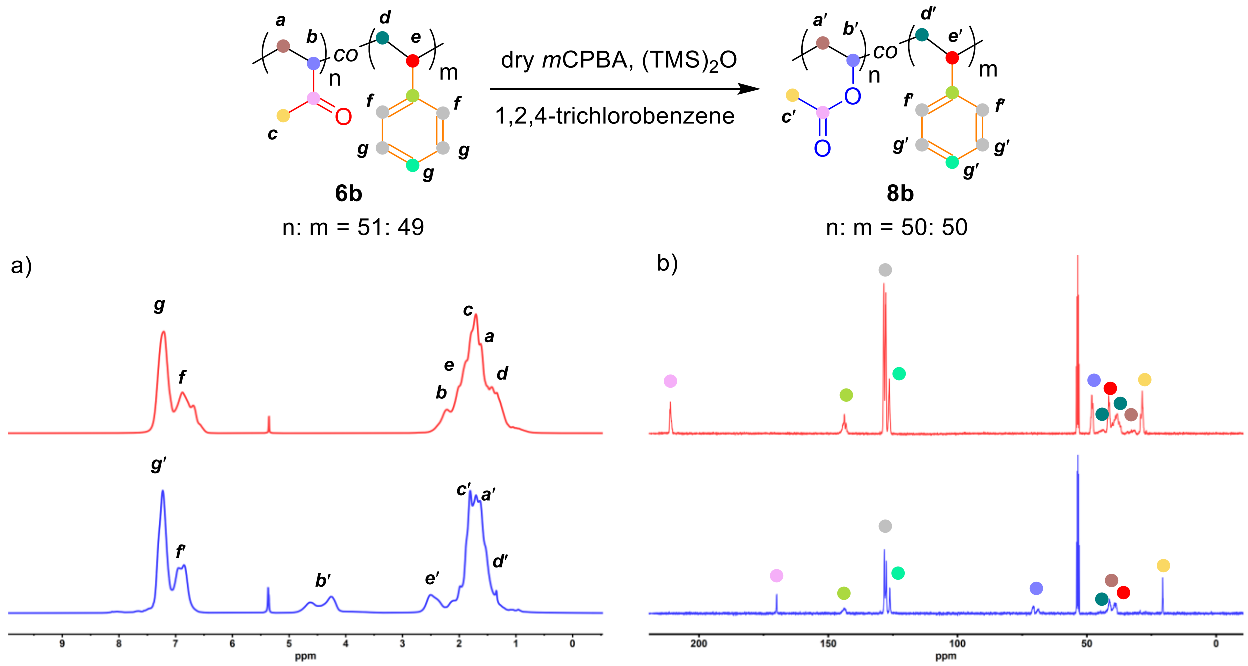


Figure S5. Exhaustive BV oxidation of PMVK-*co*-PS (51/49) statistical copolymers **6b**. Comparison of (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra before and after the exhaustive BV oxidation of **6b**. The NMR spectra were recorded using CD_2Cl_2 as a solvent.

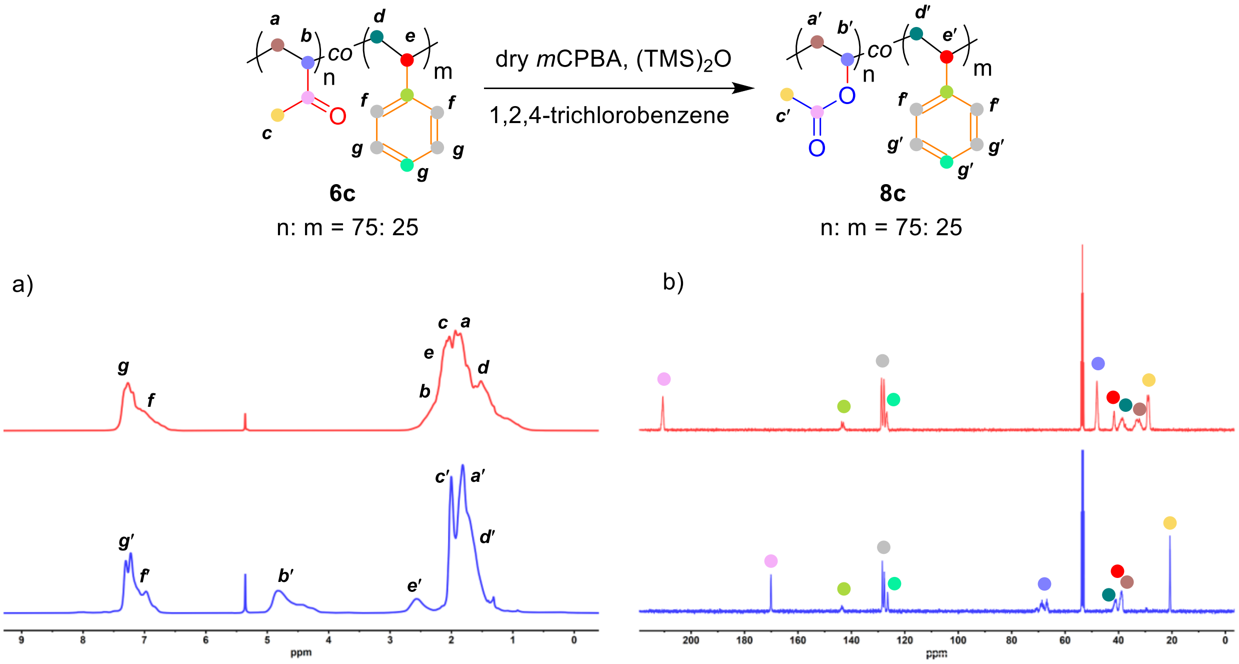


Figure S6. Exhaustive BV oxidation of PMVK-*co*-PS (75/25) statistical copolymers **6c**. Comparison of (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra before and after the exhaustive BV oxidation of **6c**. The NMR spectra were recorded using CD_2Cl_2 as a solvent.

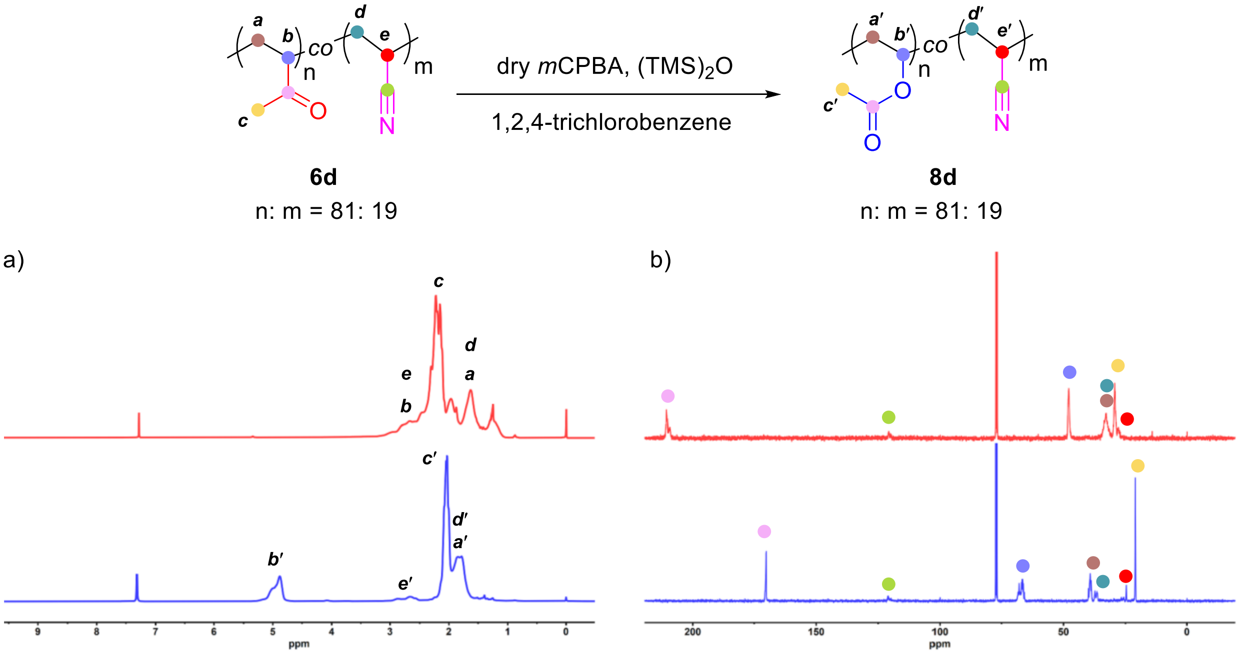


Figure S7. Exhaustive BV oxidation of PMVK-*co*-PAN (81/19) statistical copolymers **6d**. Comparison of (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra before and after the exhaustive BV oxidation of **6d**. The NMR spectra were recorded using $CDCl_3$ as a solvent.

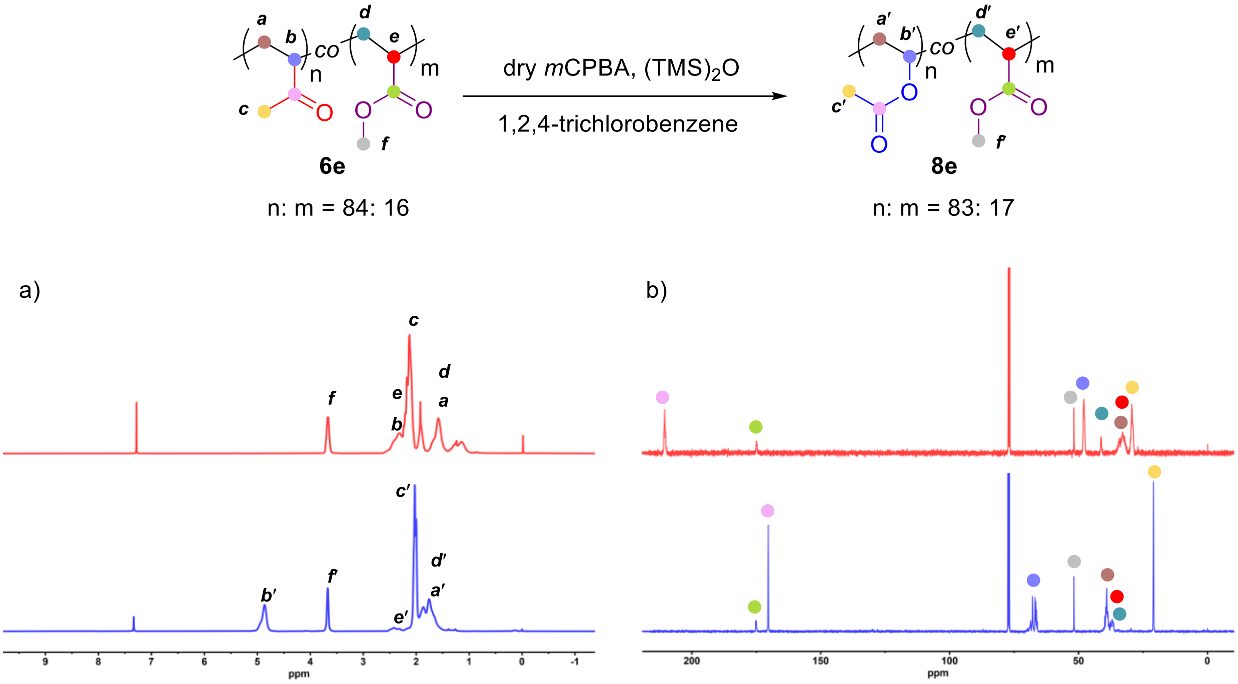


Figure S8. Exhaustive BV oxidation of PMVK-*co*-PMA (84/16) statistical copolymers **6e**. Comparison of (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra before and after the exhaustive BV oxidation of **6e**. The NMR spectra were recorded using $CDCl_3$ as a solvent.

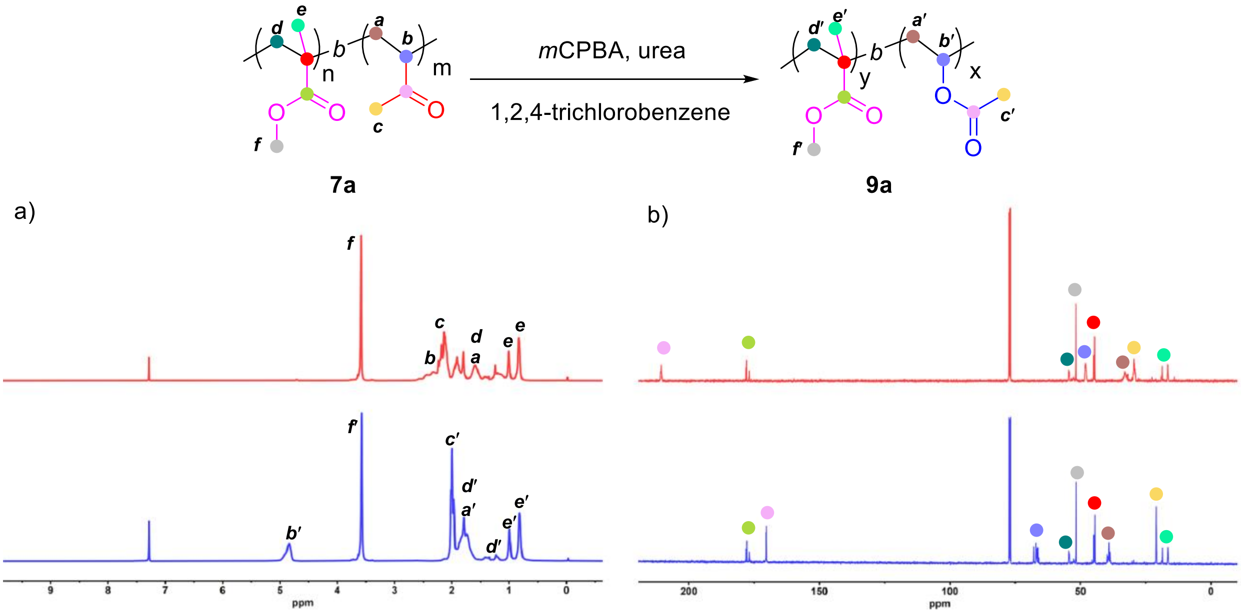


Figure S9. Exhaustive BV oxidation of PMMA-*b*-PMVK **7a**. Comparison of (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra before and after the exhaustive BV oxidation of **7a**. The NMR spectra were recorded using $CDCl_3$ as a solvent.

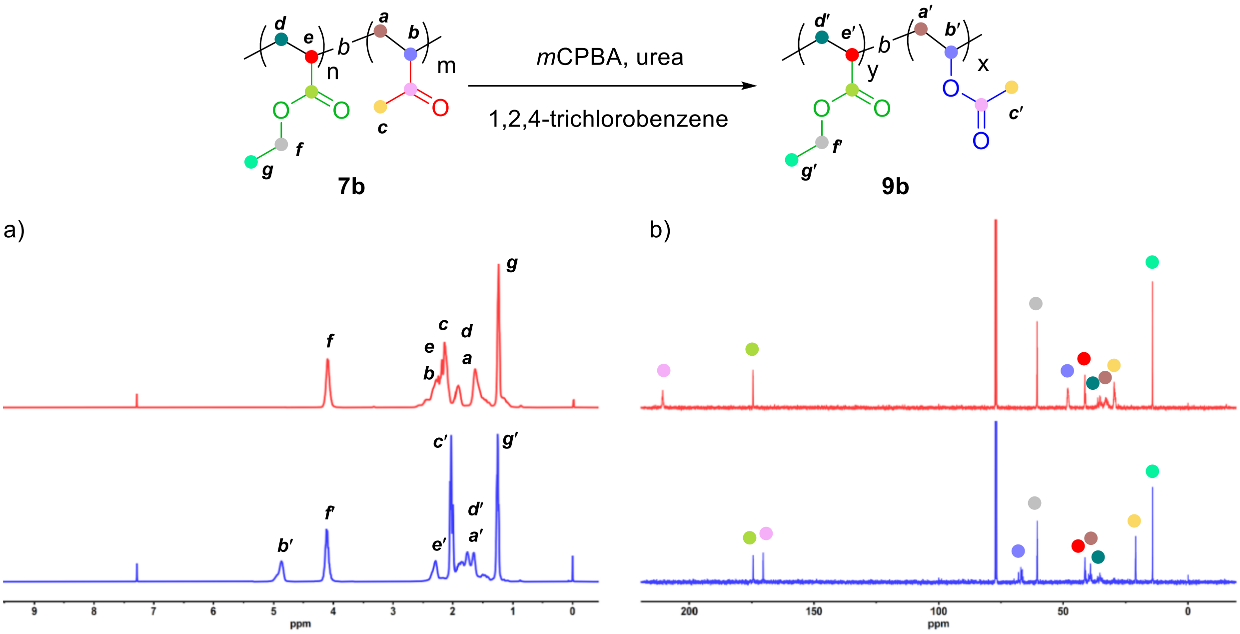


Figure S10. Exhaustive BV oxidation of PEA-*b*-PMVK **7b**. Comparison of (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra before and after the exhaustive BV oxidation of **7b**. The NMR spectra were recorded using $CDCl_3$ as a solvent.

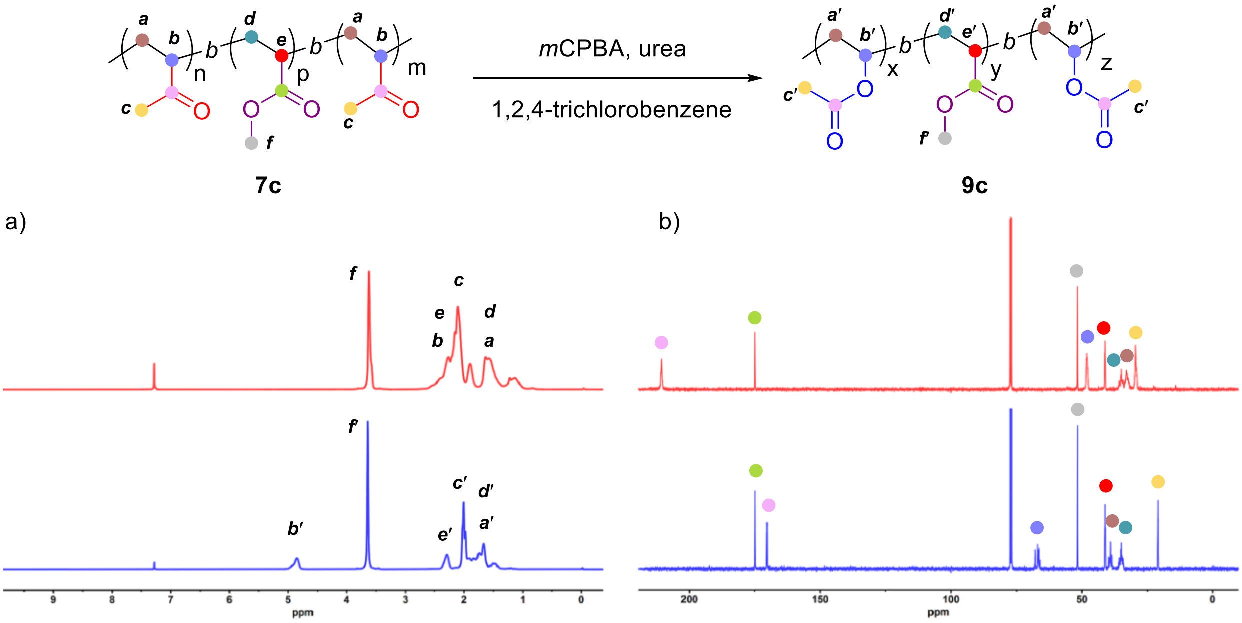


Figure S11. Exhaustive BV oxidation of PMVK-*b*-PMA-b-PMVK **7c**. Comparison of (a) ^{1}H NMR spectra and (b) ^{13}C NMR spectra before and after the exhaustive BV oxidation of **7c**. The NMR spectra were recorded using $CDCl_3$ as a solvent.

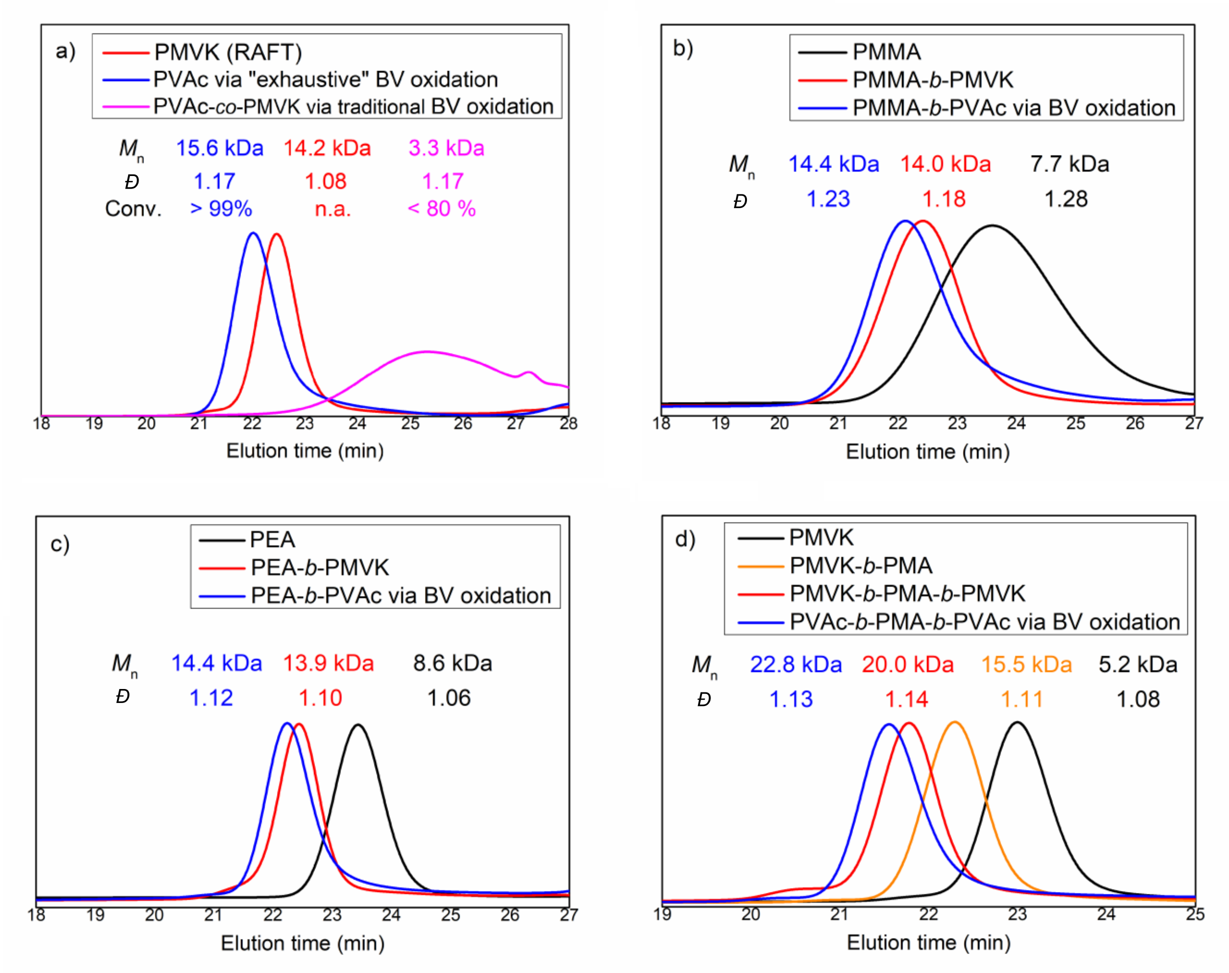


Figure S12. SEC traces of (a) RAFT homopolymer of PMVK **3b**, PVAc **5b** synthesized by the exhaustive BV protocol, PVAc-*co*-PMVK synthesized by an existing small-molecule BV protocol, (b) RAFT homopolymer of PMMA, PMMA-*b*-PMVK diblock copolymer **7a**, PMMA-*b*-PVAc diblock copolymer **9a**, (c) RAFT homopolymer of PEA, PEA-*b*-PMVK diblock copolymer **7b**, PEA-*b*-PVAc diblock copolymer **9b**, and (d) RAFT homopolymer of PMVK, PMVK-*b*-PMA diblock copolymer, PMVK-*b*-PMA-*b*-PMVK triblock copolymer **7c**, PVAc-*b*-PMA-*b*-PVAc triblock copolymer **9c**.

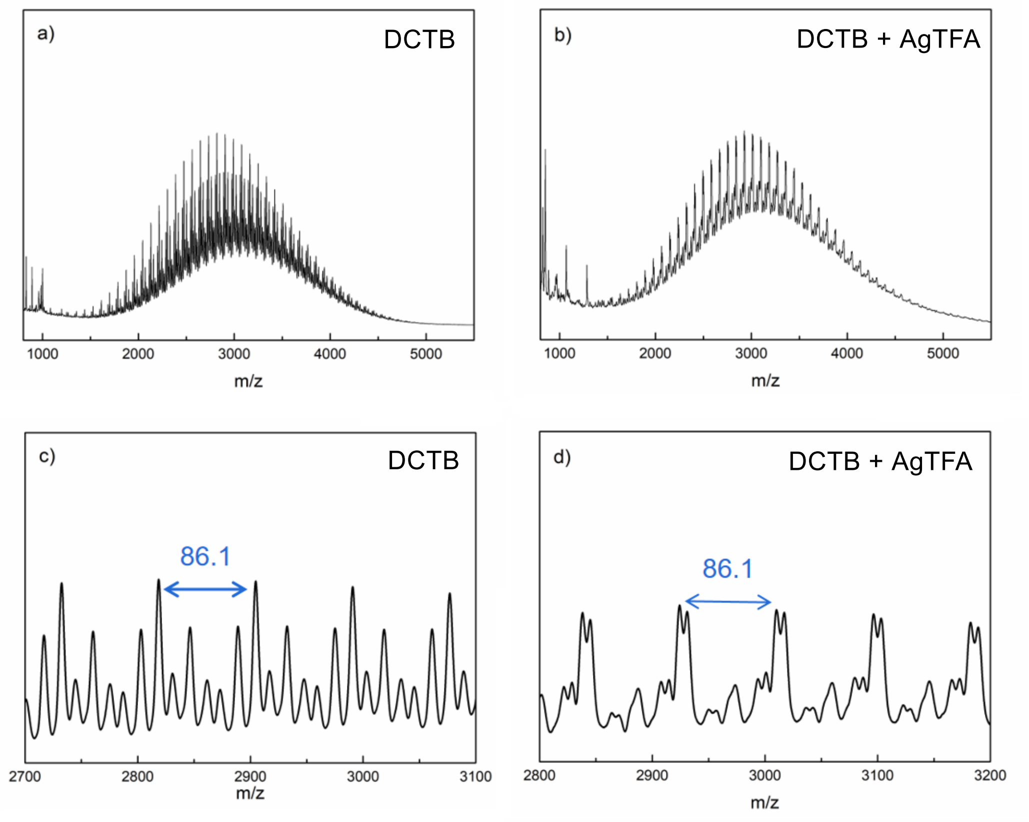


Figure S13. (a) Full MALDI–TOF spectrum of **5c** with DCTB as a matrix. (b) MALDI–TOF spectrum from 2700–3100 m/z of **5c** with DCTB as a matrix. (c) Full MALDI–TOF spectrum of **5c** with DCTB as a matrix and AgTFA as a cationic reagent. (d) MALDI–TOF spectrum from 2800–3200 m/z of **5c** with DCTB as a matrix and AgTFA as a cationic reagent.

12. Supplemental References

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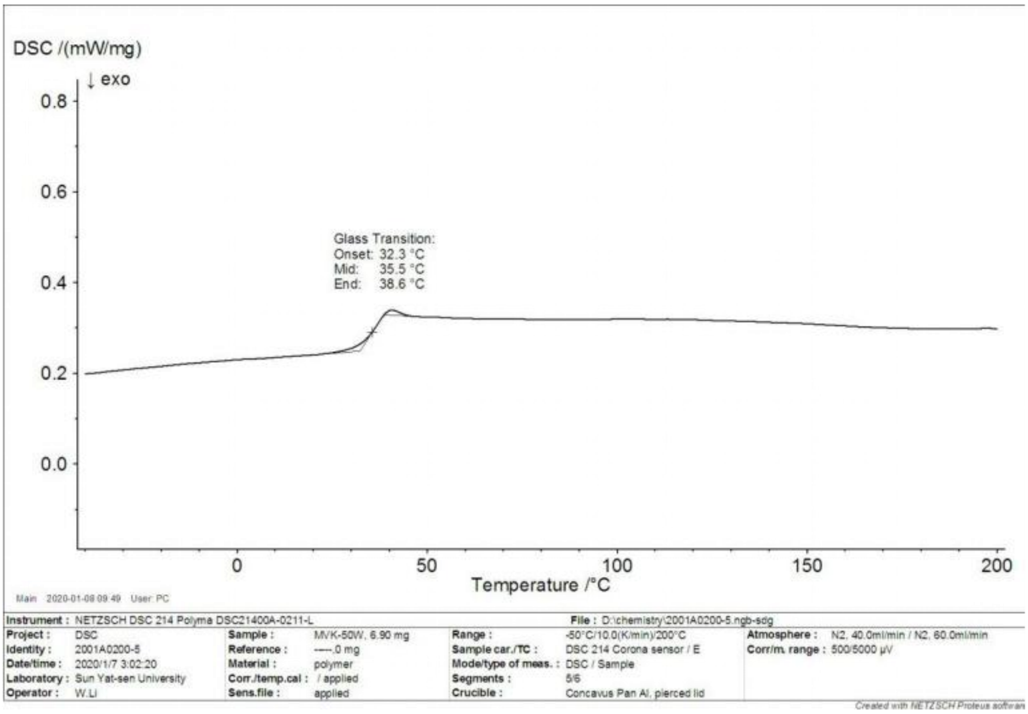
13. Differential Scanning Calorimetry



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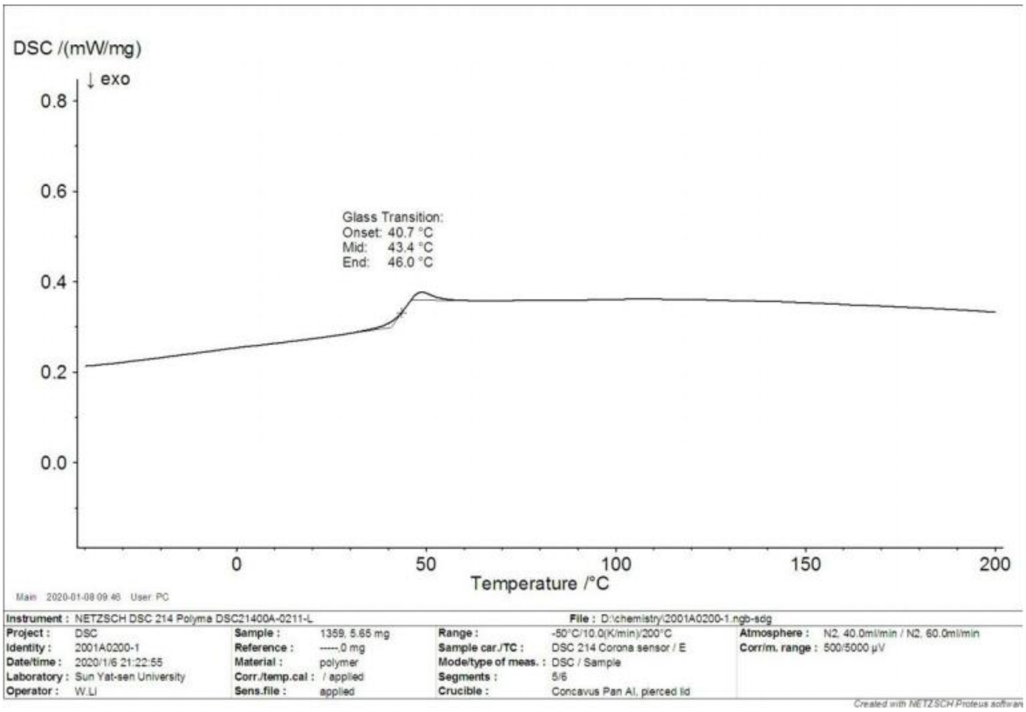
Laboratory :	Sun Yat-sen University	**Corr./temp.cal :**	/ applied	**Segments :**	5/6		
Operator :	W.Li	**Sens.file :**	applied	**Crucible :**	Concavus Pan Al, pierced lid		

Created with NETZSCH Proteus softwar

Figure S14. DSC of commercial PMVK **3a**.



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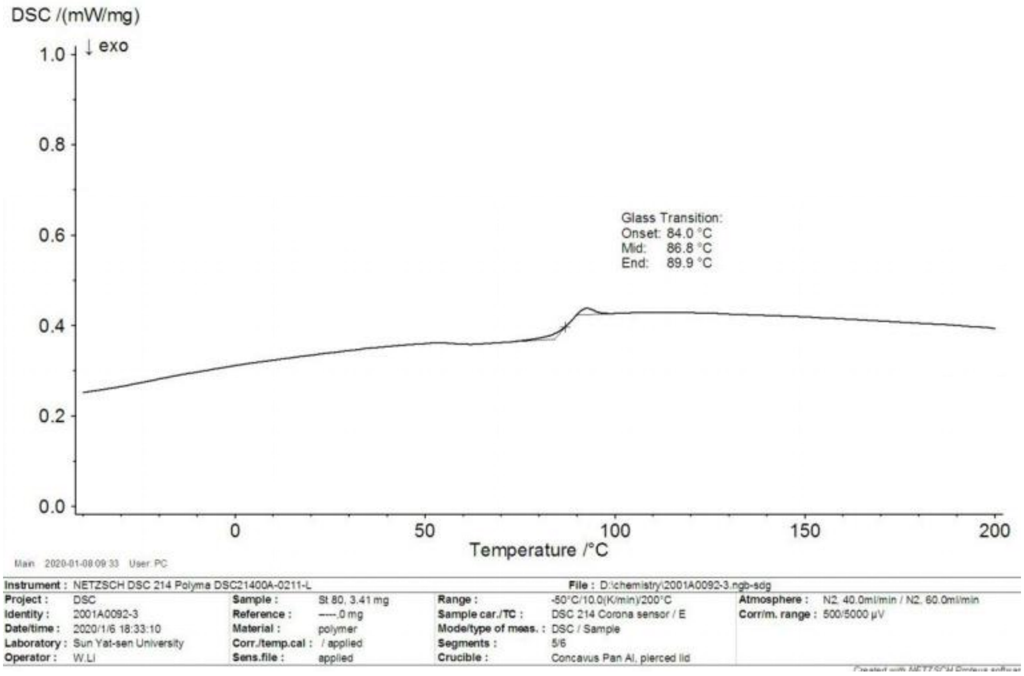
Created with NETZSCH Proteus softwar

Figure S15. DSC of PVAc **5a**.



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Operator : W.Li
Sample : St 80, 3.41 mg
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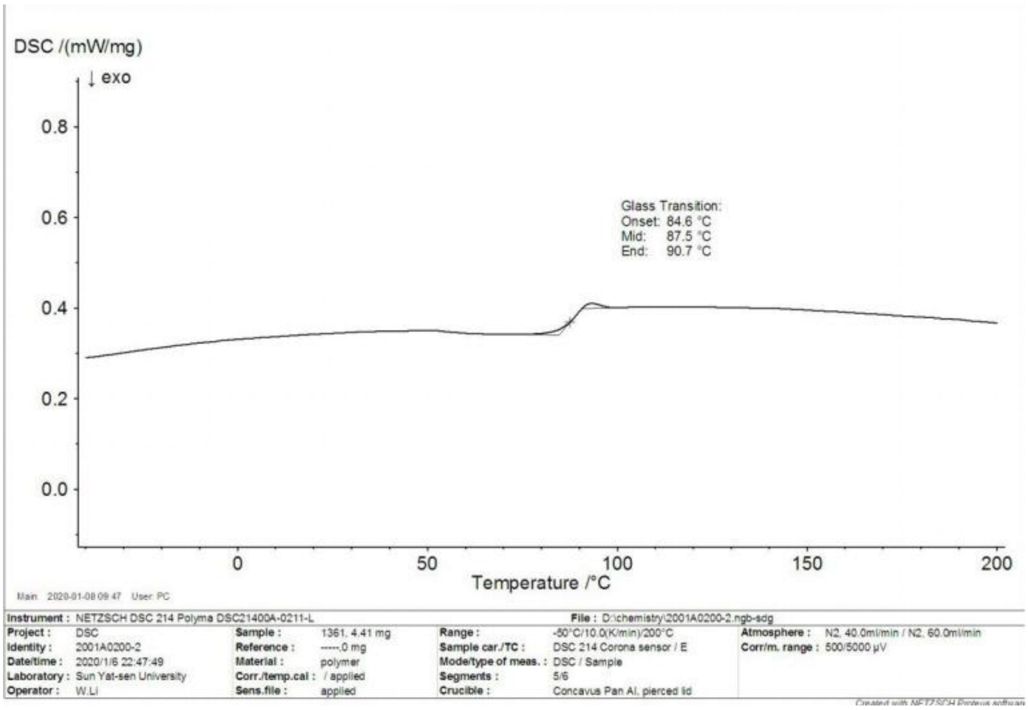
Corr./temp.cal : / applied
Sens.file : applied
Range : -50°C/10.0(K/min)/200°C
Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

Figure S16. DSC of PMVK-*co*-PS (28/72) **6a**.



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Sens.file : applied
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Crucible : Concavus Pan Al, pierced lid
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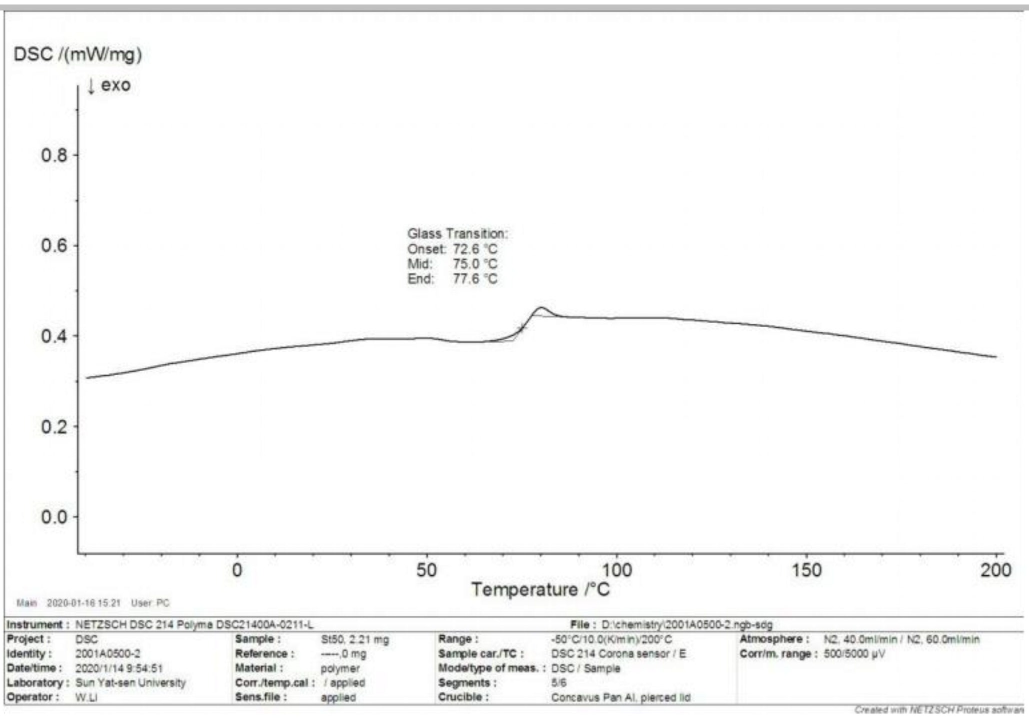
Corr/m. range : 500/5000 µV

Figure S17. DSC of PVAc-*co*-PS (28/72) **8a**.



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Sens.file : applied
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Mode/type of meas. : DSC / Sample
Segments : 5/6
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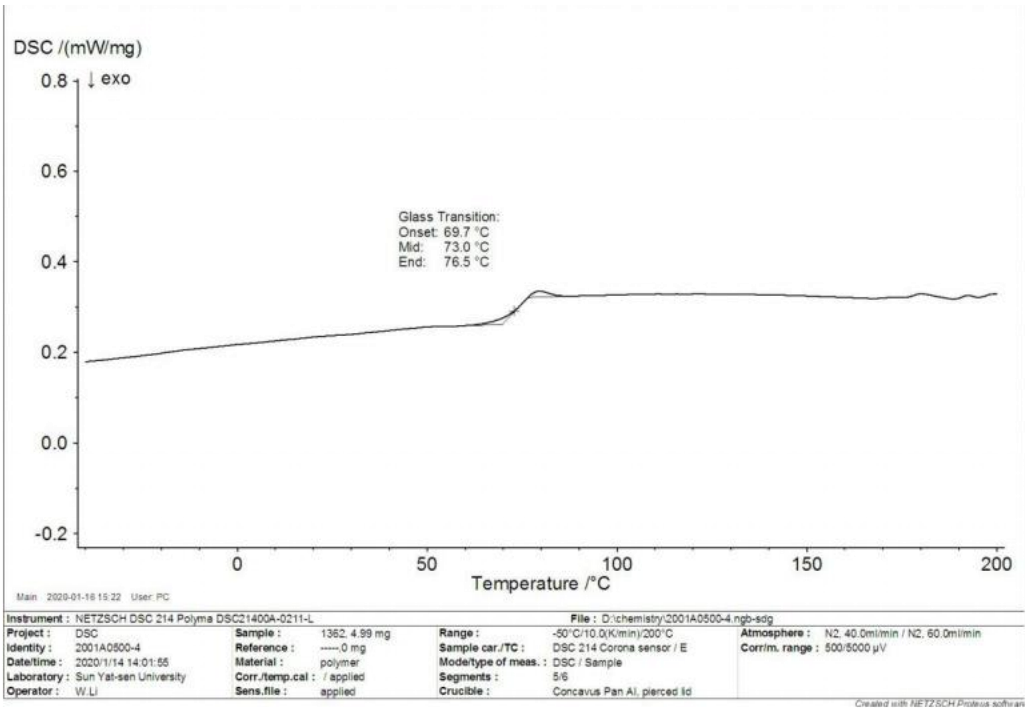
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

Figure S18. DSC of PMVK-*co*-PS (50/50) **6b**.



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Operator : W.Li
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Sens.file : applied
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Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
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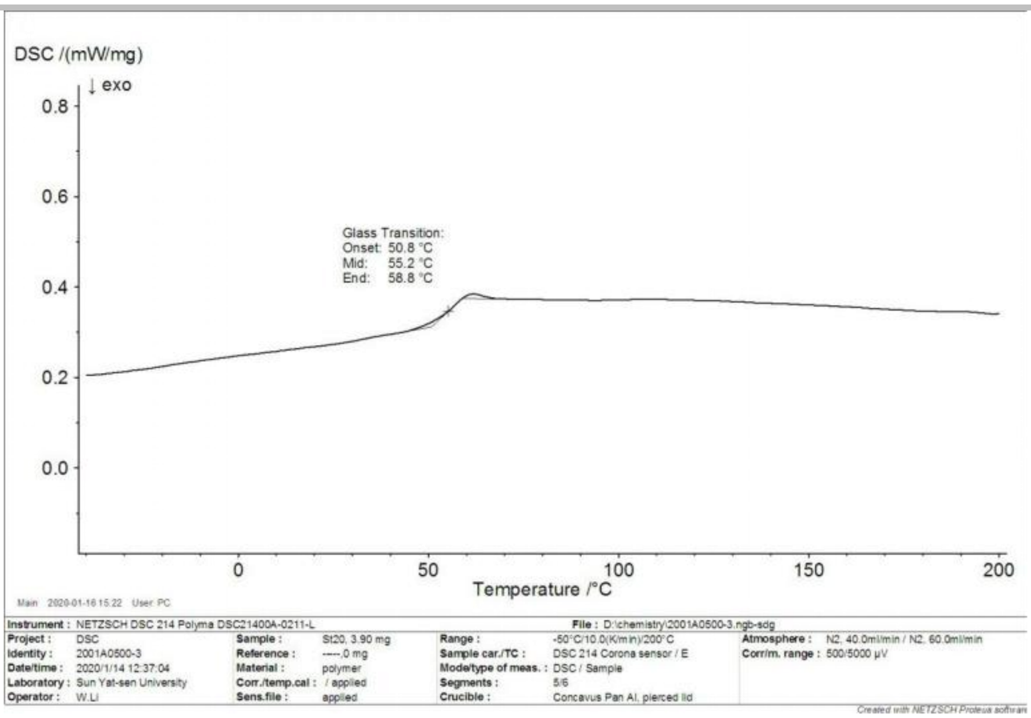
Corr/m. range : 500/5000 µV

Figure S19. DSC of PVAc-*co*-PS (50/50) **8b**.



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Operator : W.Li
Sample : St20, 3.90 mg
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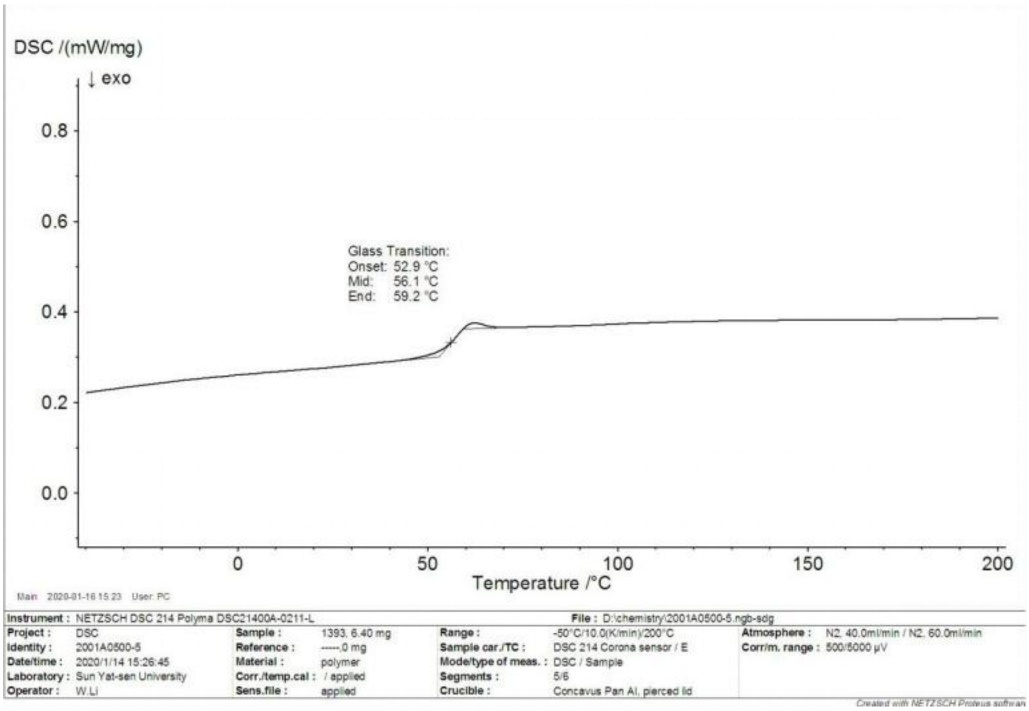
Material : polymer
Corr./temp.cal : / applied
Sens.file : applied
Range : -50°C/10.0(K/min)/200°C
Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

Figure S20. DSC of PMVK-*co*-PS (75/25) **6c**.



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Sens.file : applied
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Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
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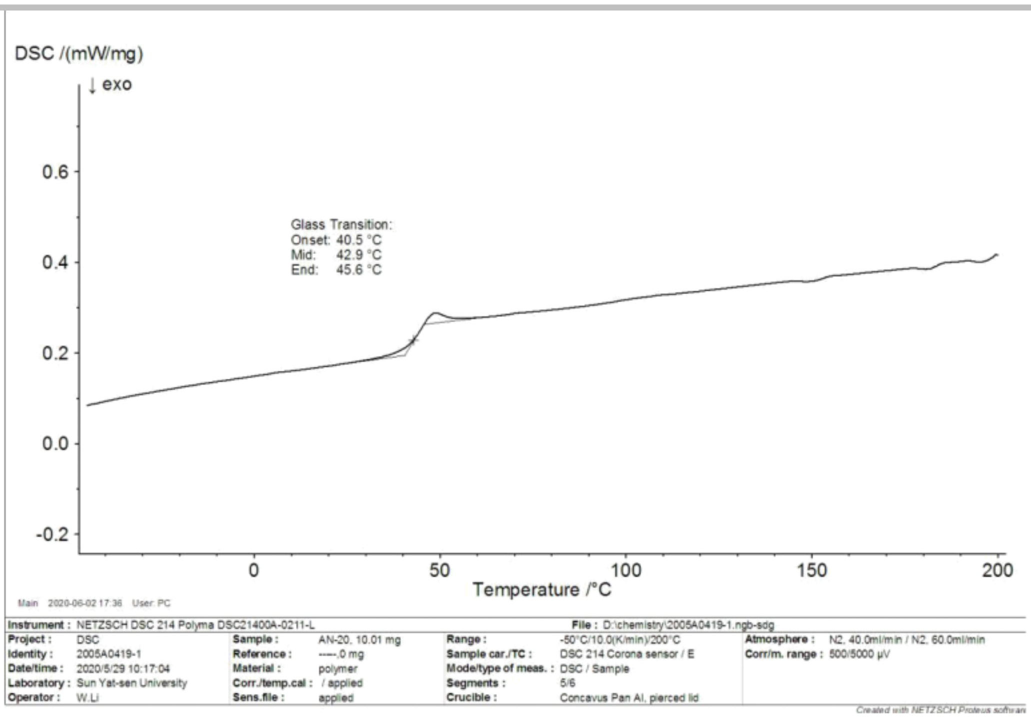
Corr/m. range : 500/5000 µV

Figure S21. DSC of PVAc-*co*-PS (75/25) **8c**.



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Onset: 40.5 °C
Mid: 42.9 °C
End: 45.6 °C

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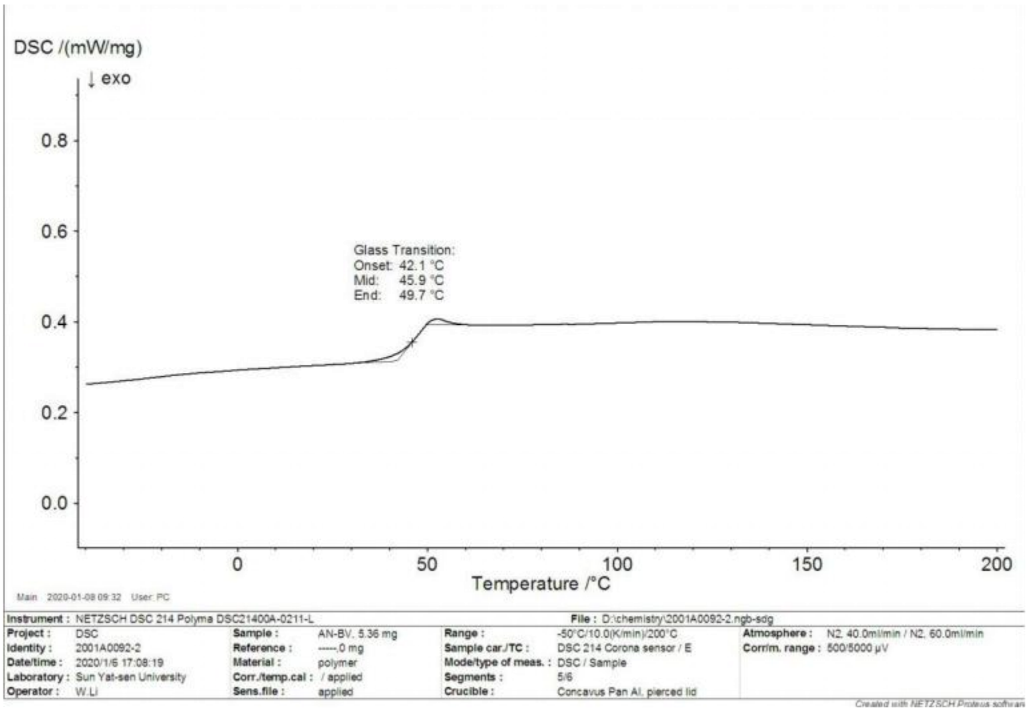
Laboratory : Sun Yat-sen University
Operator : W.Li
Sample : AN-20, 10.01 mg
Reference : -----,0 mg
Material : polymer
Corr./temp.cal : / applied
Sens.file : applied
Range : -50°C/10.0(K/min)/200°C
Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

Created with NETZSCH Proteus softwar

Figure S22. DSC of PMVK-*co*-PAN (81/19) **6d**.



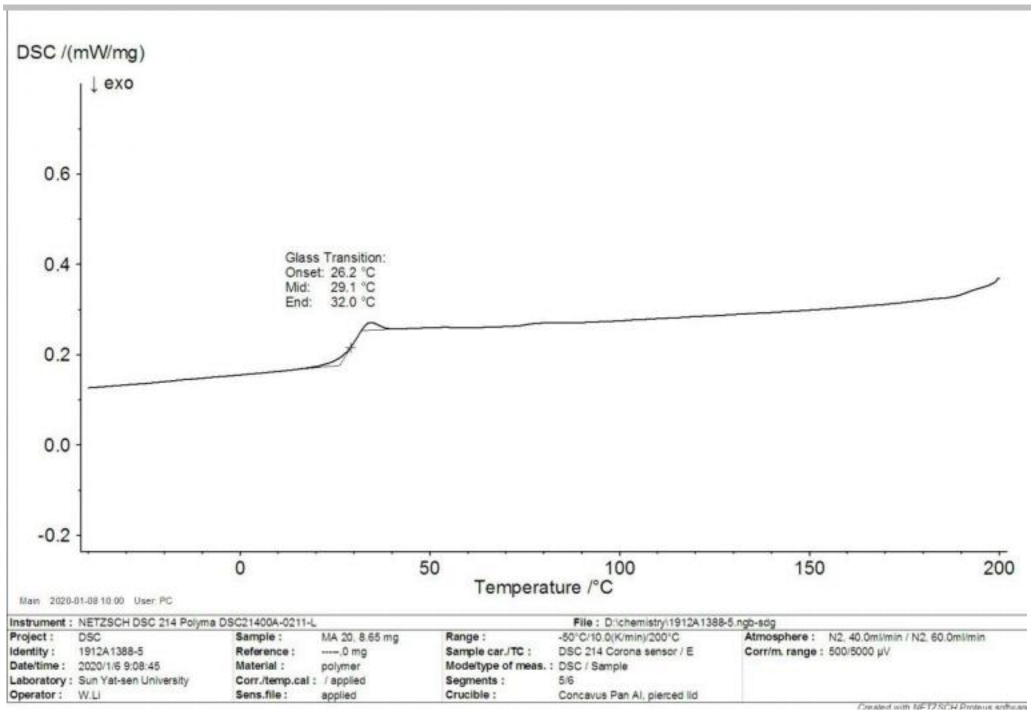
Glass Transition:
Onset: 42.1 °C
Mid: 45.9 °C
End: 49.7 °C

Main 2020-01-08 09:32 User: PC

Instrument : NETZSCH DSC 214 Polyma DSC21400A-0211-L
File : D:\chemistry\2001A0092-2.ngb-sdg
Project : DSC
Identity : 2001A0092-2
Date/time : 2020/1/6 17:08:19
Laboratory : Sun Yat-sen University
Operator : W.Li
Sample : AN-BV, 5.36 mg
Reference : -----,0 mg
Material : polymer
Corr./temp.cal : / applied
Sens.file : applied
Range : -50°C/10.0(K/min)/200°C
Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

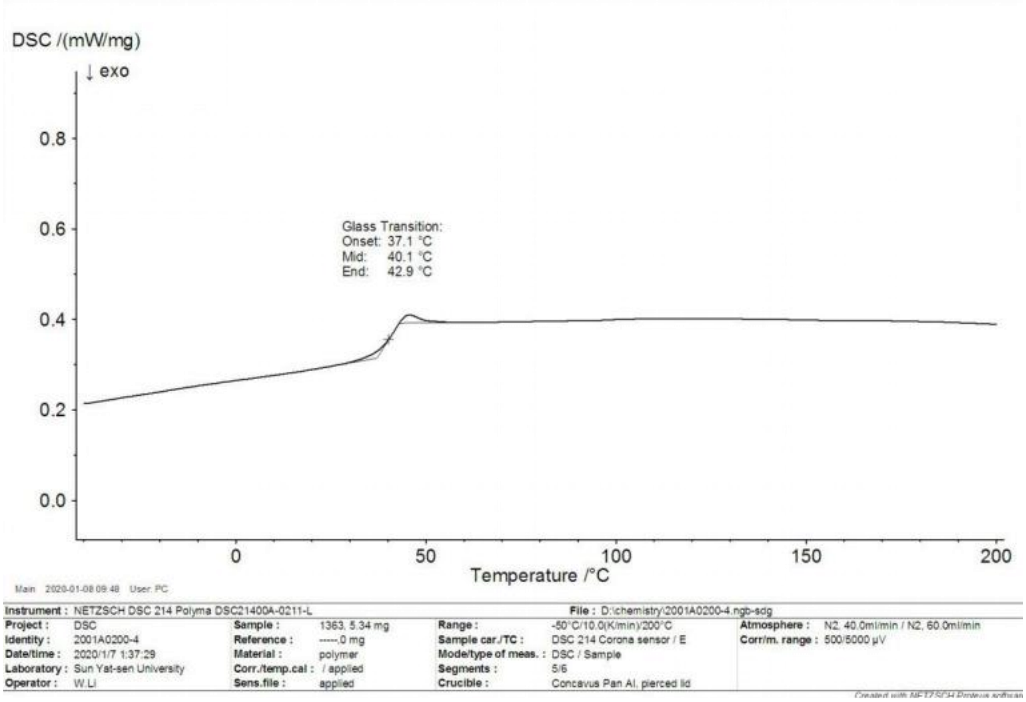
Created with NETZSCH Proteus softwar

Figure S23. DSC of PVAc-*co*-PAN (81/19) **8d**.



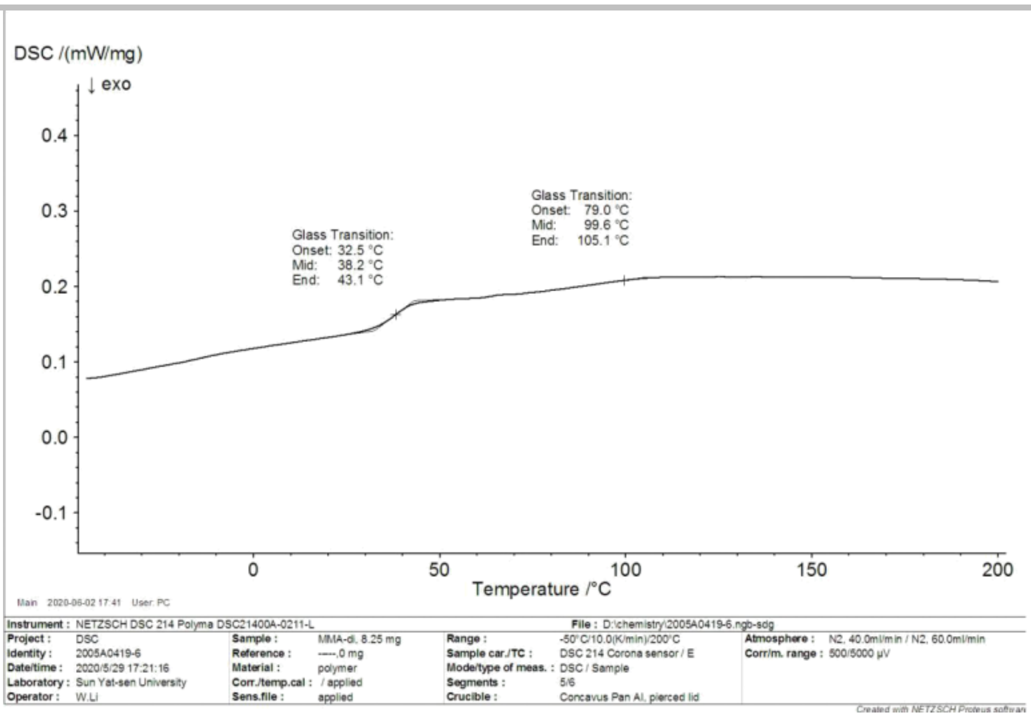
Instrument : NETZSCH DSC 214 Polyma DSC21400A-0211-L
File : D:\chemistry\1912A1388-5.ngb-sdg
Project : DSC
Identity : 1912A1388-5
Date/time : 2020/1/6 9:08:45
Laboratory : Sun Yat-sen University
Operator : W.Li
Sample : MA 20, 8.65 mg
Reference : -----,0 mg
Material : polymer
Corr./temp.cal : / applied
Sens.file : applied
Range : -50°C/10.0(K/min)/200°C
Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

Figure S24. DSC of PMVK-*co*-PMA (83/17) **6e**.



Instrument : NETZSCH DSC 214 Polyma DSC21400A-0211-L
File : D:\chemistry\2001A0200-4.ngb-sdg
Project : DSC
Identity : 2001A0200-4
Date/time : 2020/1/7 1:37:29
Laboratory : Sun Yat-sen University
Operator : W.Li
Sample : 1363, 5.34 mg
Reference : -----,0 mg
Material : polymer
Corr./temp.cal : / applied
Sens.file : applied
Range : -50°C/10.0(K/min)/200°C
Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

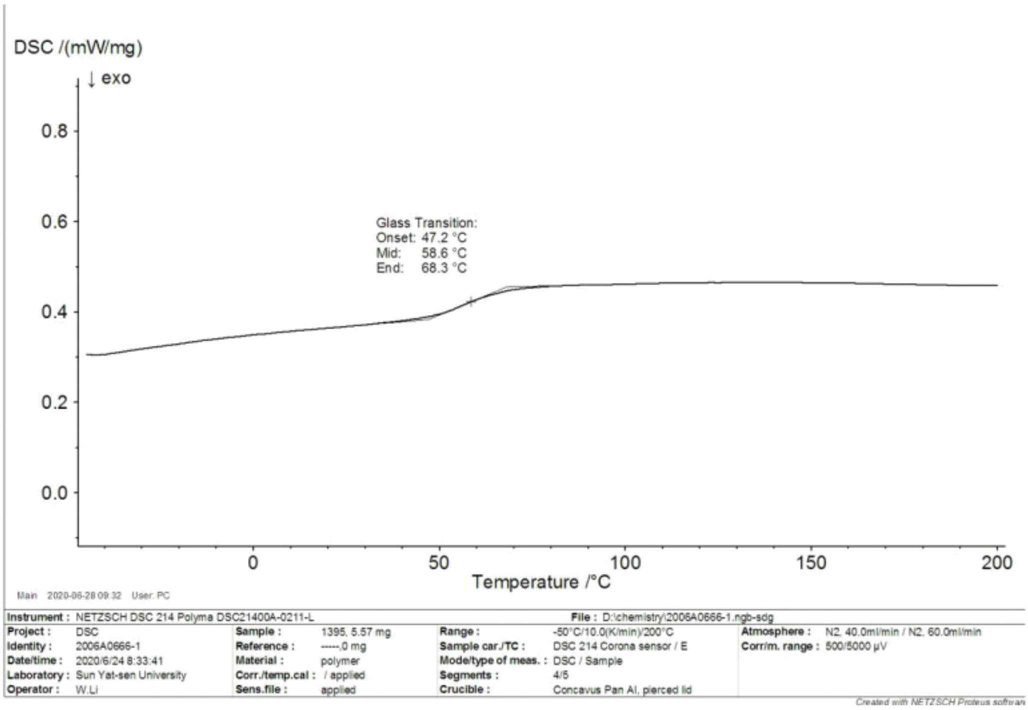
Figure S25. DSC of PVAc-*co*-PMA (83/17) **8e**.



Instrument : NETZSCH DSC 214 Polyma DSC21400A-0211-L
File : D:\chemistry\2005A0419-6.ngb-sdg

Project : DSC
Identity : 2005A0419-6
Date/time : 2020/5/29 17:21:16
Laboratory : Sun Yat-sen University
Operator : W.Li
Sample : MMA-di, 8.25 mg
Reference : -----,0 mg
Material : polymer
Corr./temp.cal : / applied
Sens.file : applied
Range : -50°C/10.0(K/min)/200°C
Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

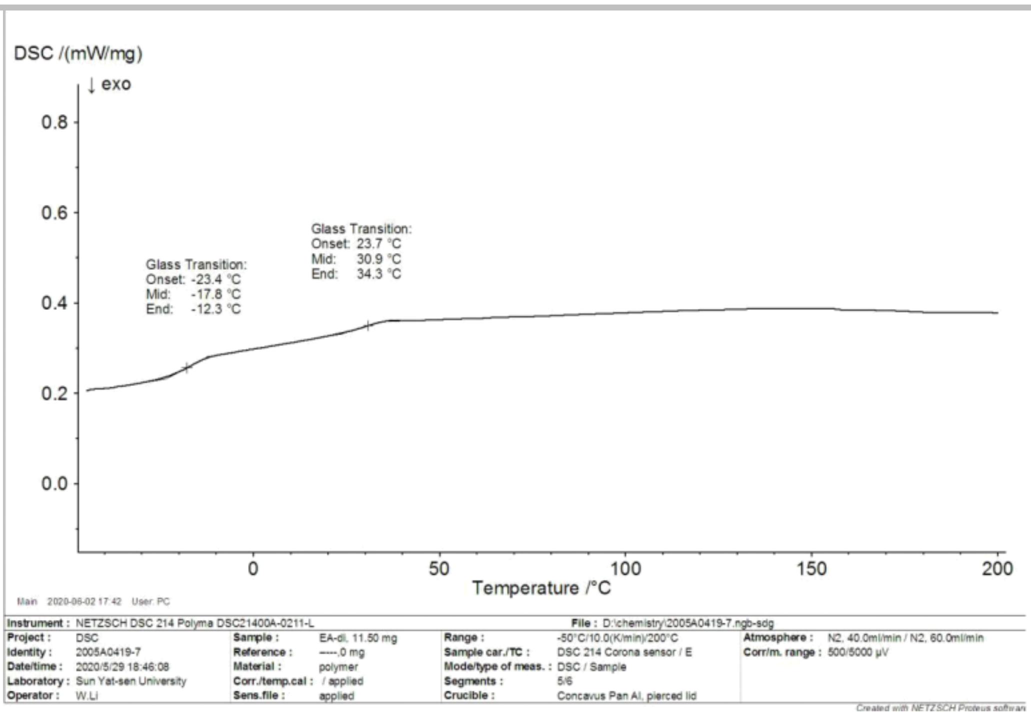
Figure S26. DSC of PMMA-*b*-PMVK diblock copolymer **7a**.



Instrument : NETZSCH DSC 214 Polyma DSC21400A-0211-L
File : D:\chemistry\2006A0666-1.ngb-sdg

Project : DSC
Identity : 2006A0666-1
Date/time : 2020/6/24 8:33:41
Laboratory : Sun Yat-sen University
Operator : W.Li
Sample : 1395, 5.57 mg
Reference : -----,0 mg
Material : polymer
Corr./temp.cal : / applied
Sens.file : applied
Range : -50°C/10.0(K/min)/200°C
Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 4/5
Crucible : Concavus Pan Al, pierced lid
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

Figure S27. DSC of PMMA-*b*-PVAc diblock copolymer **9a**.



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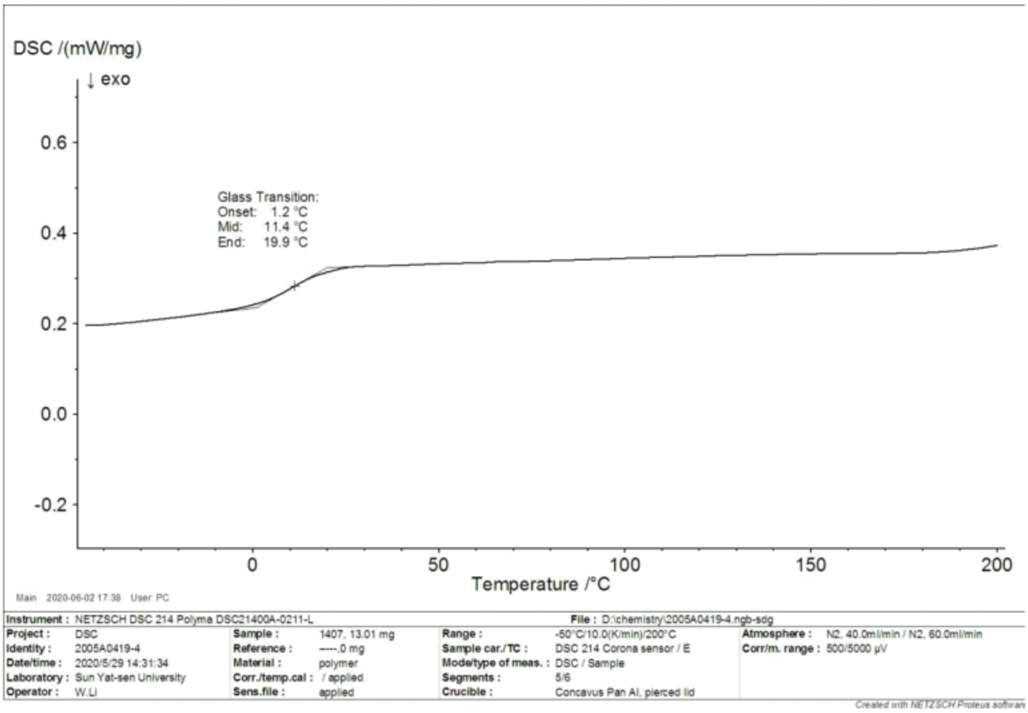
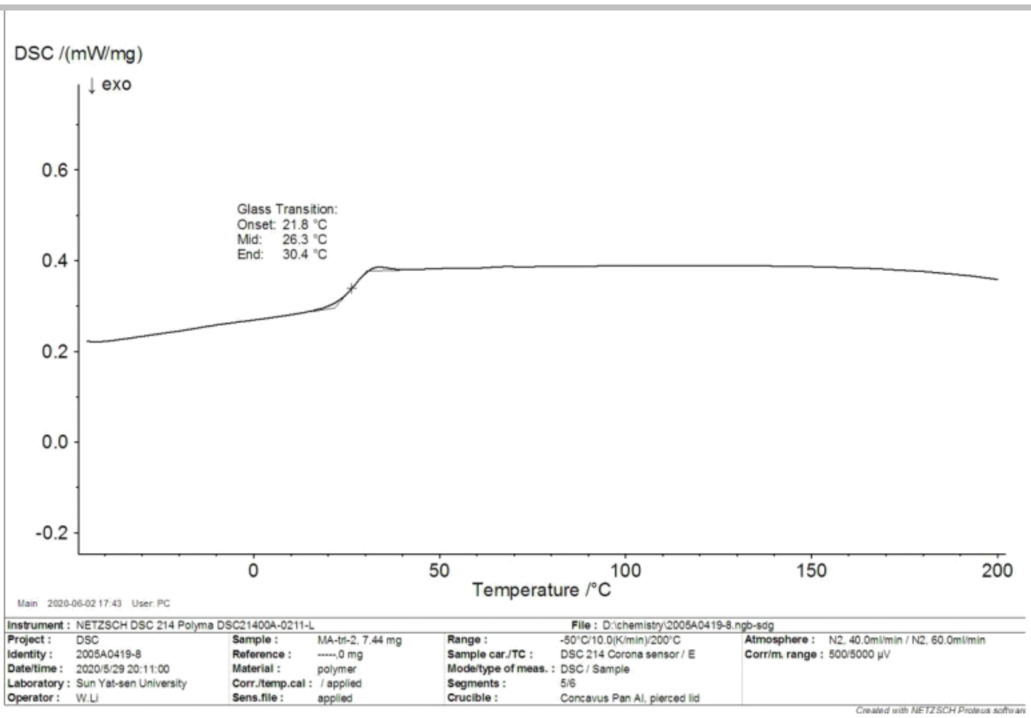
Project : DSC
Identity : 2005A0419-7
Date/time : 2020/5/29 18:46:08
Laboratory : Sun Yat-sen University
Operator : W.Li
Sample : EA-di, 11.50 mg
Reference : ----,0 mg
Material : polymer
Corr./temp.cal : / applied
Sens.file : applied
Range : -50°C/10.0(K/min)/200°C
Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

Figure S28. DSC of PEA-*b*-PMVK diblock copolymer **7b**.



Instrument : NETZSCH DSC 214 Polyma DSC21400A-0211-L
File : D:\chemistry\2005A0419-4.ngb-sdg
Project : DSC
Identity : 2005A0419-4
Date/time : 2020/5/29 14:31:34
Laboratory : Sun Yat-sen University
Operator : W.Li
Sample : 1407, 13.01 mg
Reference : ----,0 mg
Material : polymer
Corr./temp.cal : / applied
Sens.file : applied
Range : -50°C/10.0(K/min)/200°C
Sample car./TC : DSC 214 Corona sensor / E
Mode/type of meas. : DSC / Sample
Segments : 5/6
Crucible : Concavus Pan Al, pierced lid
Atmosphere : N2, 40.0ml/min / N2, 60.0ml/min
Corr/m. range : 500/5000 µV

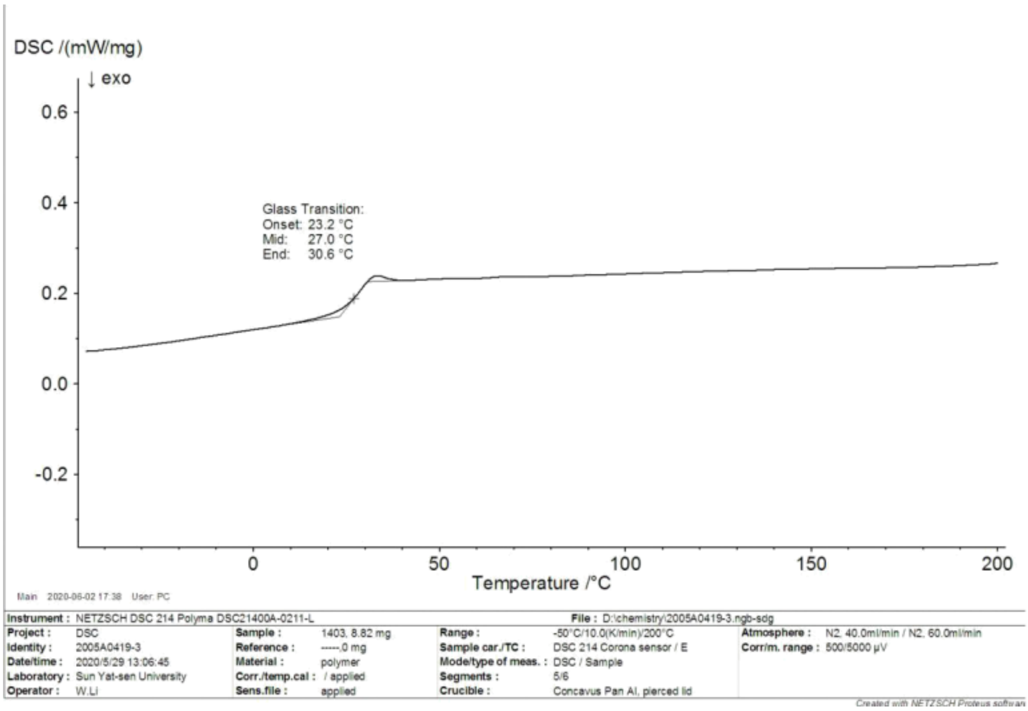
Figure S29. DSC of PEA-*b*-PVAc diblock copolymer **9b**.



Instrument : NETZSCH DSC 214 Polyma DSC21400A-0211-L **File :** D:\chemistry\2005A0419-8.ngb-sdg

Project :	DSC	**Sample :**	MA-tri-2, 7.44 mg	**Range :**	-50°C/10.0(K/min)/200°C	**Atmosphere :**	N2, 40.0ml/min / N2, 60.0ml/min
Identity :	2005A0419-8	**Reference :**	-----,0 mg	**Sample car./TC :**	DSC 214 Corona sensor / E	**Corr/m. range :**	500/5000 µV
Date/time :	2020/5/29 20:11:00	**Material :**	polymer	**Mode/type of meas. :**	DSC / Sample		
Laboratory :	Sun Yat-sen University	**Corr./temp.cal :**	/ applied	**Segments :**	5/6		
Operator :	W.Li	**Sens.file :**	applied	**Crucible :**	Concavus Pan Al, pierced lid		

Figure S30. DSC of PMVK-*b*-PMA-*b*-PMVK triblock copolymer **7c**.



Instrument : NETZSCH DSC 214 Polyma DSC21400A-0211-L **File :** D:\chemistry\2005A0419-3.ngb-sdg

Project :	DSC	**Sample :**	1403, 8.82 mg	**Range :**	-50°C/10.0(K/min)/200°C	**Atmosphere :**	N2, 40.0ml/min / N2, 60.0ml/min
Identity :	2005A0419-3	**Reference :**	-----,0 mg	**Sample car./TC :**	DSC 214 Corona sensor / E	**Corr/m. range :**	500/5000 µV
Date/time :	2020/5/29 13:06:45	**Material :**	polymer	**Mode/type of meas. :**	DSC / Sample		
Laboratory :	Sun Yat-sen University	**Corr./temp.cal :**	/ applied	**Segments :**	5/6		
Operator :	W.Li	**Sens.file :**	applied	**Crucible :**	Concavus Pan Al, pierced lid		

Figure S31. DSC of PVAc-*b*-PMA-*b*-PVAc triblock copolymer **9c**.

14. Thermogravimetric Analysis

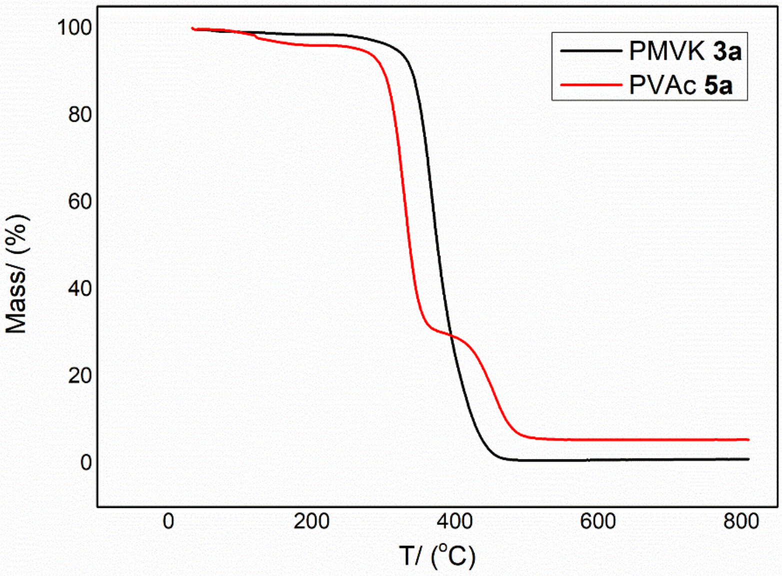


Figure S32. TGA of commercial PMVK **3a** and PVAc **5a**.

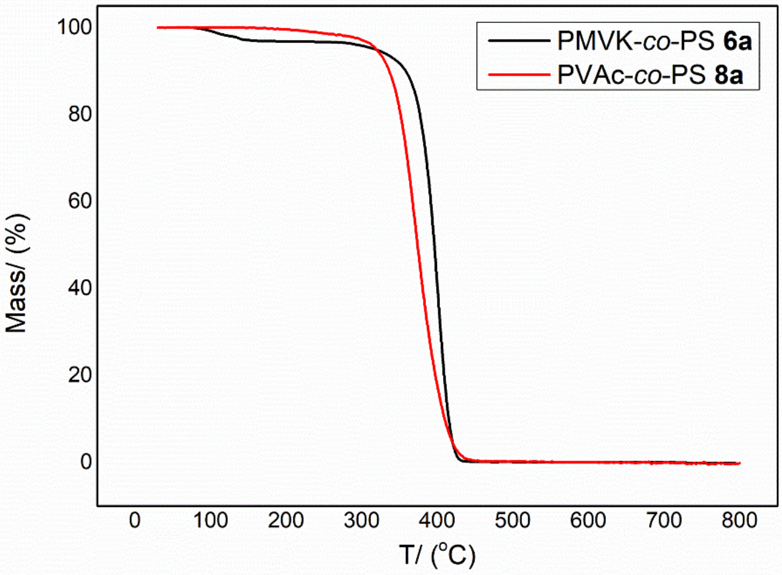


Figure S33. TGA of PMVK-*co*-PS (28/72) **6a** and PVAc-*co*-PS (28/72) **8a**.

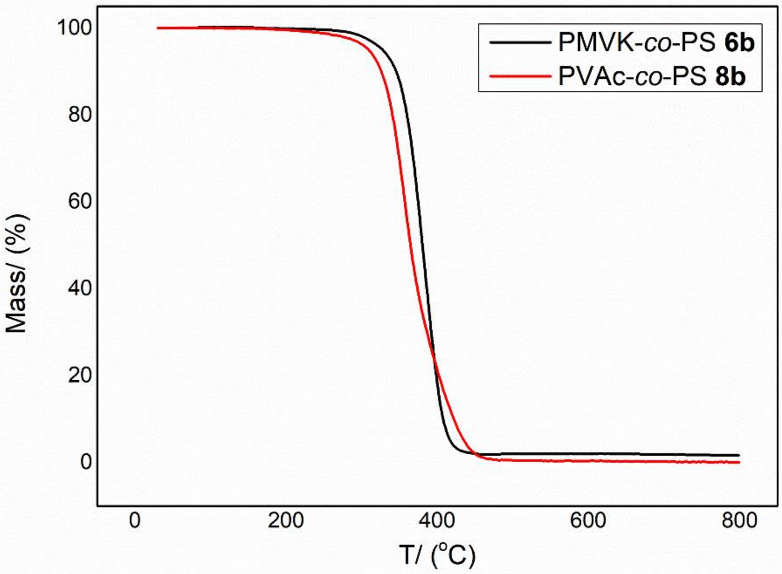


Figure S34. TGA of PMVK-*co*-PS (51/49) **6b** and PVAc-*co*-PS (50/50) **8b**.

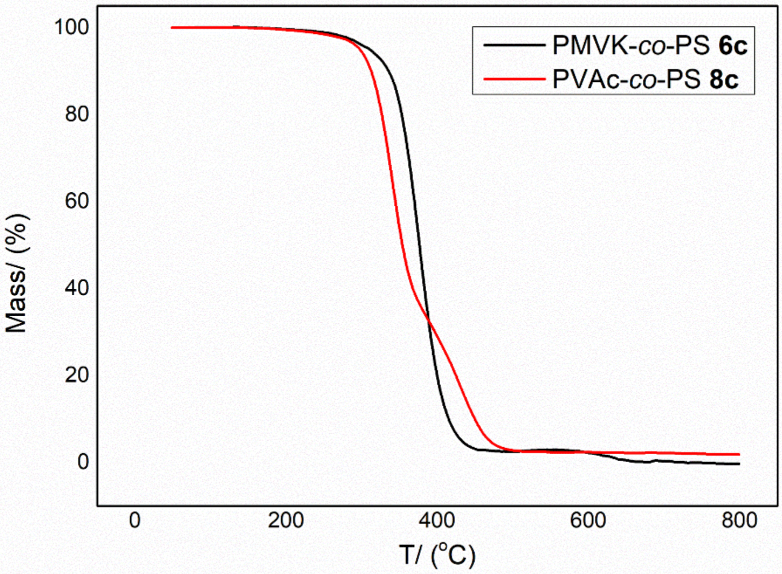


Figure S35. TGA of PMVK-*co*-PS (75/25) **6c** and PVAc-*co*-PS (75/25) **8c**.

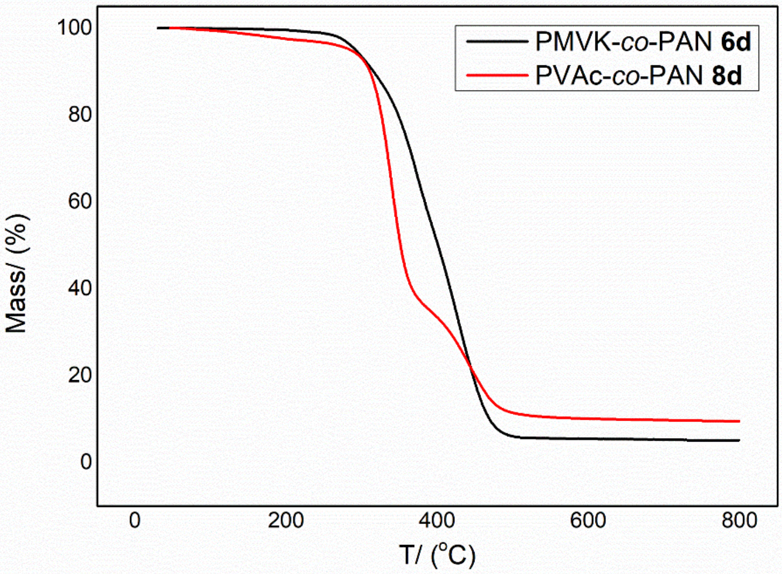


Figure S36. TGA of PMVK-*co*-PAN (81/19) **6d** and PVAc-*co*-PAN (81/19) **8d**.

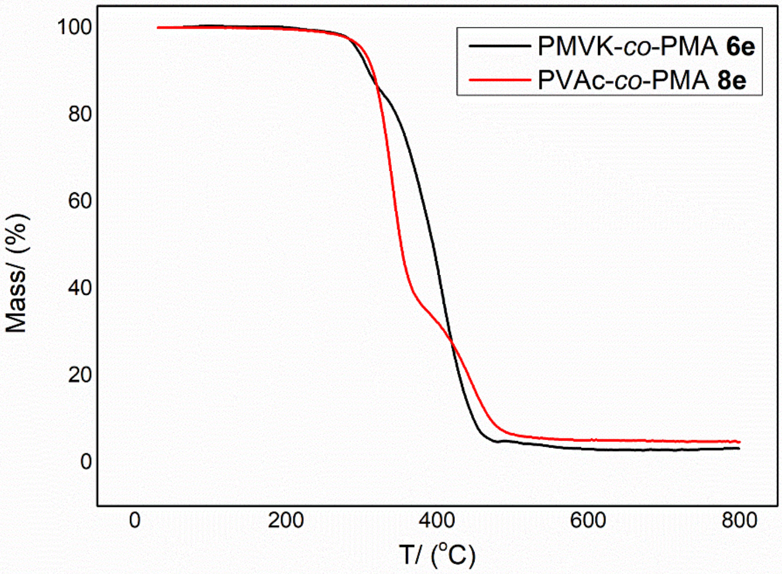


Figure S37. TGA of PMVK-*co*-PMA (83/17) **6e** and PVAc-*co*-PMA (83/17) **8e**.

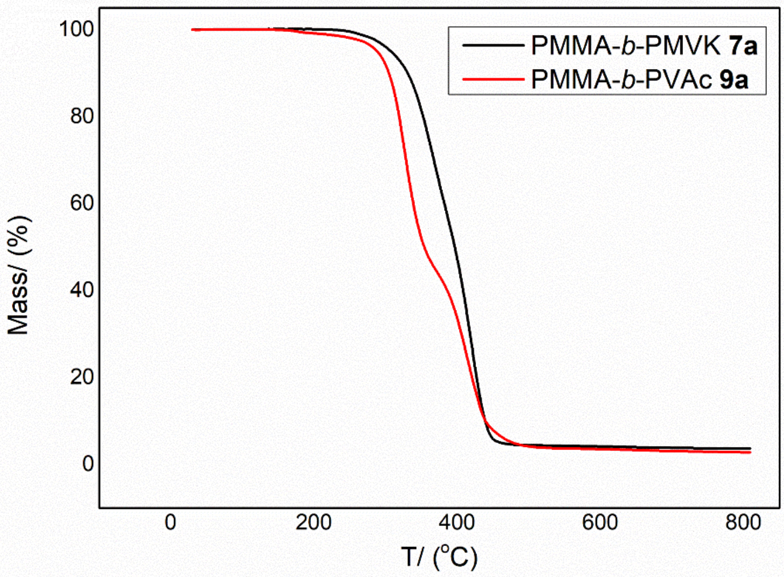


Figure S38. TGA of PMMA-*b*-PMVK diblock copolymer **7a** and PMMA-*b*-PVAc diblock copolymer **9a**.

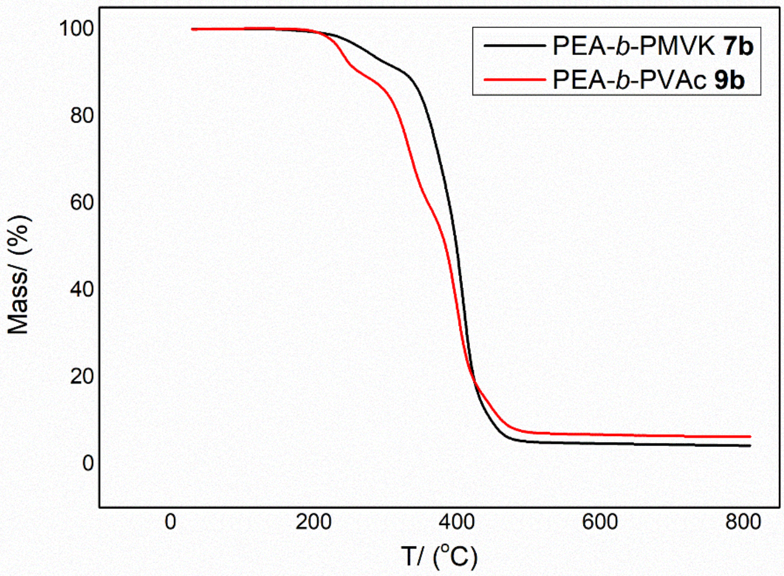


Figure S39. TGA of PEA-*b*-PMVK diblock copolymer **7b** and PEA-*b*-PVAc diblock copolymer **9b**.

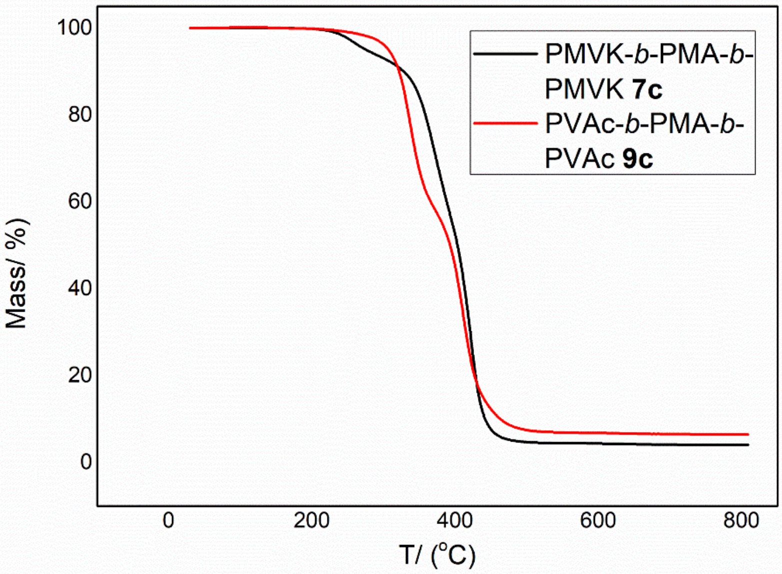


Figure S40. TGA of PMVK-*b*-PMA-*b*-PMVK triblock copolymer **7c** and PVAc-*b*-PMA-*b*-PVAc triblock copolymer **9c**.

15. Infrared Spectroscopy

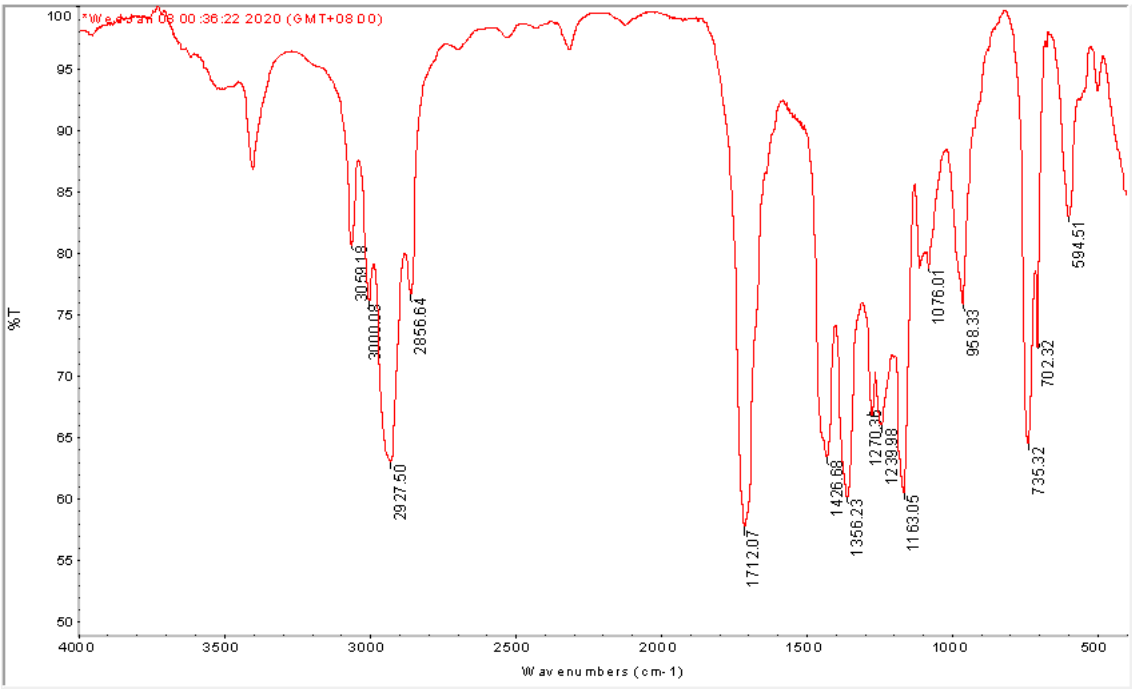


Figure S41. FT–IR of commercial PMVK **3a**.

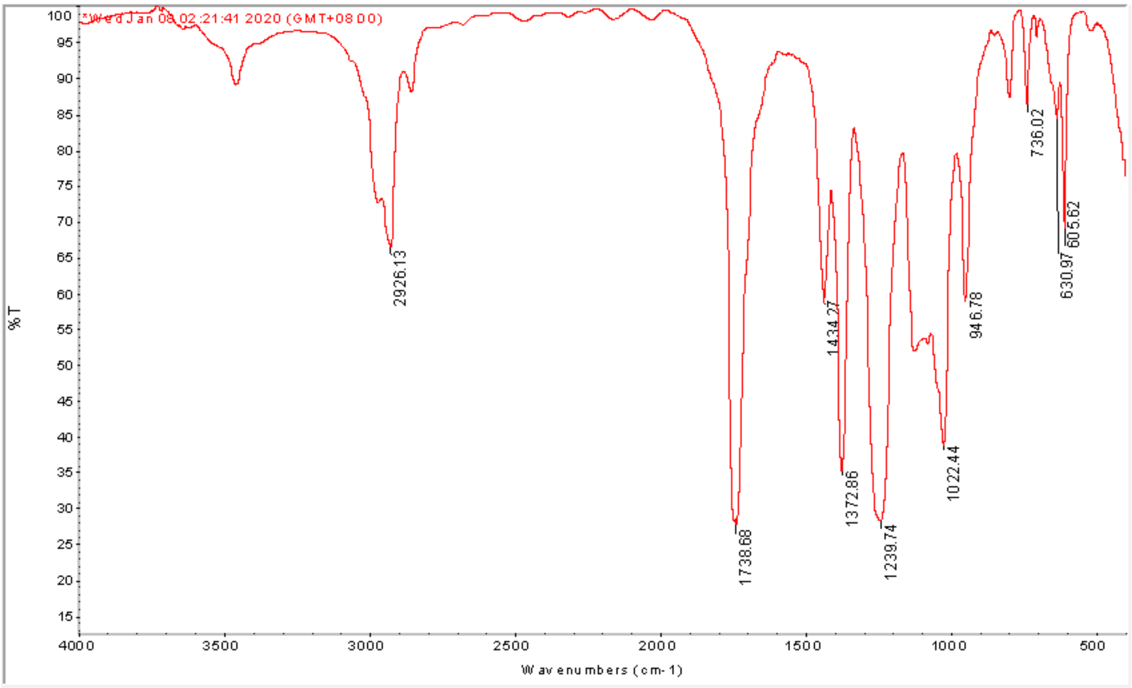


Figure S42. FT–IR of PVAc **5a**.

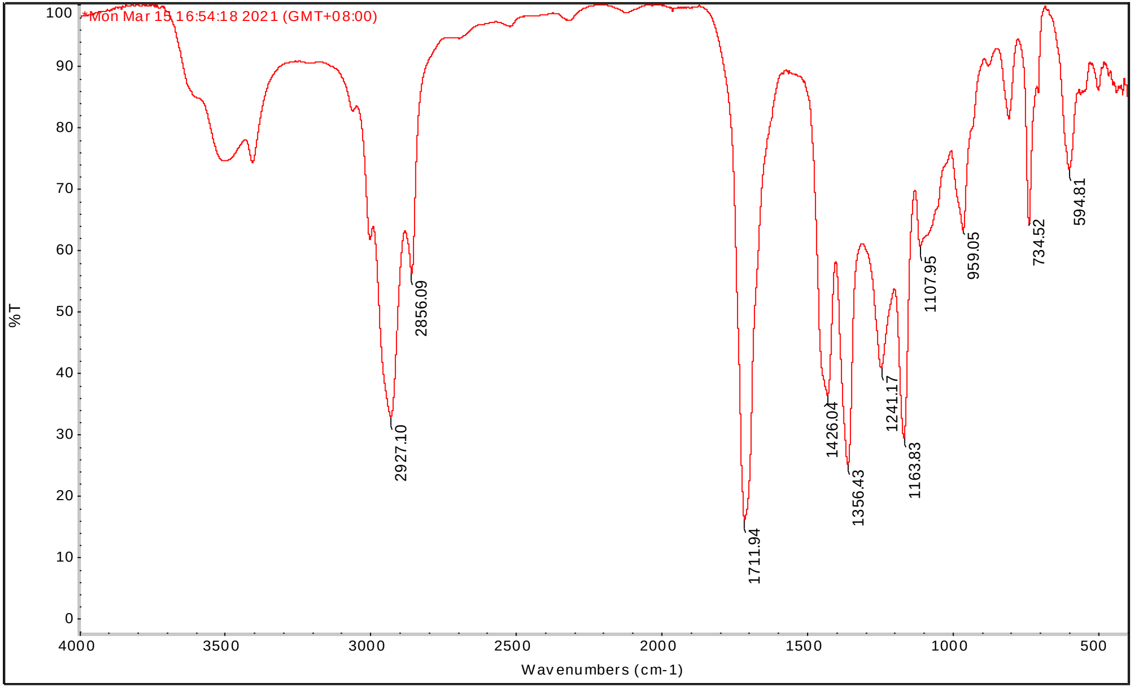


Figure S43. FT–IR of PMVK (RAFT) **3b**.

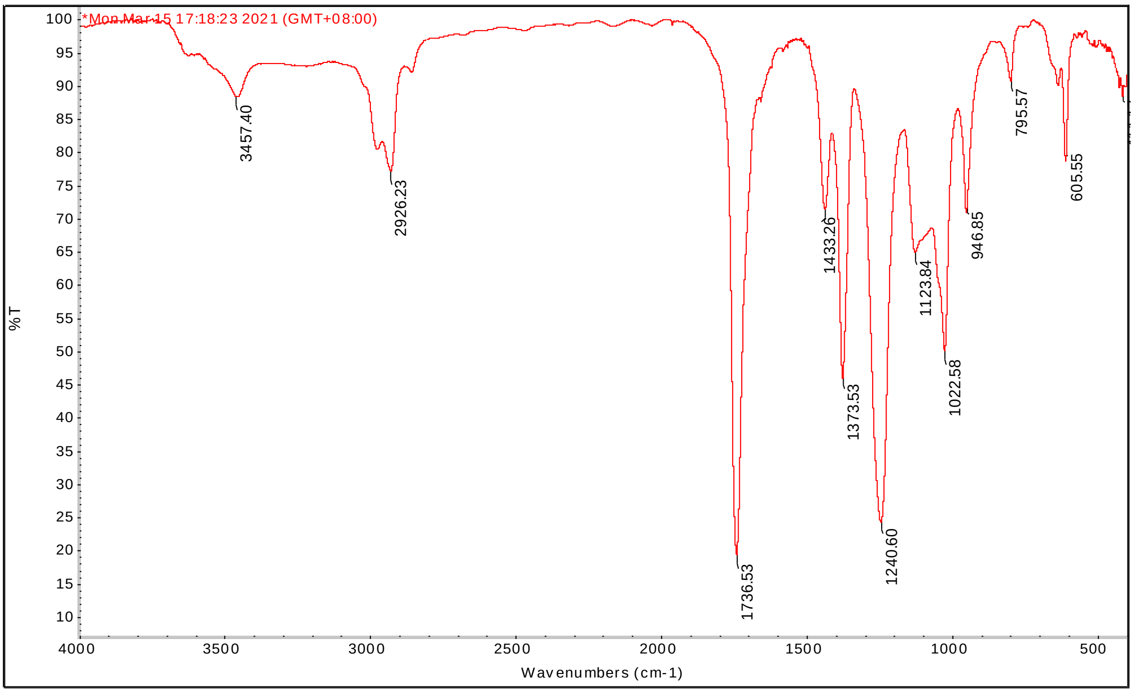


Figure S44. FT–IR of PVAc **5b**.

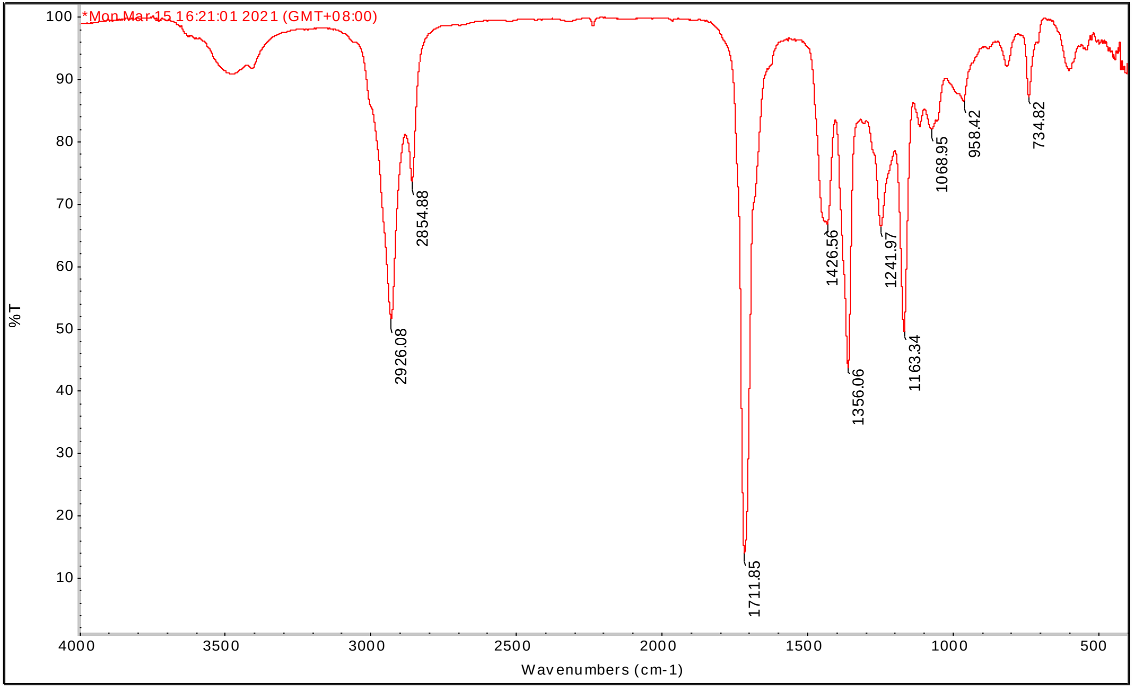


Figure S45. FT–IR of PMVK (RAFT) **3c**.

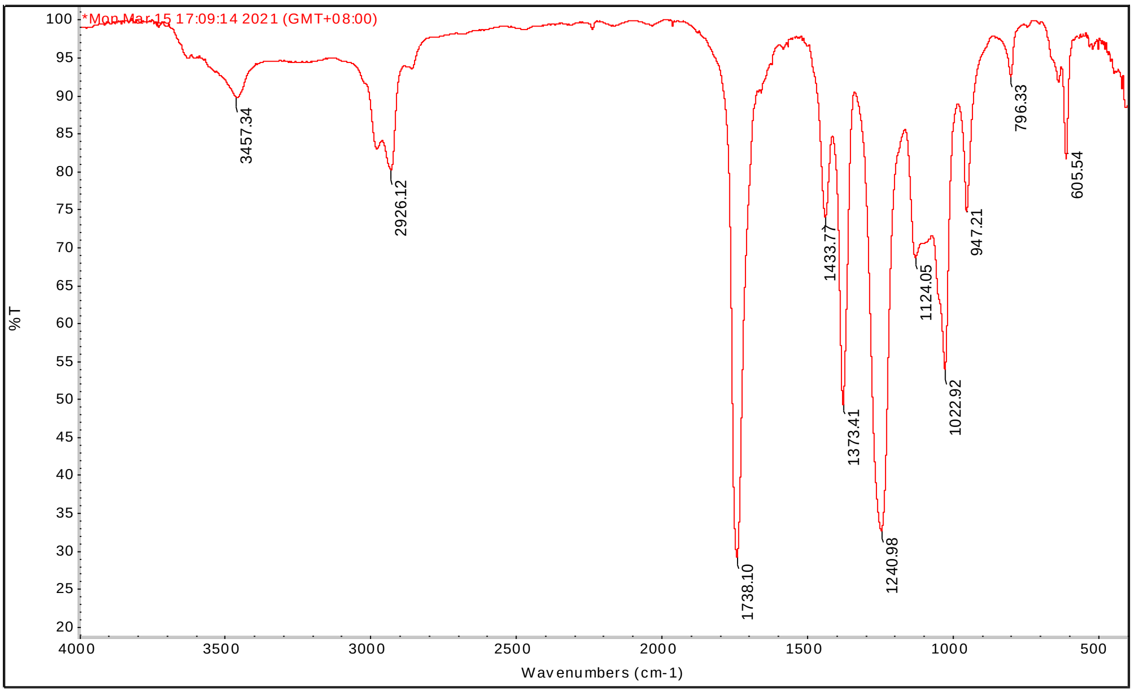


Figure S46. FT–IR of PVAc **5c**.

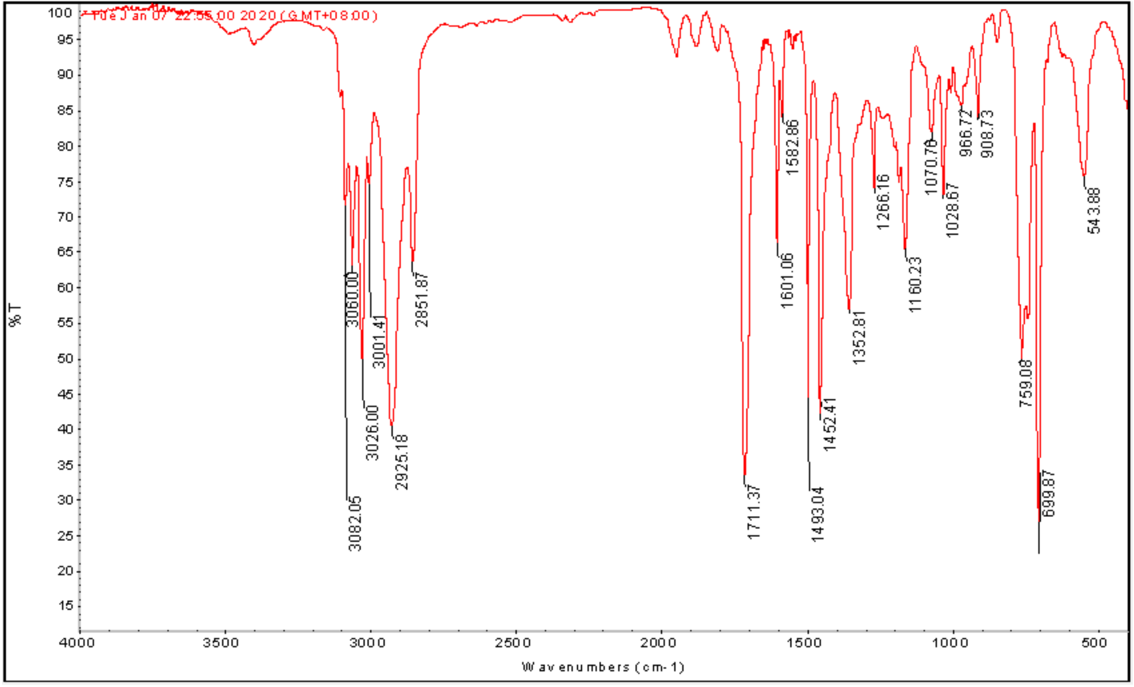


Figure S47. FT–IR of PMVK-*co*-PS (28/72) **6a**.

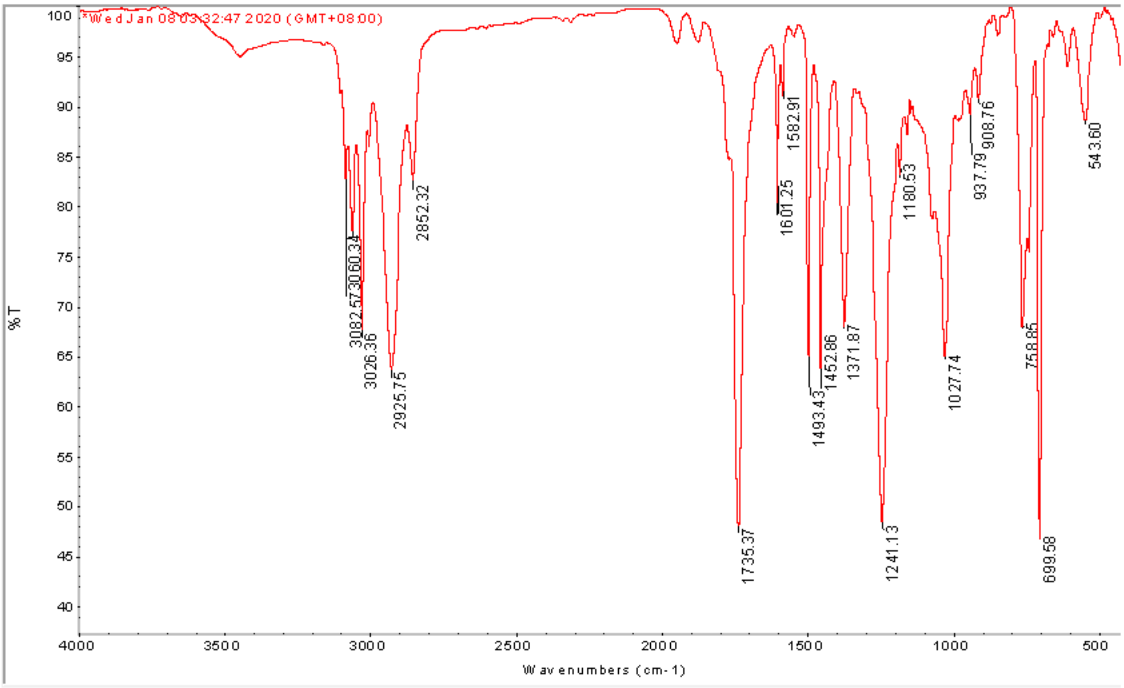


Figure S48. FT–IR of PVAc-*co*-PS (28/72) **8a**.

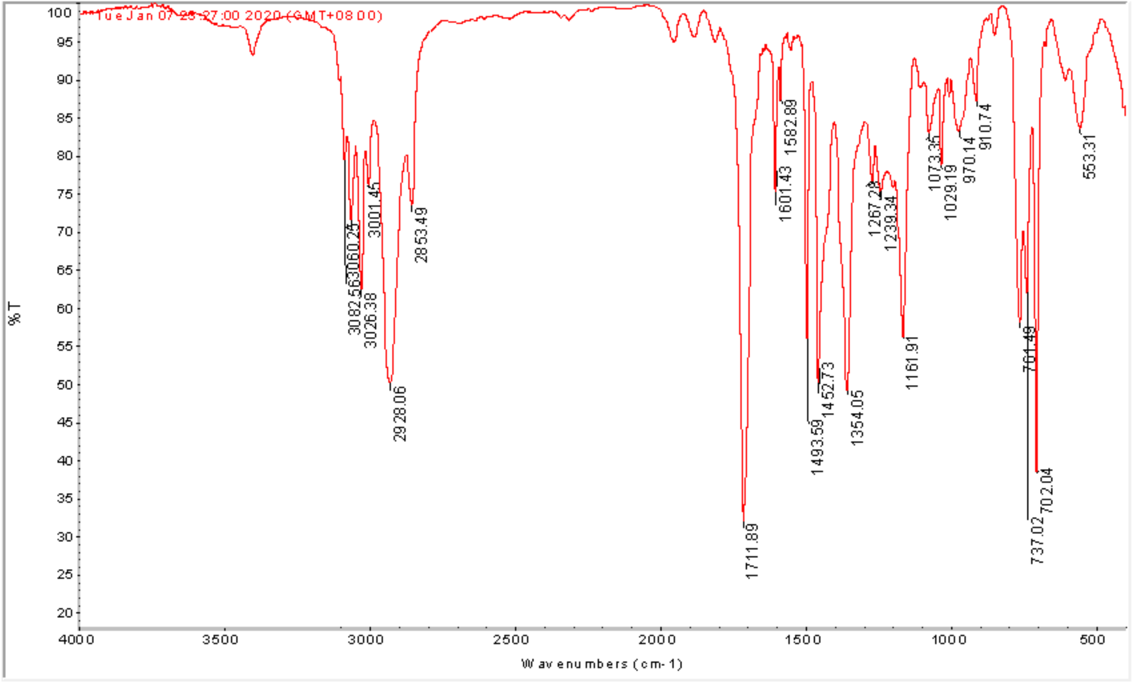


Figure S49. FT–IR of PMVK-*co*-PS (50/50) **6b**.

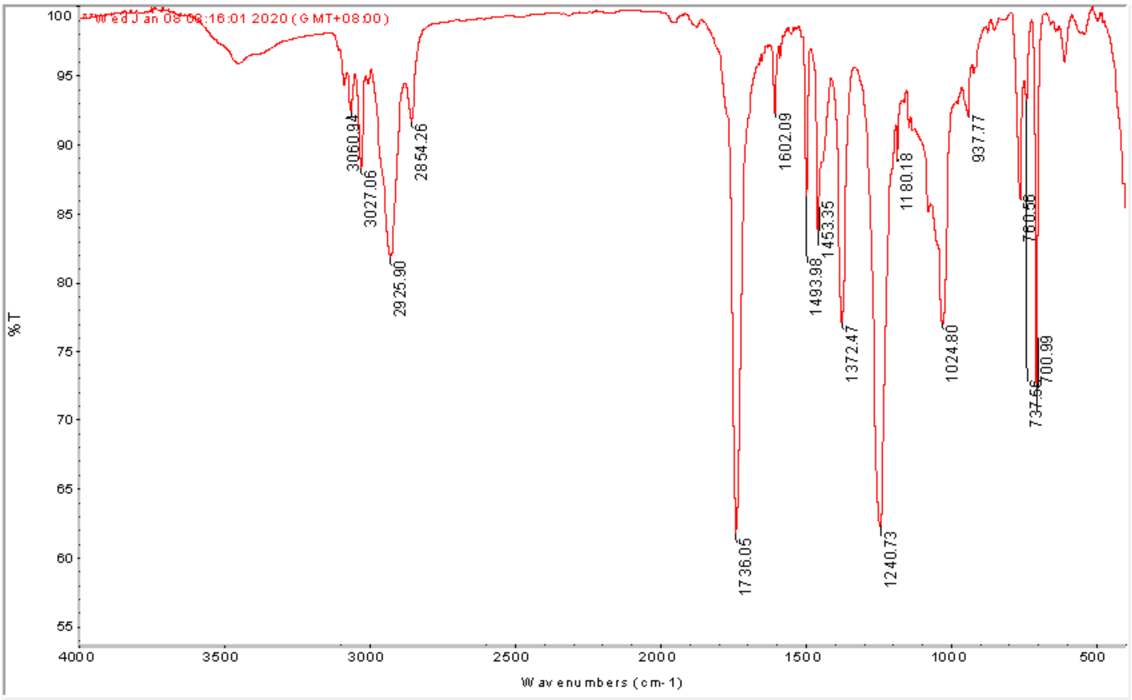


Figure S50. FT–IR of PVAc-*co*-PS (50/50) **8b**.

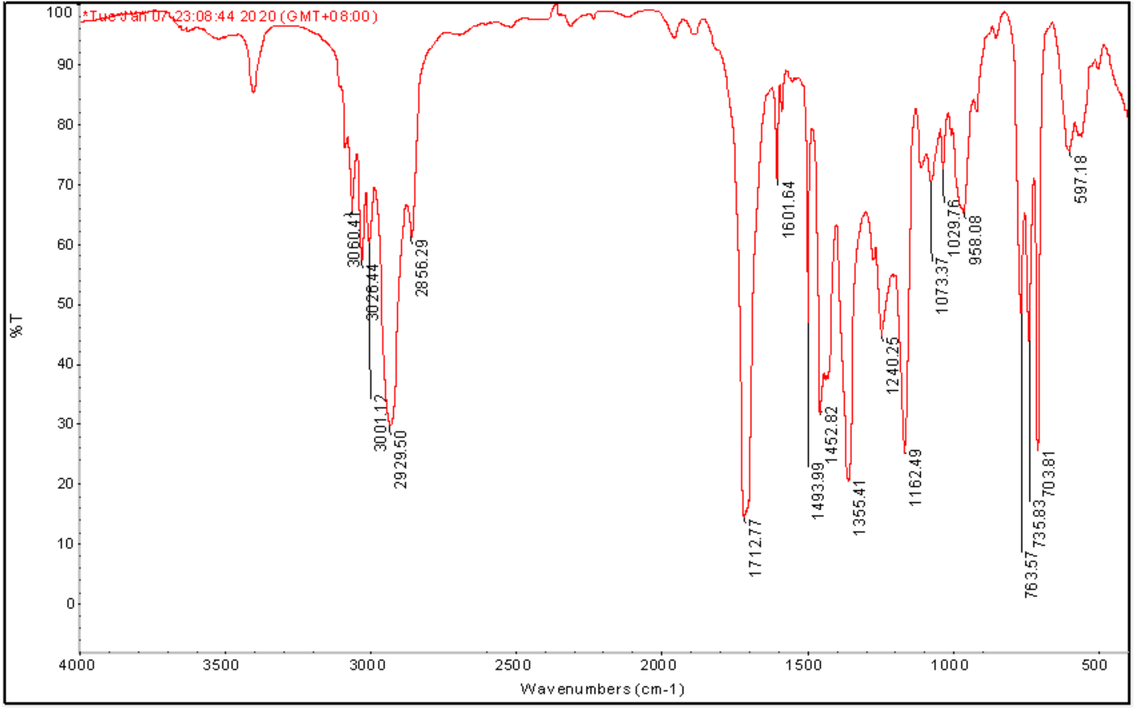


Figure S51. FT–IR of PMVK-*co*-PS (75/25) **6c**.

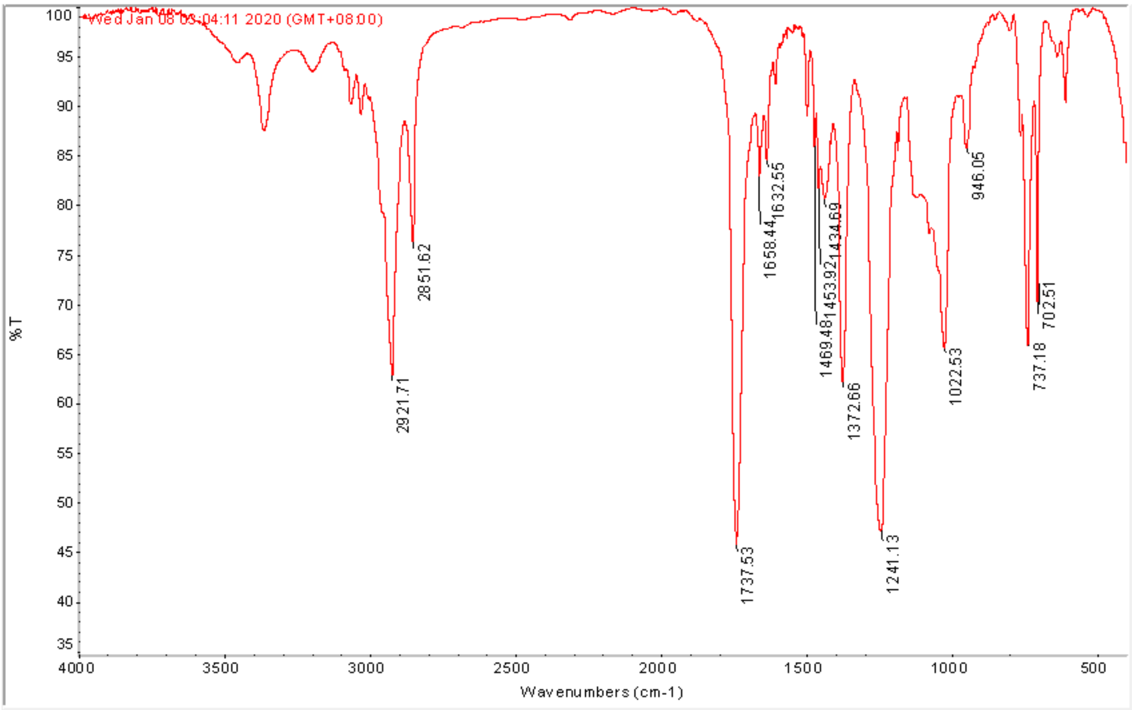


Figure S52. FT–IR of PVAc-*co*-PS (75/25) **8c**.

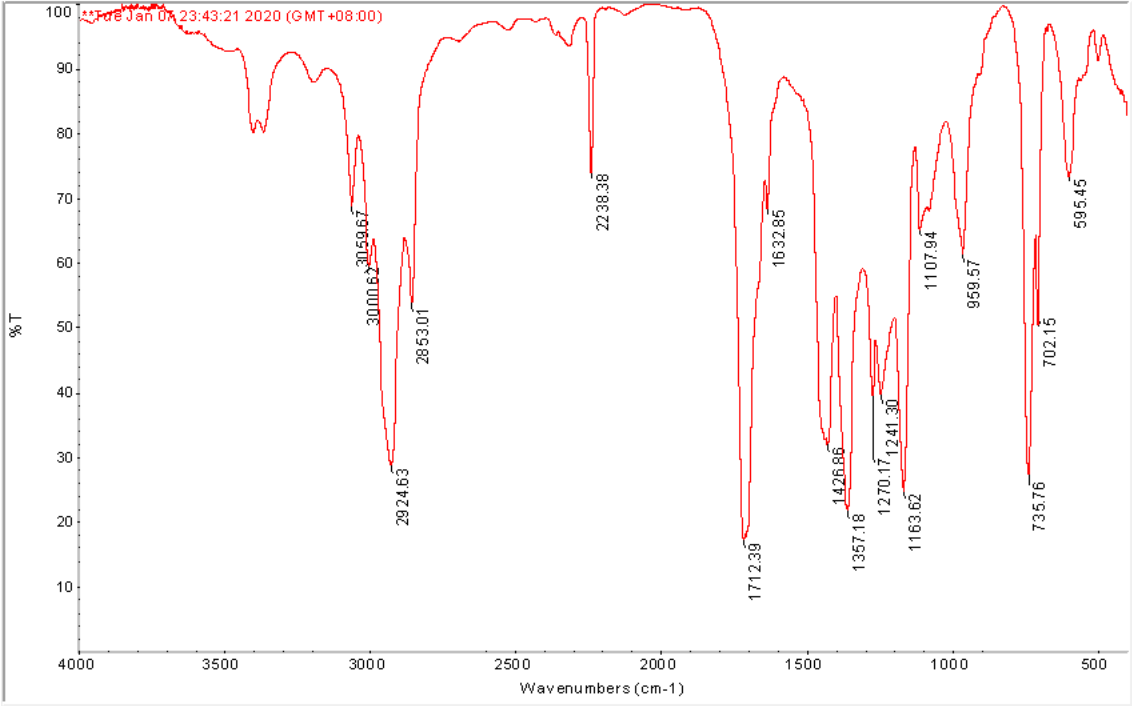


Figure S53. FT–IR of PMVK-*co*-PAN (81/19) **6d**.

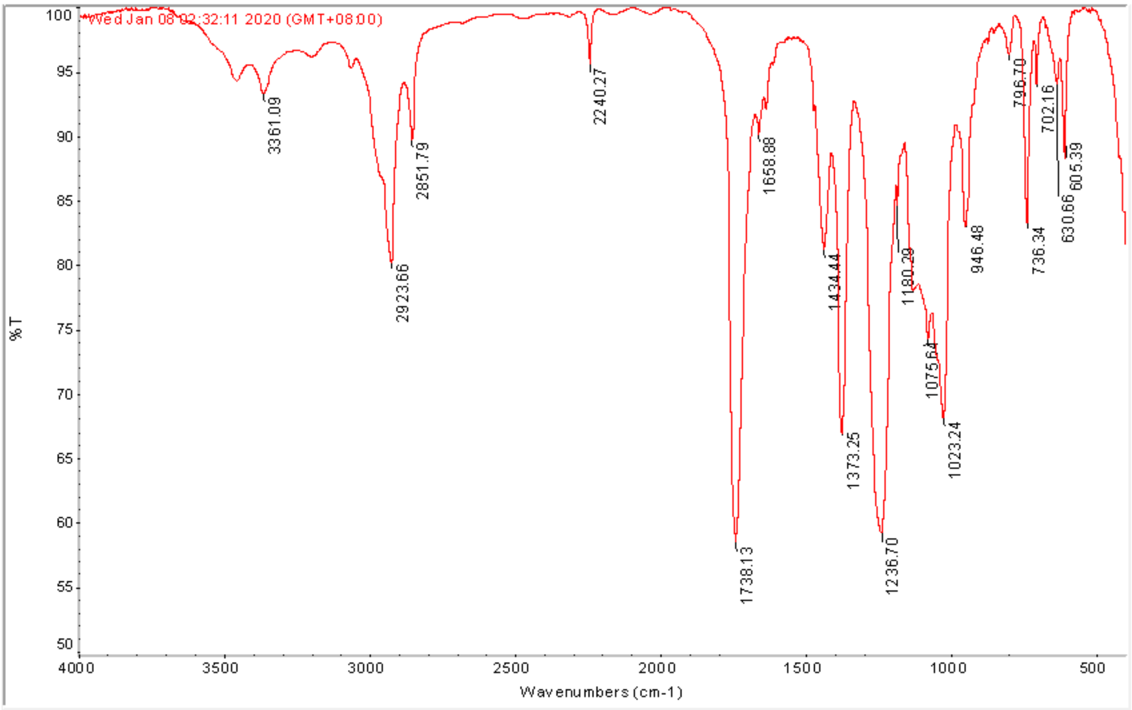


Figure S54. FT–IR of PVAc-*co*-PAN (81/19) **8d**.

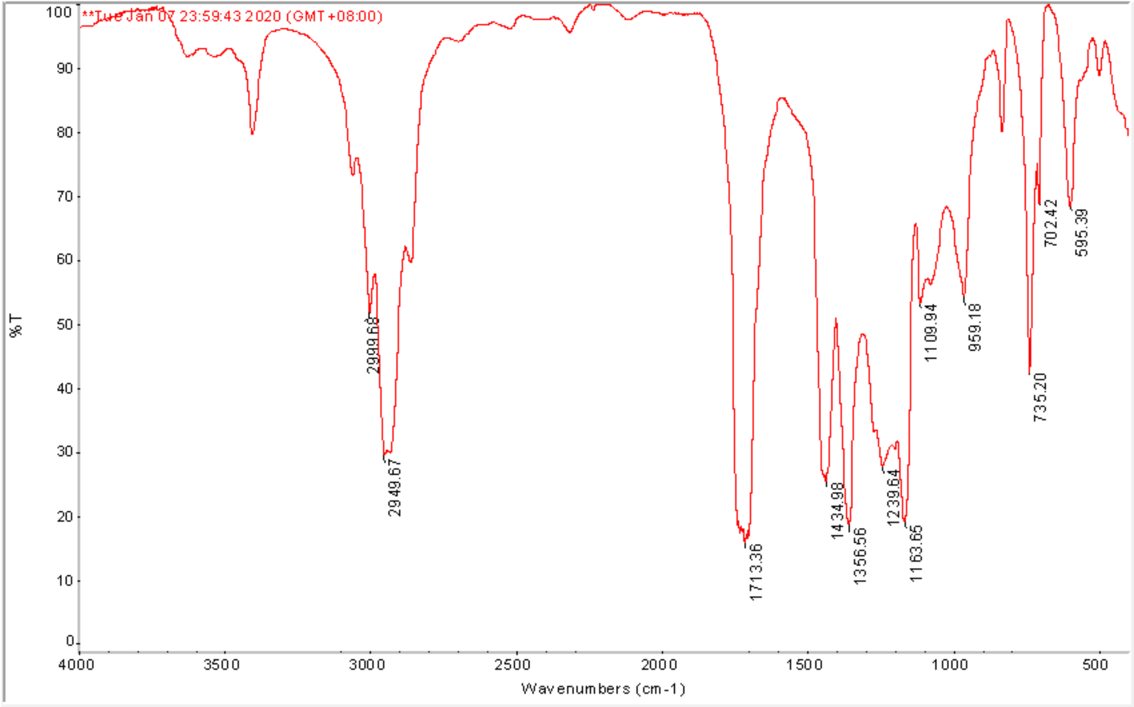


Figure S55. FT–IR of PMVK-*co*-PMA (83/17) **6e**.

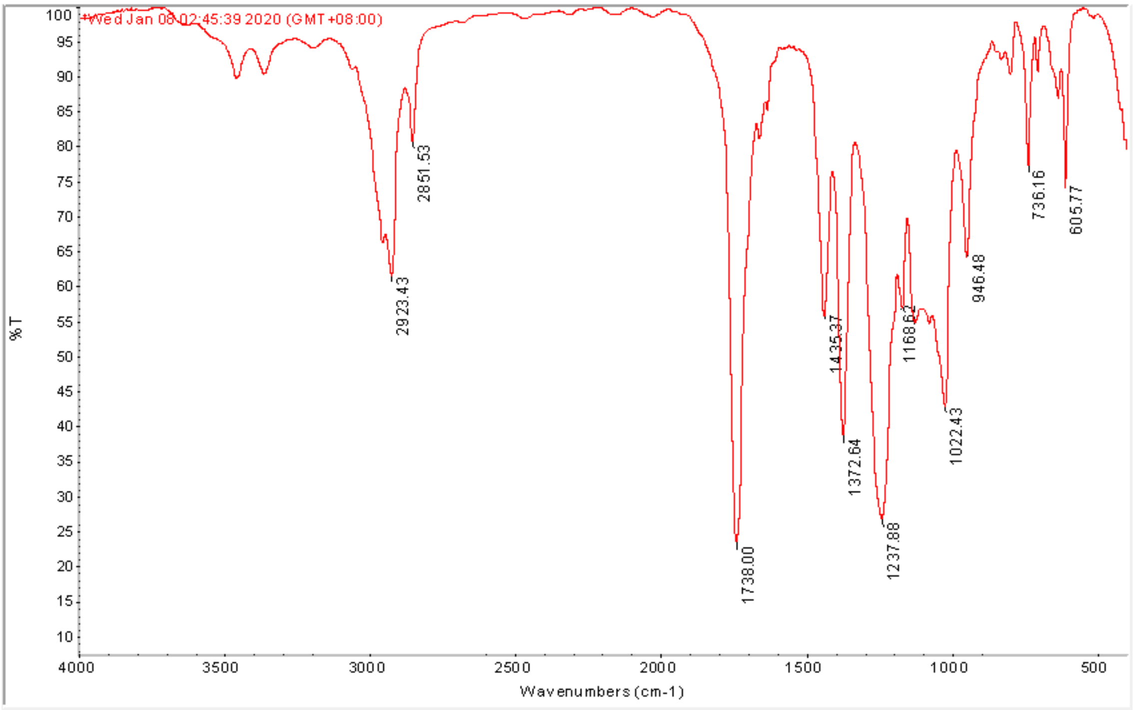


Figure S56. FT–IR of PVAc-*co*-PMA (83/17) **8e**.

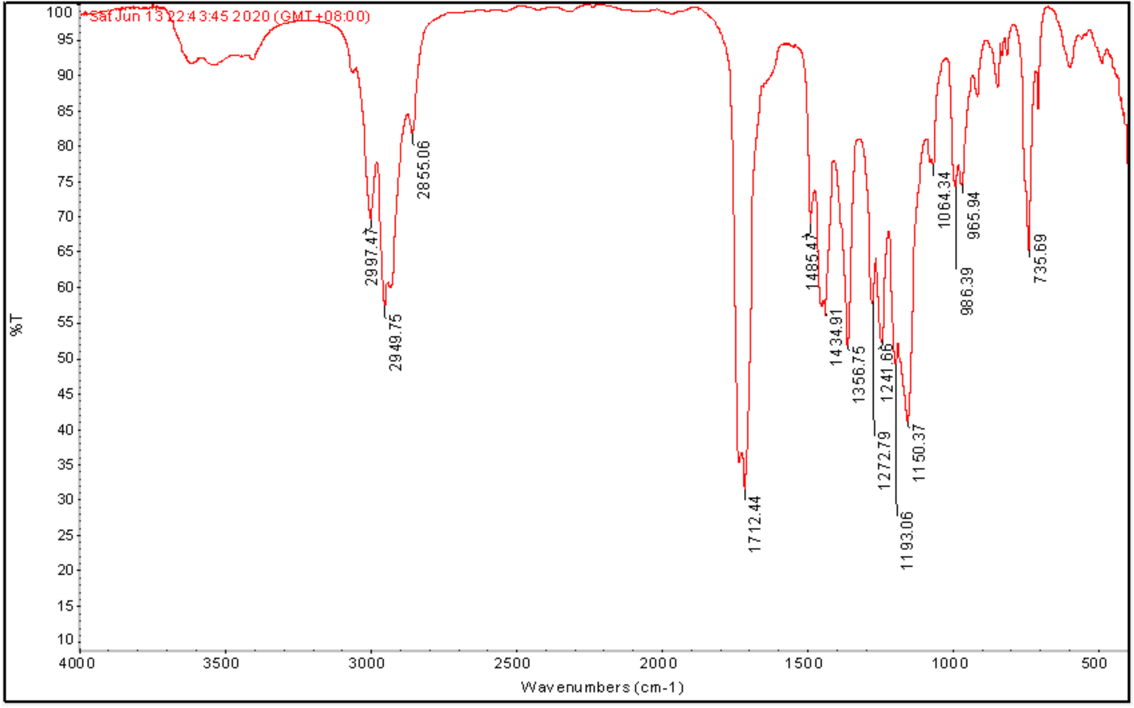


Figure S57. FT–IR of PMMA-*b*-PMVK diblock copolymer **7a**.

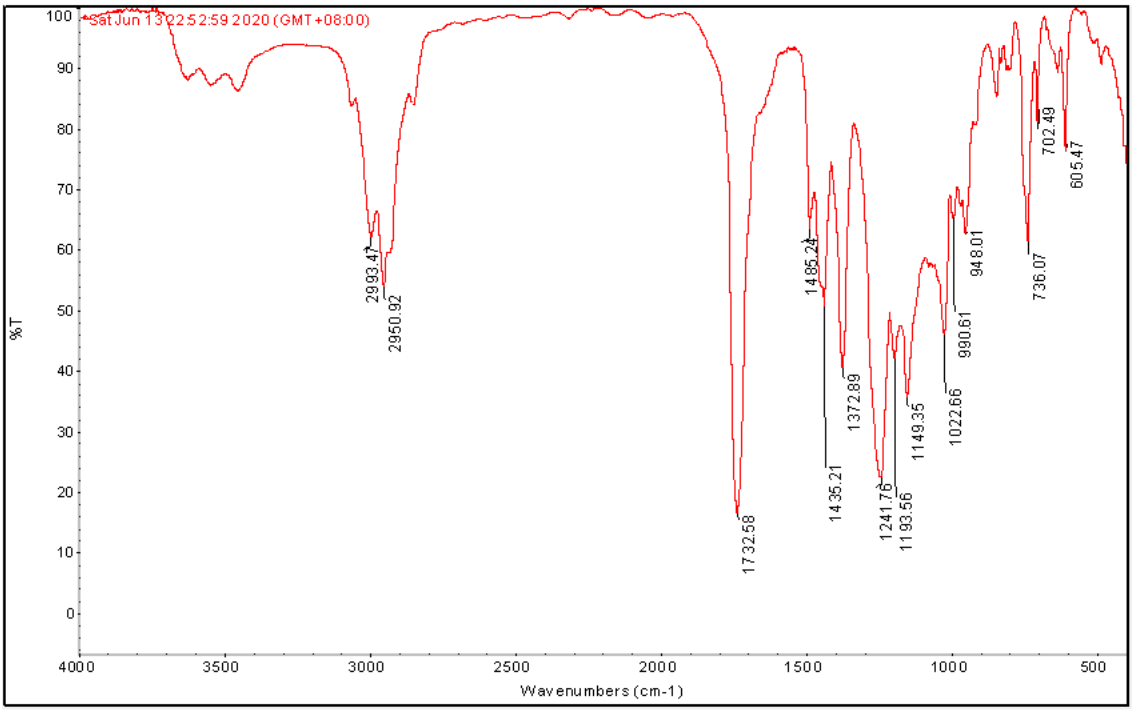


Figure S58. FT–IR of PMMA-*b*-PVAc diblock copolymer **9a**.

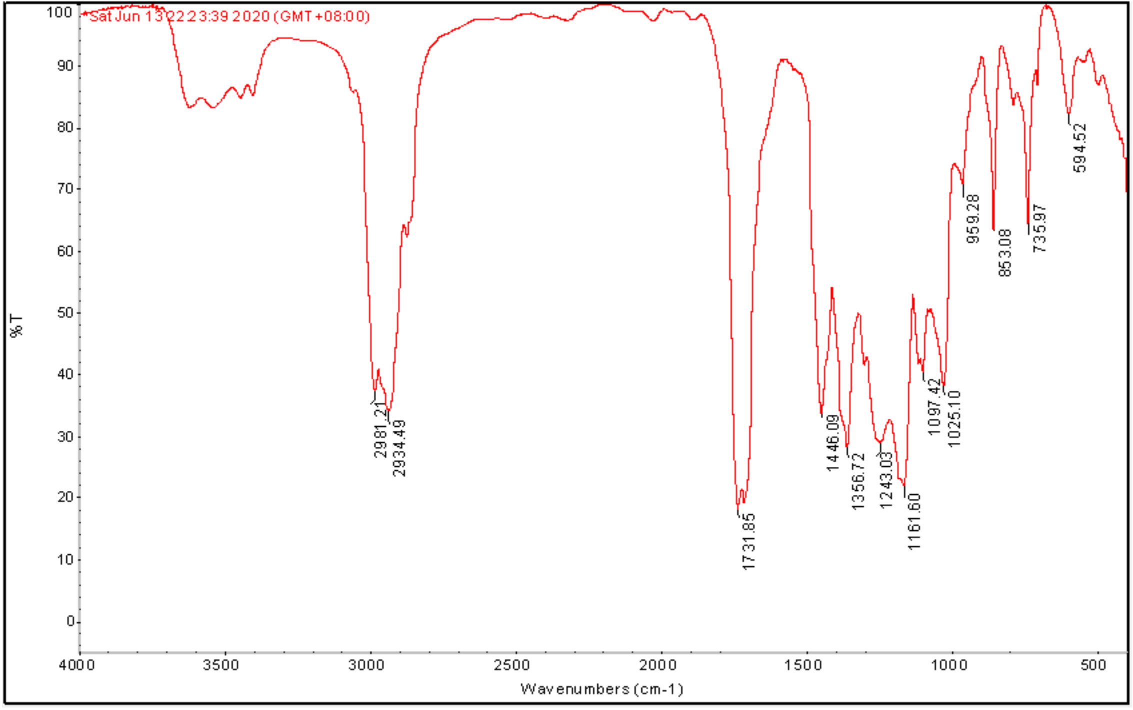


Figure S59. FT–IR of PEA-*b*-PMVK diblock copolymer **7b**.

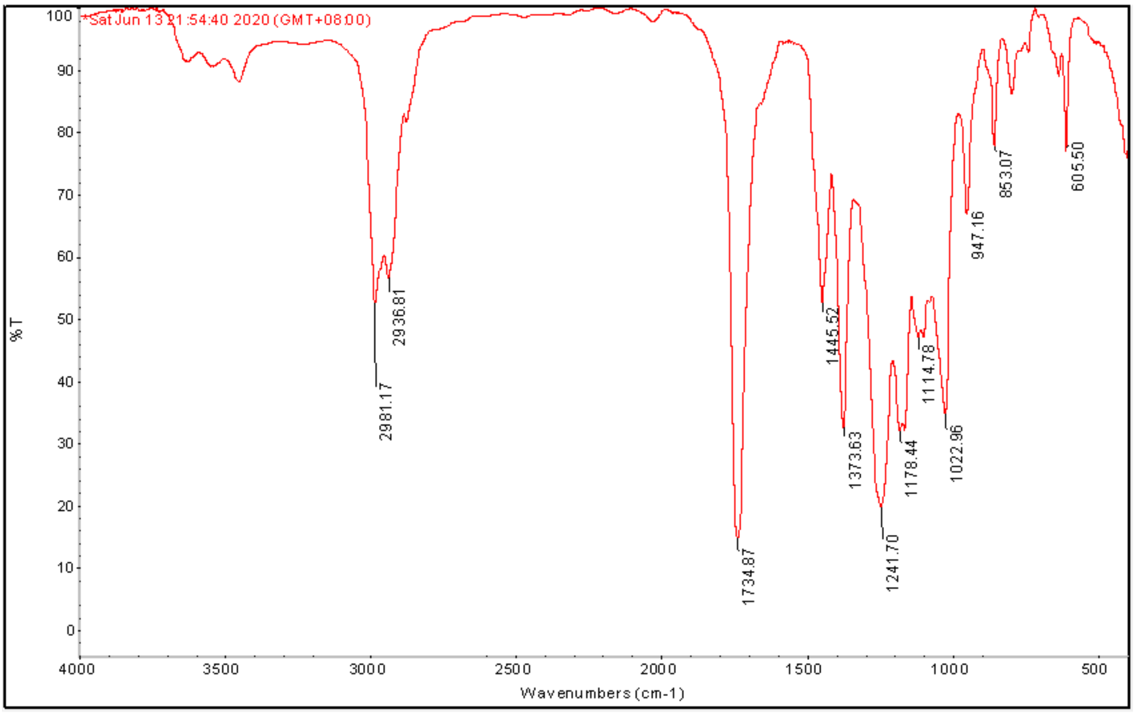


Figure S60. FT–IR of PEA-*b*-PVAc diblock copolymer **9b**.

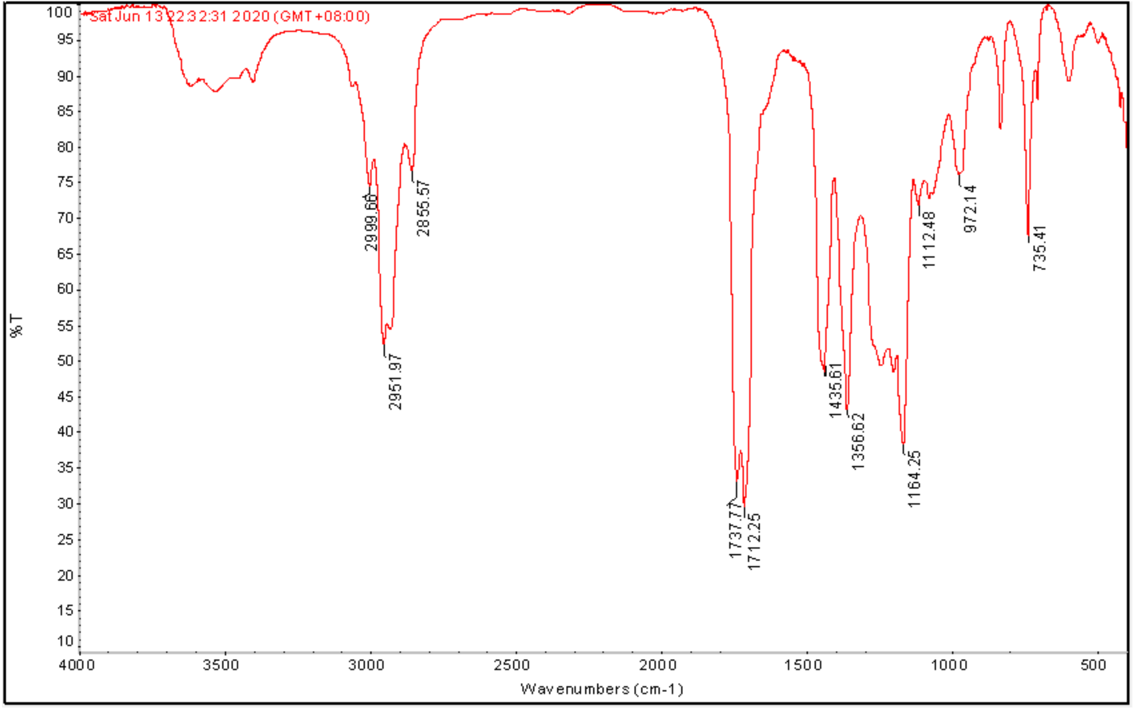


Figure S61. FT–IR of PMVK-*b*-PMA-*b*-PMVK triblock copolymer **7c**.

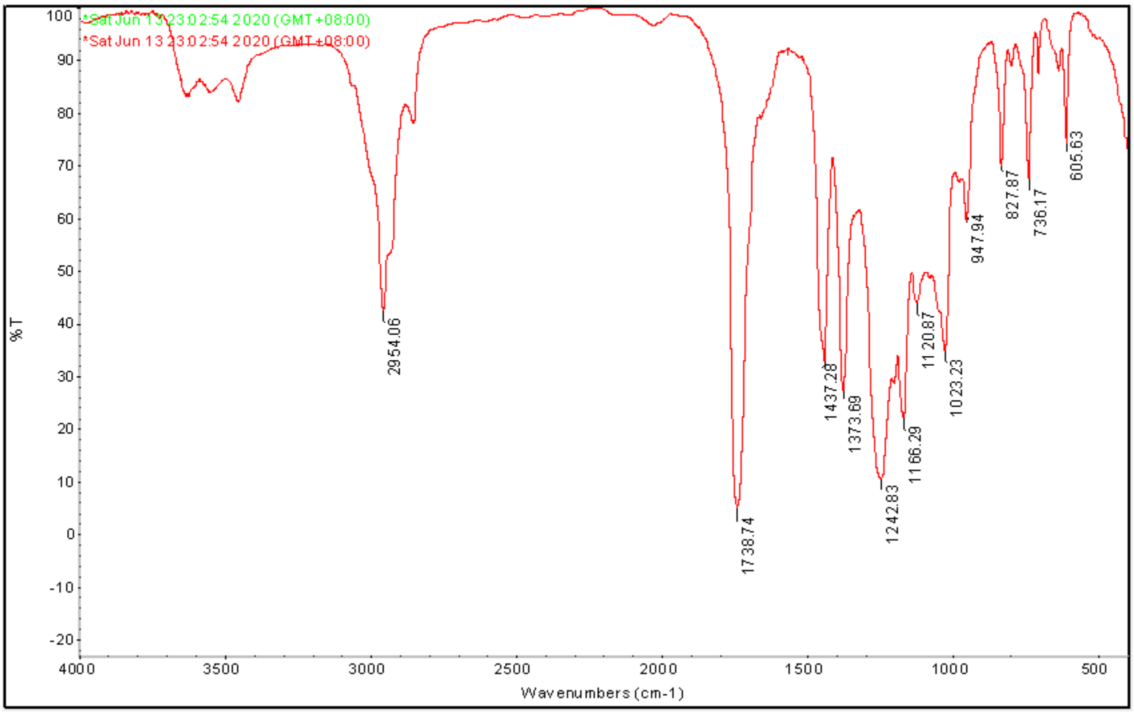


Figure S62. FT–IR of PVAc-*b*-PMA-*b*-PVAc triblock copolymer **9c**.

16. NMR Spectra

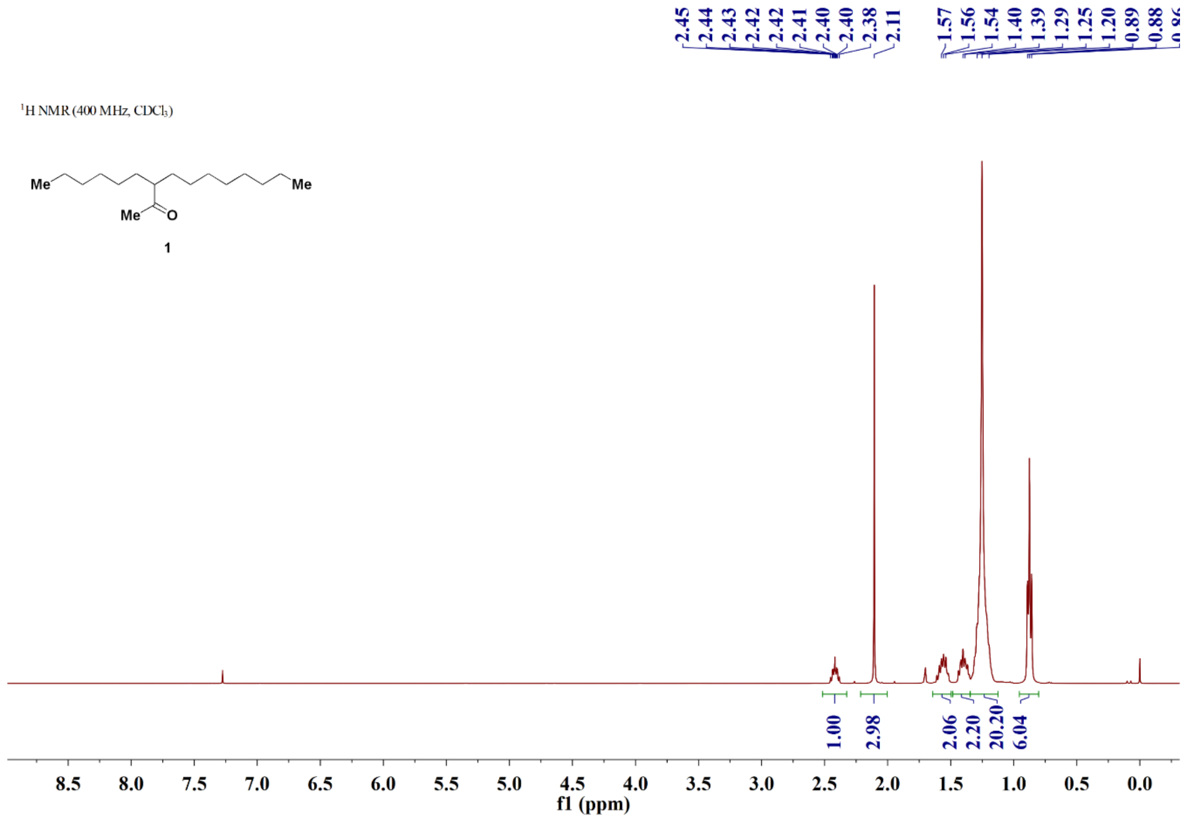


Figure S63. ^{1}H NMR spectrum of 3-hexylundecan-2-one **1**.

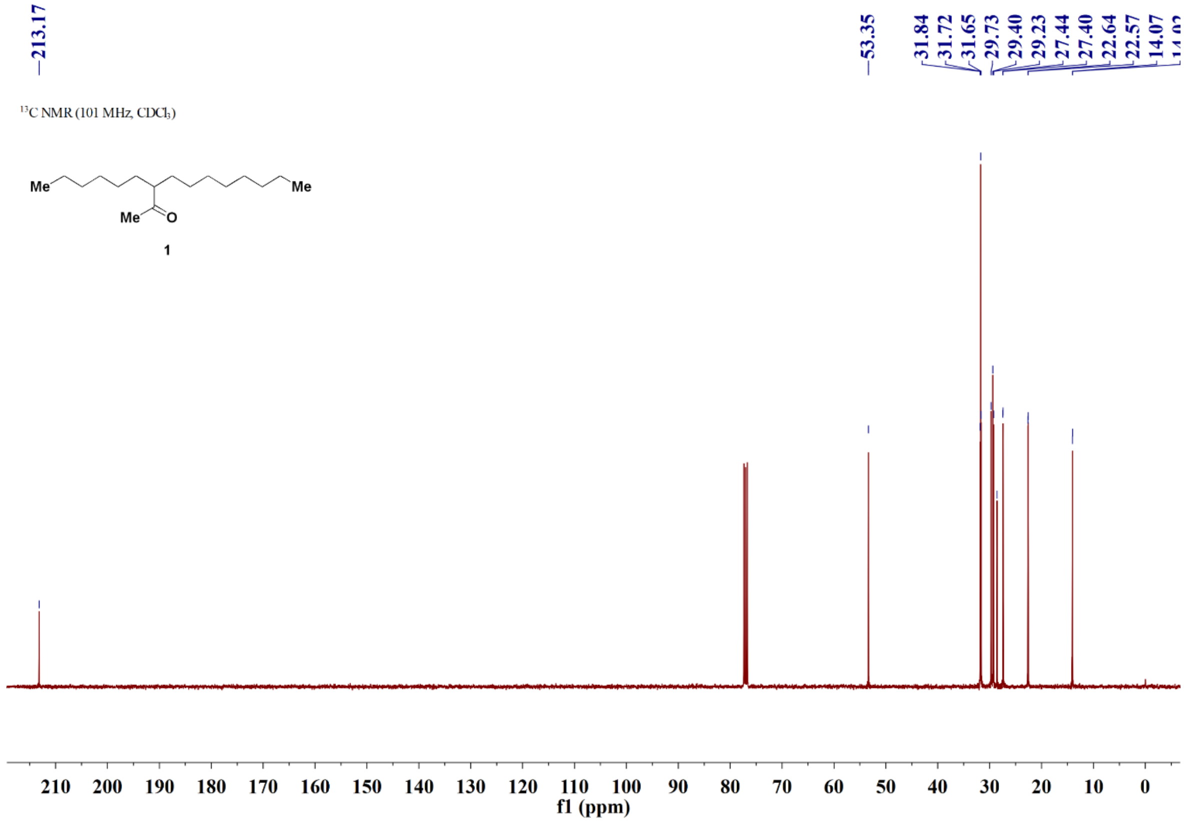


Figure S64. ^{13}C NMR spectrum of 3-hexylundecan-2-one **1**.

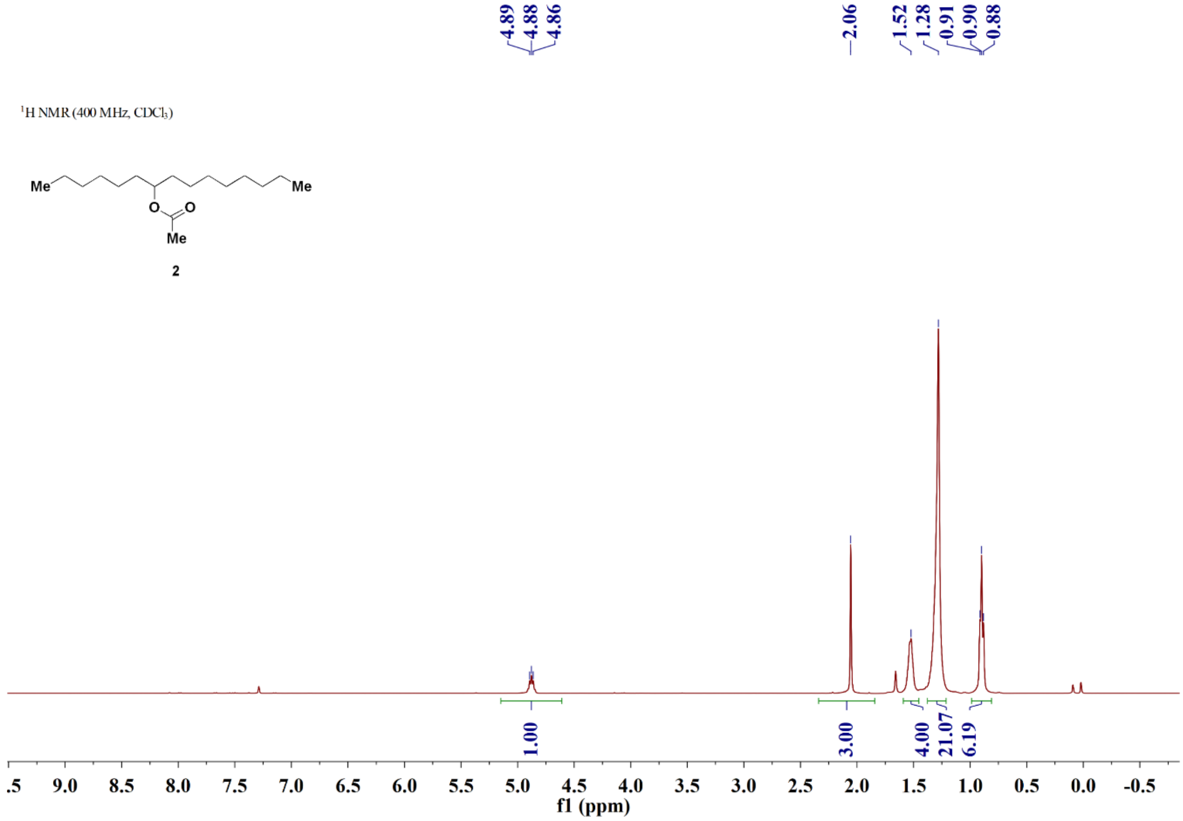


Figure S65. ^{1}H NMR spectrum of pentadecan-7-yl acetate **2**.

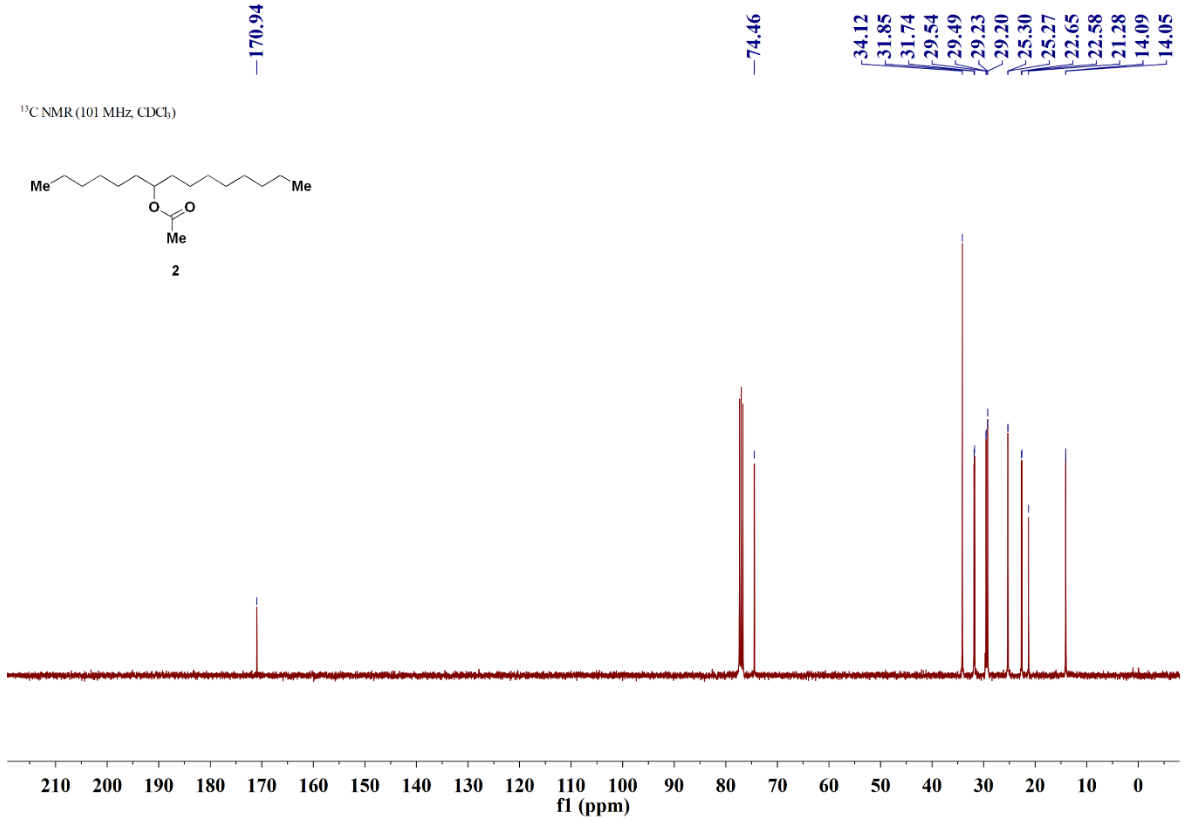


Figure S66. ^{13}C NMR spectrum of pentadecan-7-yl acetate **2**.

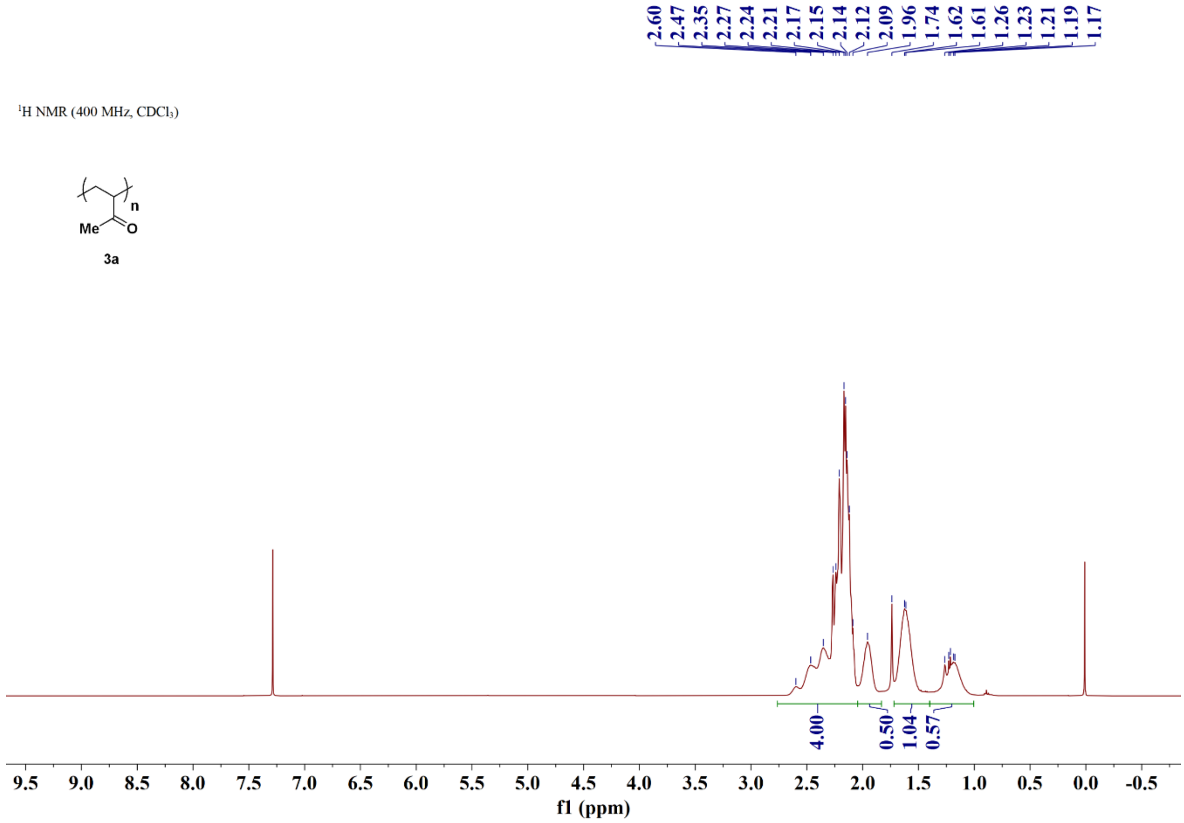


Figure S67. ^{1}H NMR spectrum of commercial PMVK **3a**.

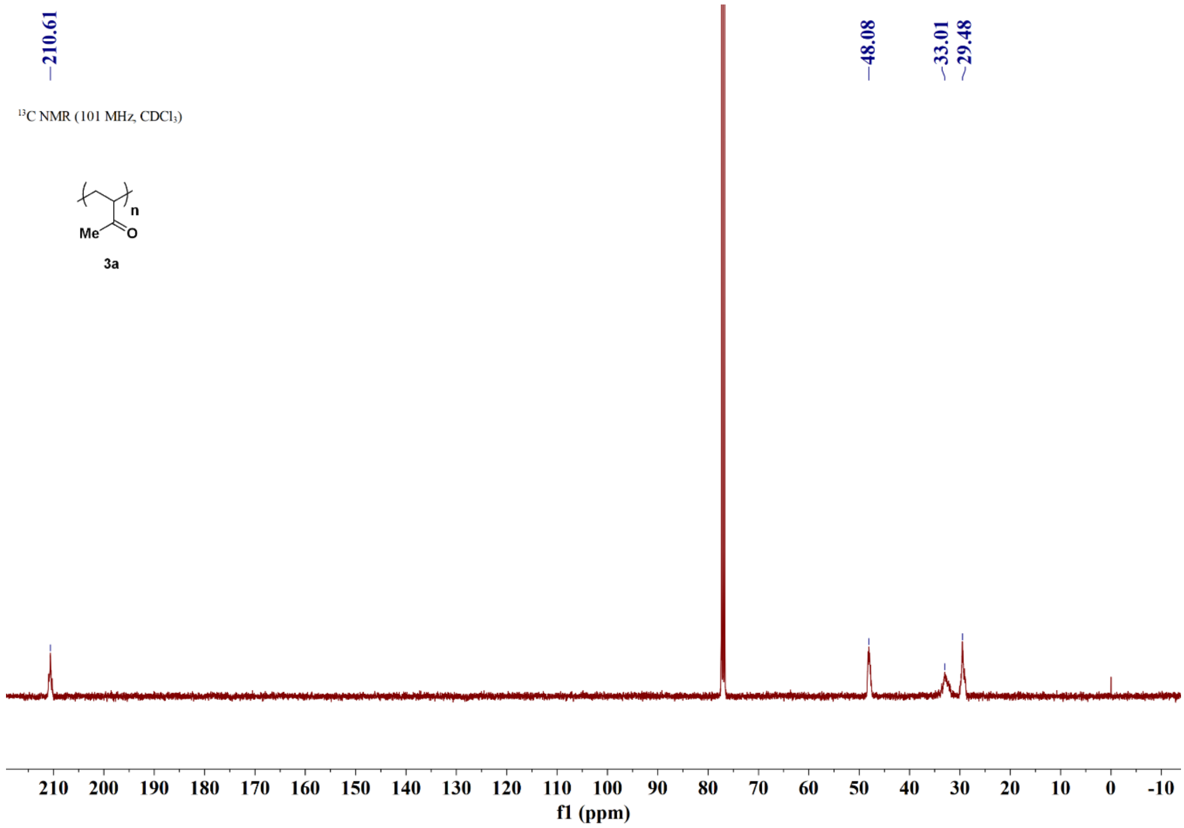


Figure S68. ^{13}C NMR spectrum of commercial PMVK **3a**.

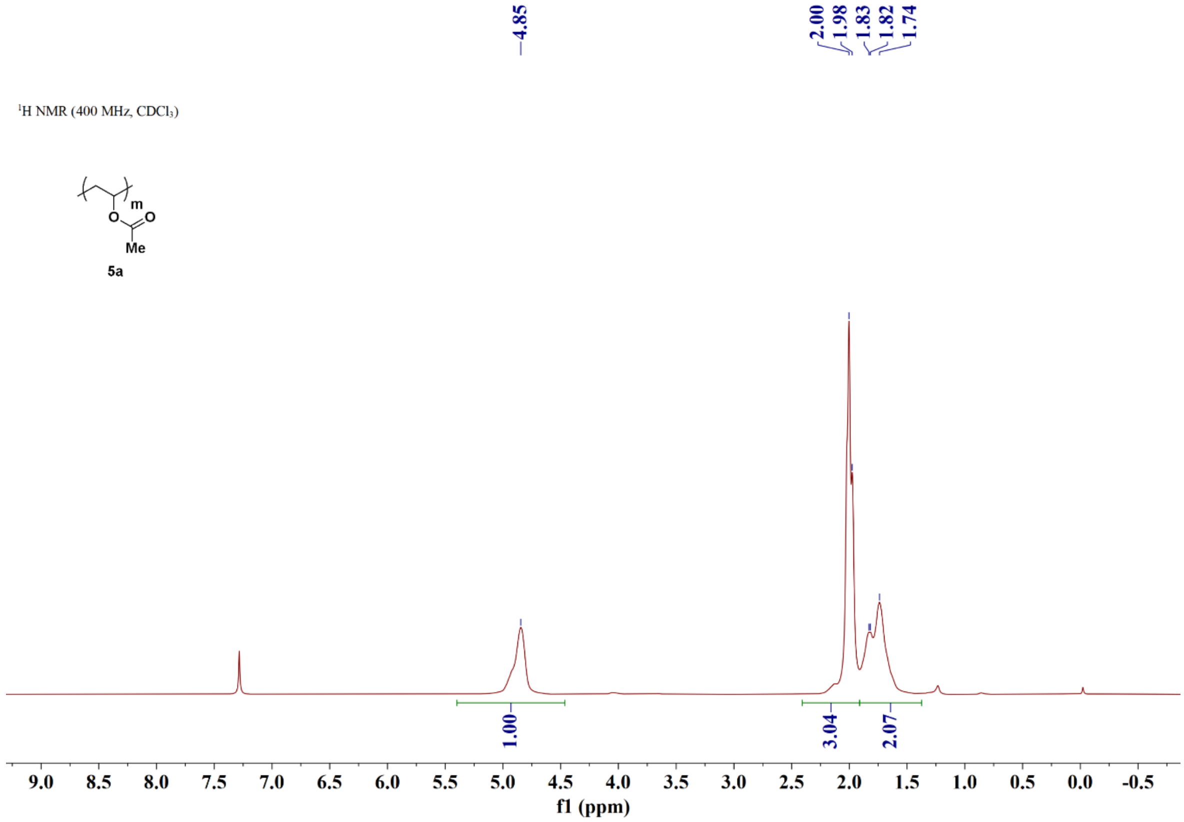


Figure S69. ^{1}H NMR spectrum of PVAc **5a**.

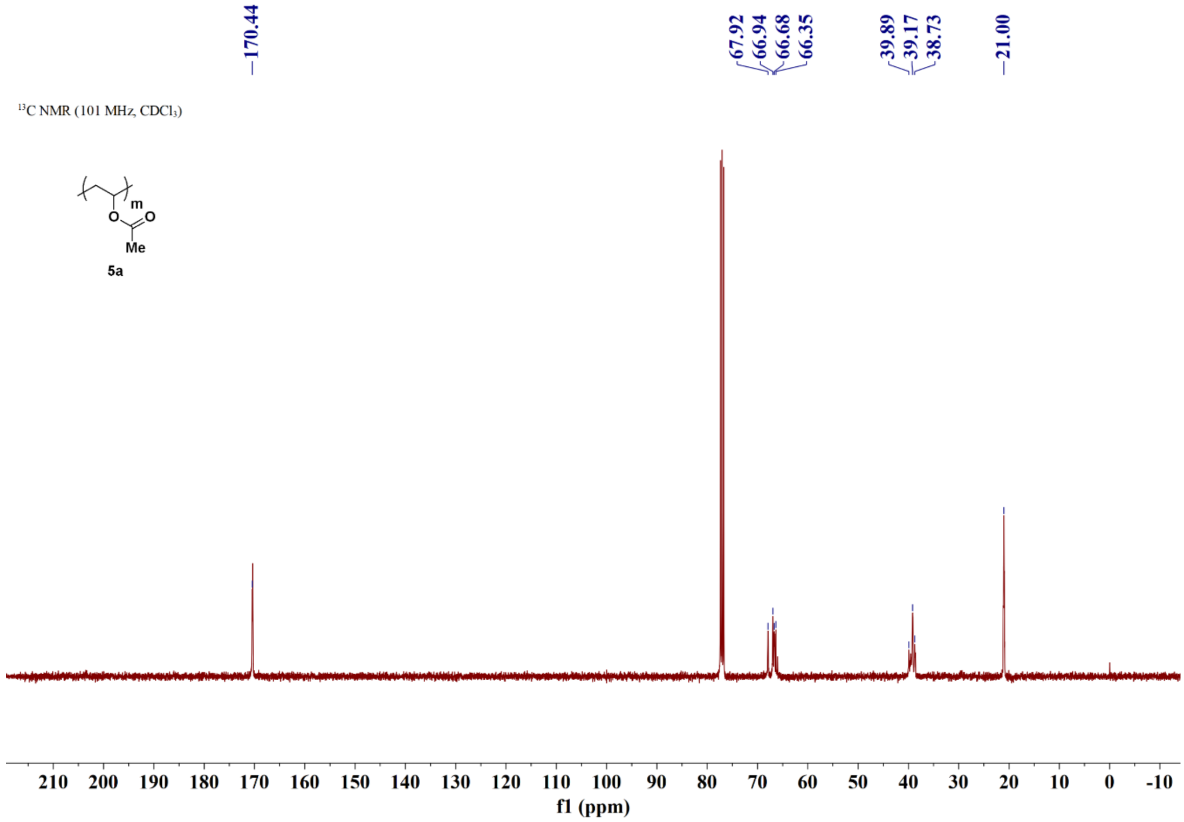


Figure S70. ^{13}C NMR spectrum of PVAc **5a**.

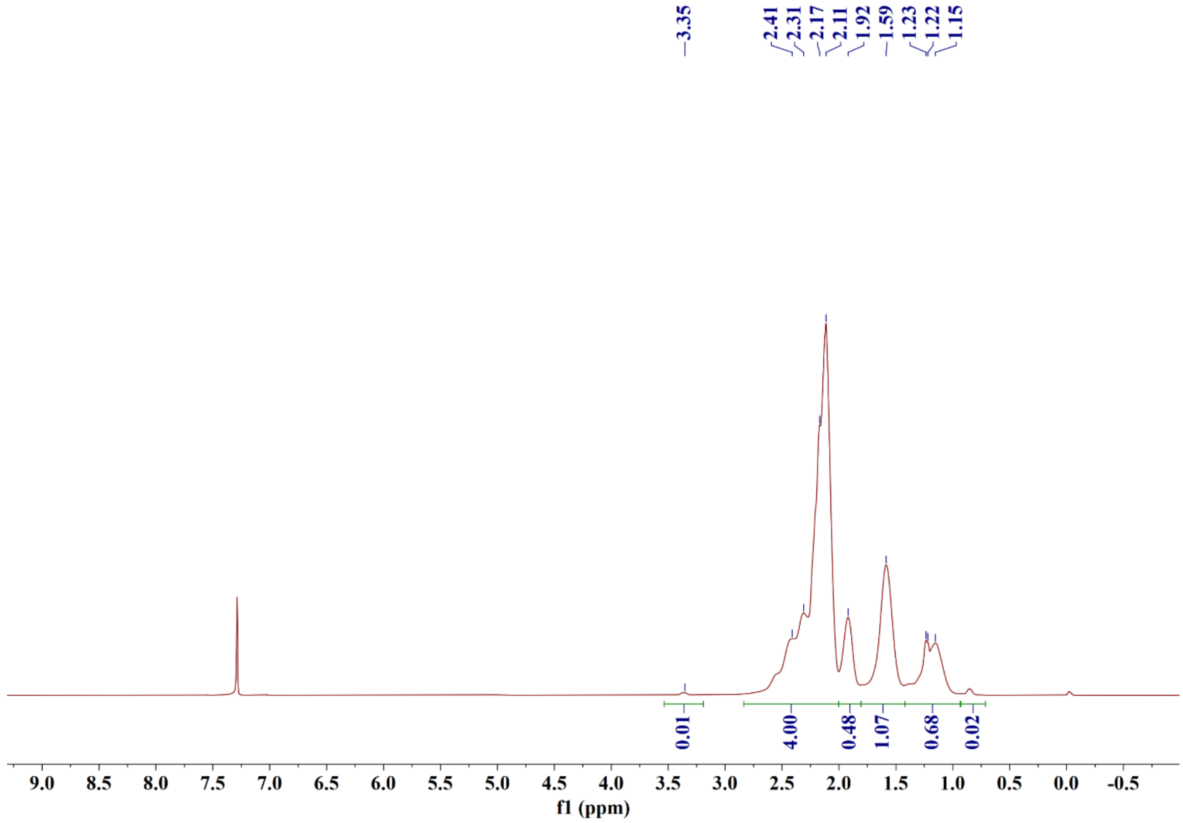


Figure S71. ^{1}H NMR spectrum of PMVK **3b**.

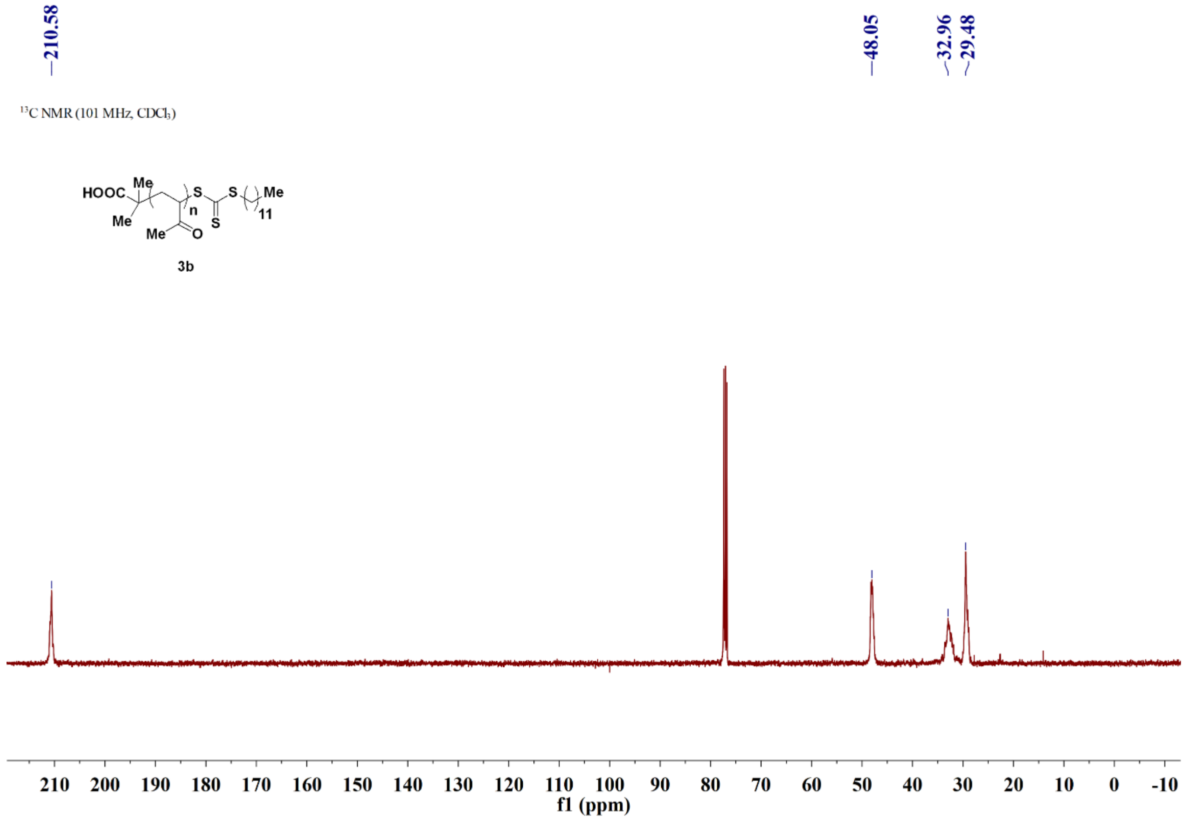


Figure S72. ^{13}C NMR spectrum of PMVK **3b**.

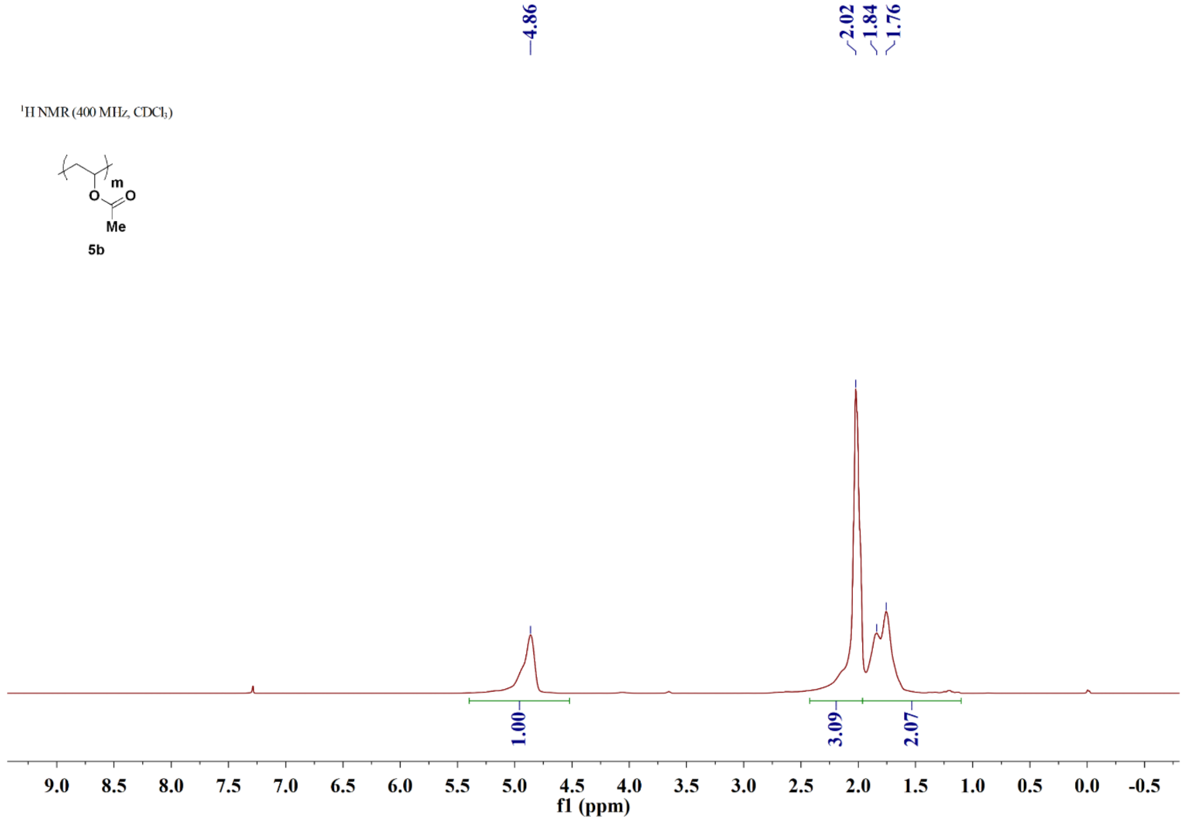


Figure S73. ^{1}H NMR spectrum of PVAc **5b**.

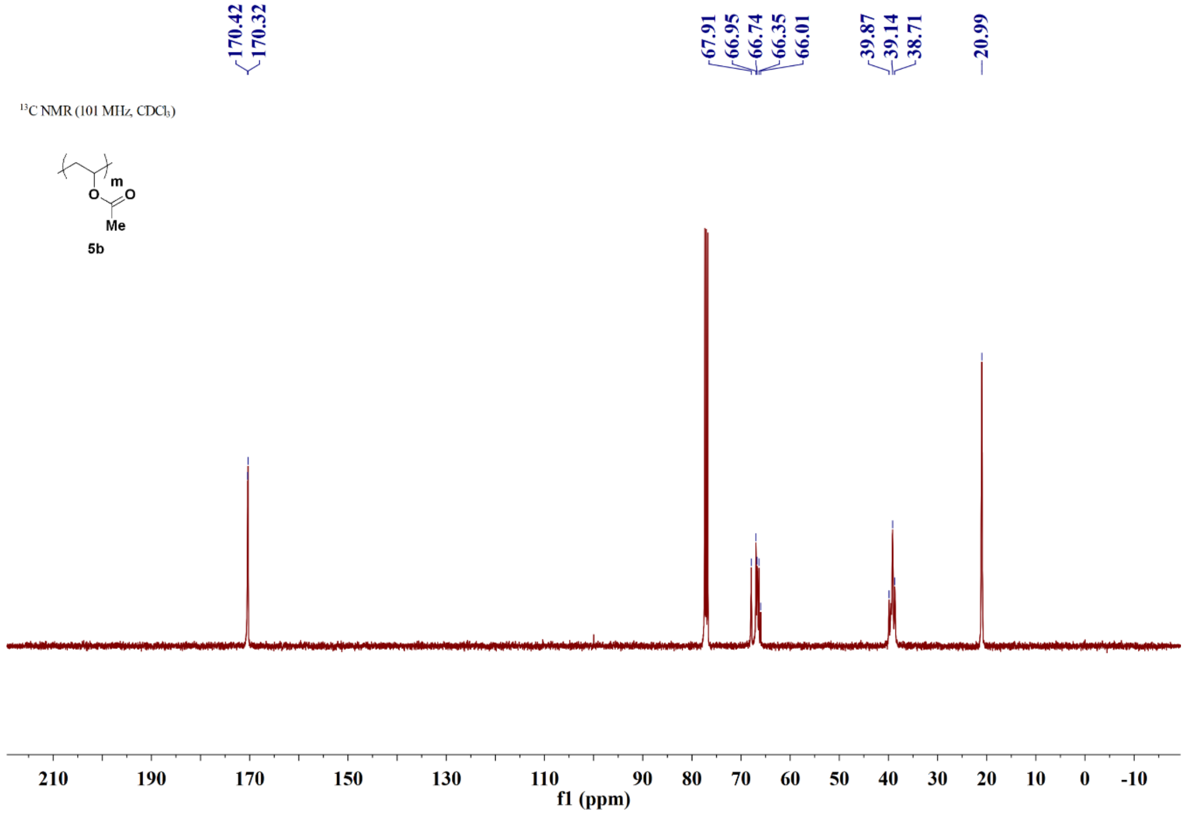


Figure S74. ^{13}C NMR spectrum of PVAc **5b**.

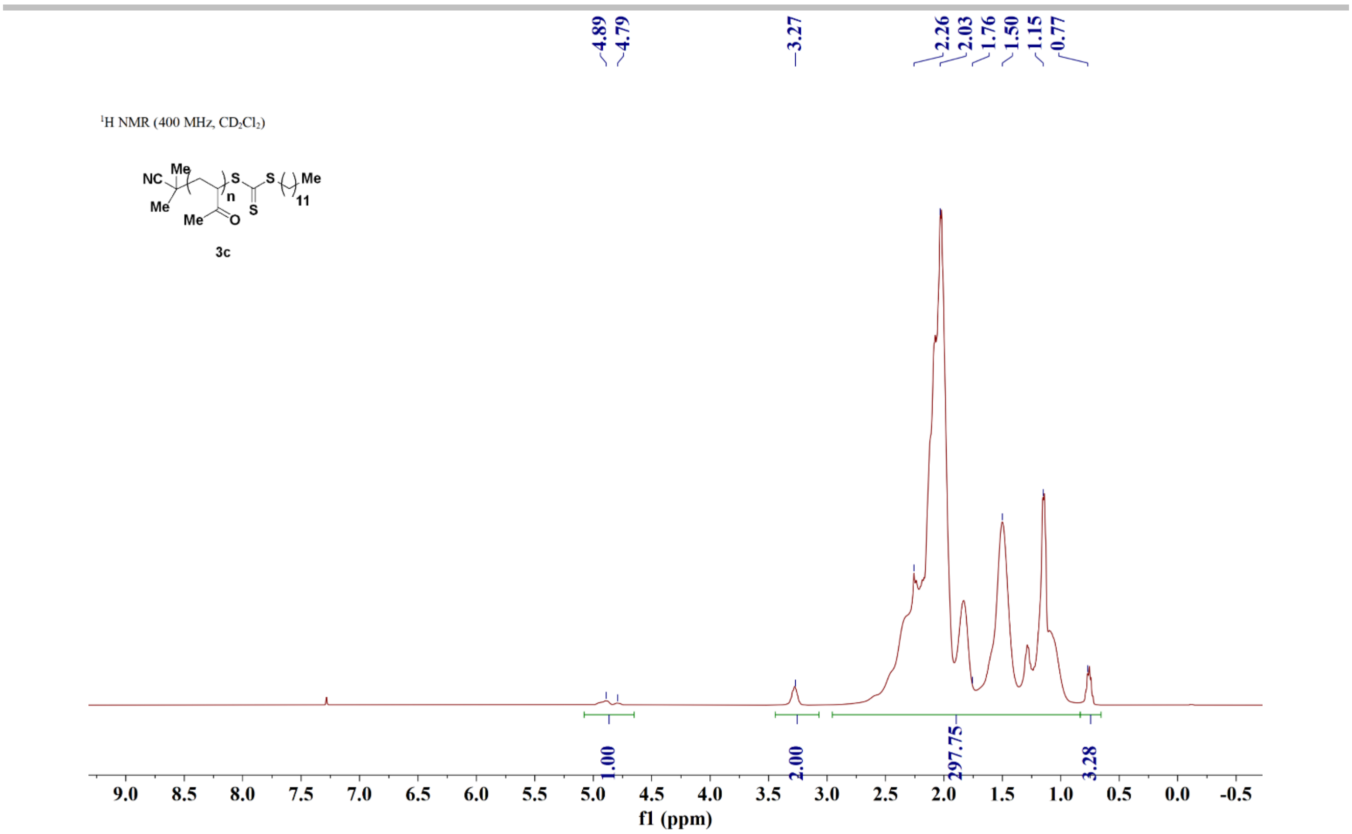


Figure S75. ^{1}H NMR spectrum of PMVK **3c**.

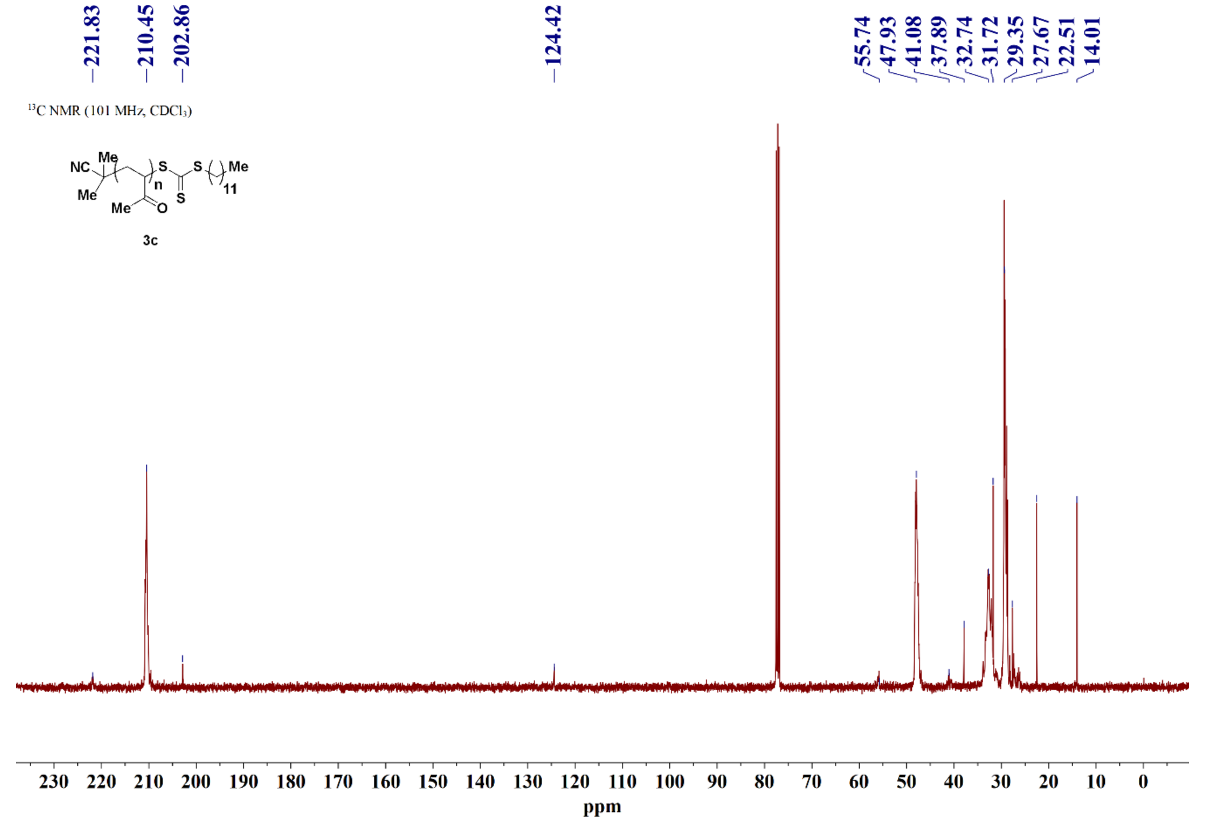


Figure S76. ^{13}C NMR spectrum of PMVK **3c**.

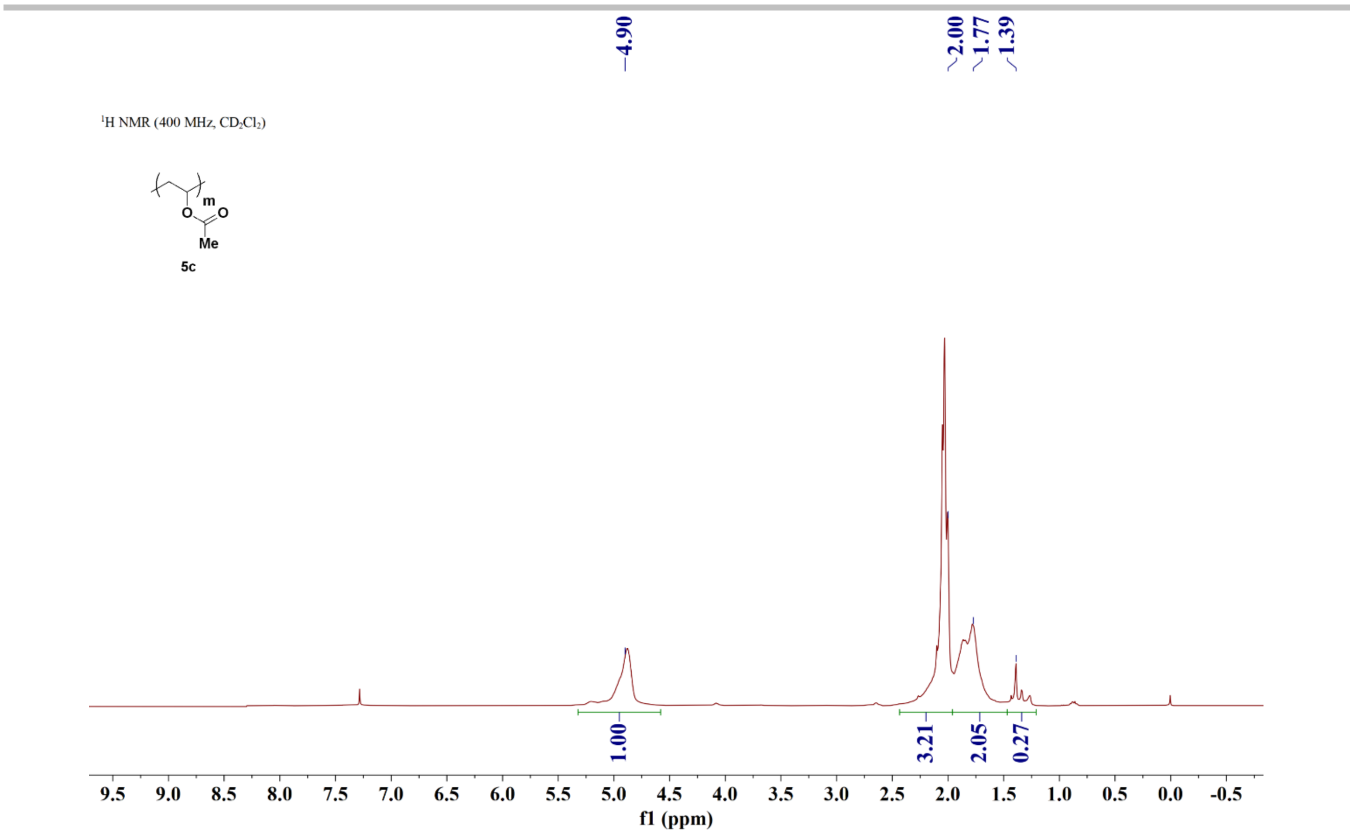


Figure S77. ^{1}H NMR spectrum of PVAc **5c**.

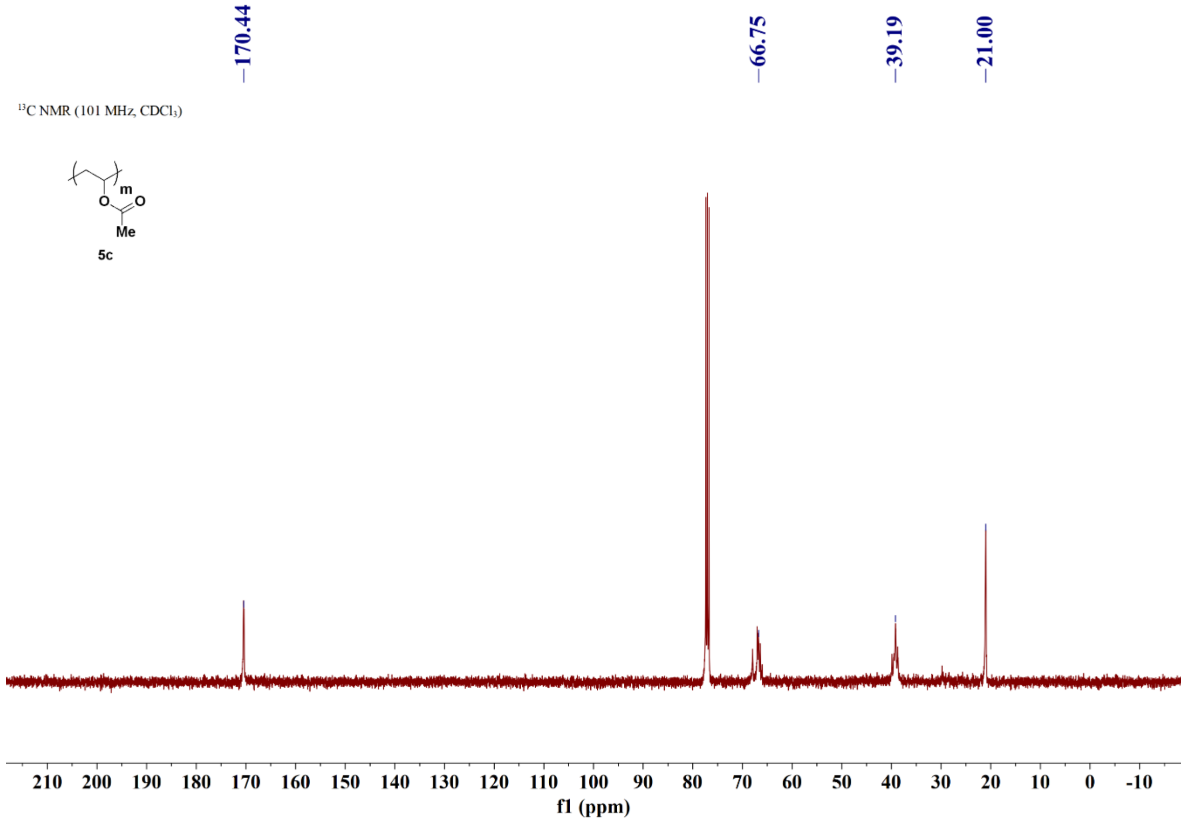


Figure S78. ^{13}C NMR spectrum of PVAc **5c**.

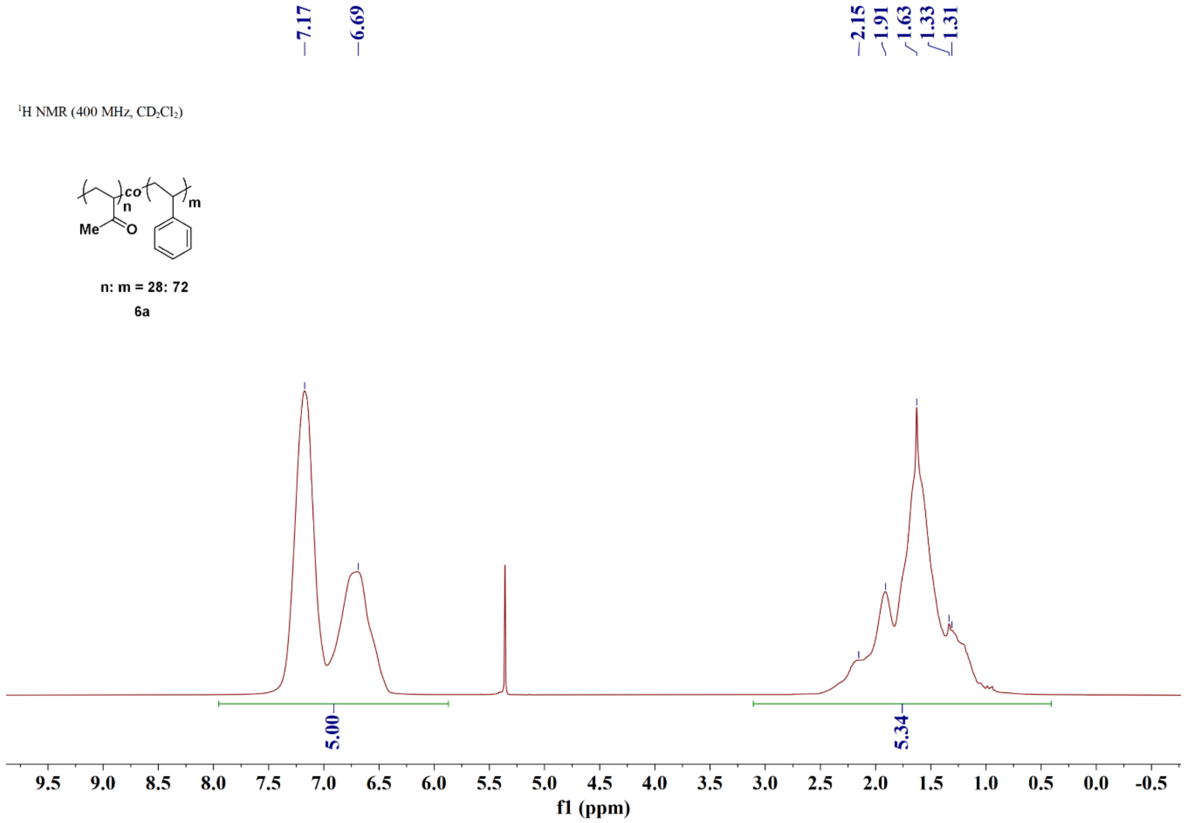


Figure S79. ^{1}H NMR spectrum of PMVK-*co*-PS (28/72) **6a**.

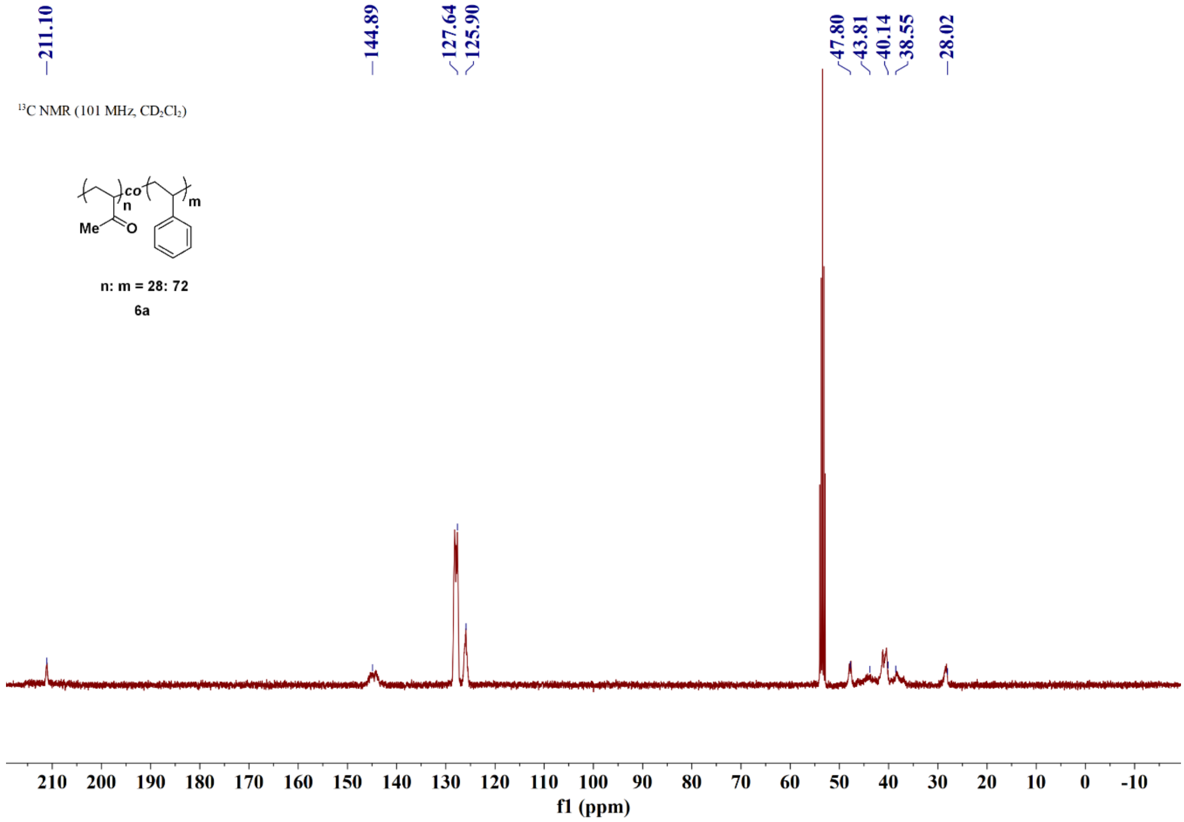


Figure S80. ^{13}C NMR spectrum of PMVK-*co*-PS (28/72) **6a**.

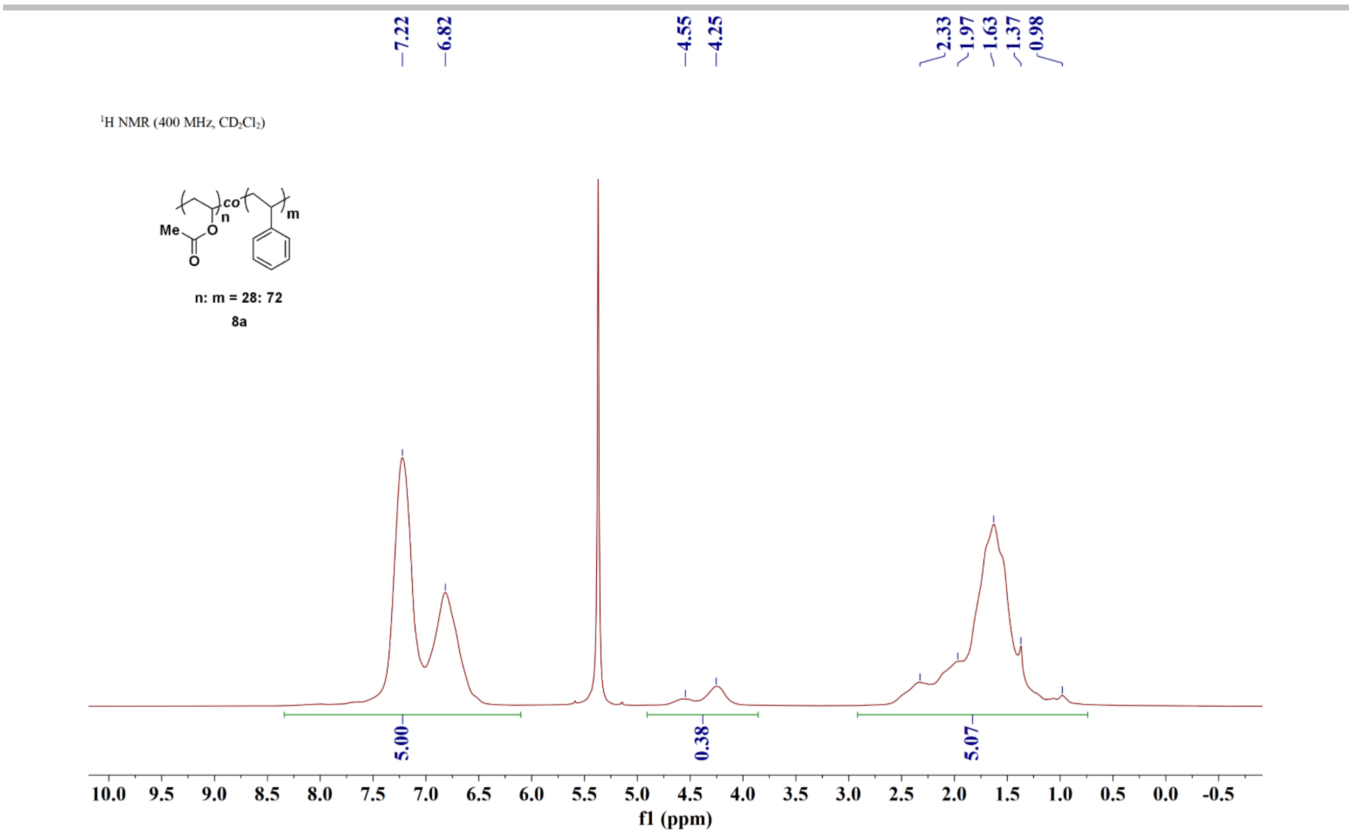


Figure S81. ^{1}H NMR spectrum of PVAc-*co*-PS (28/72) **8a**.

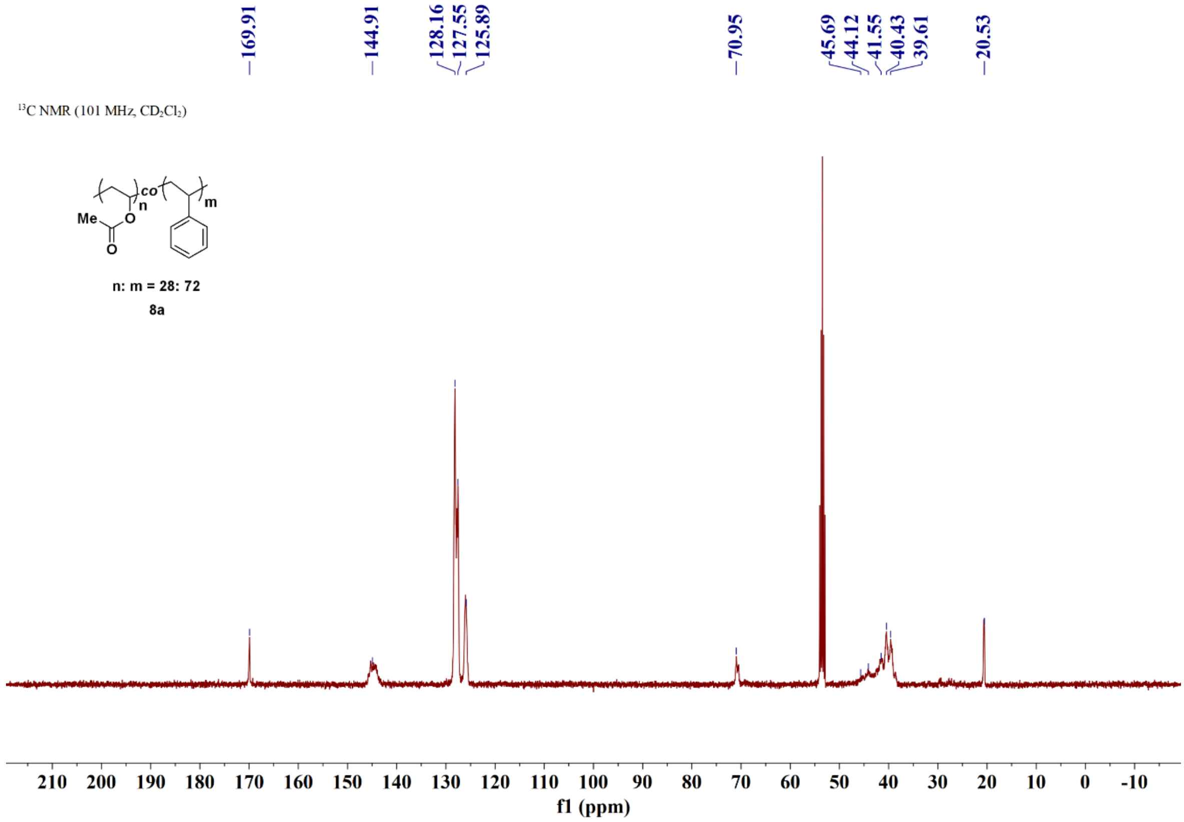


Figure S82. ^{13}C NMR spectrum of PVAc-*co*-PS (28/72) **8a**.

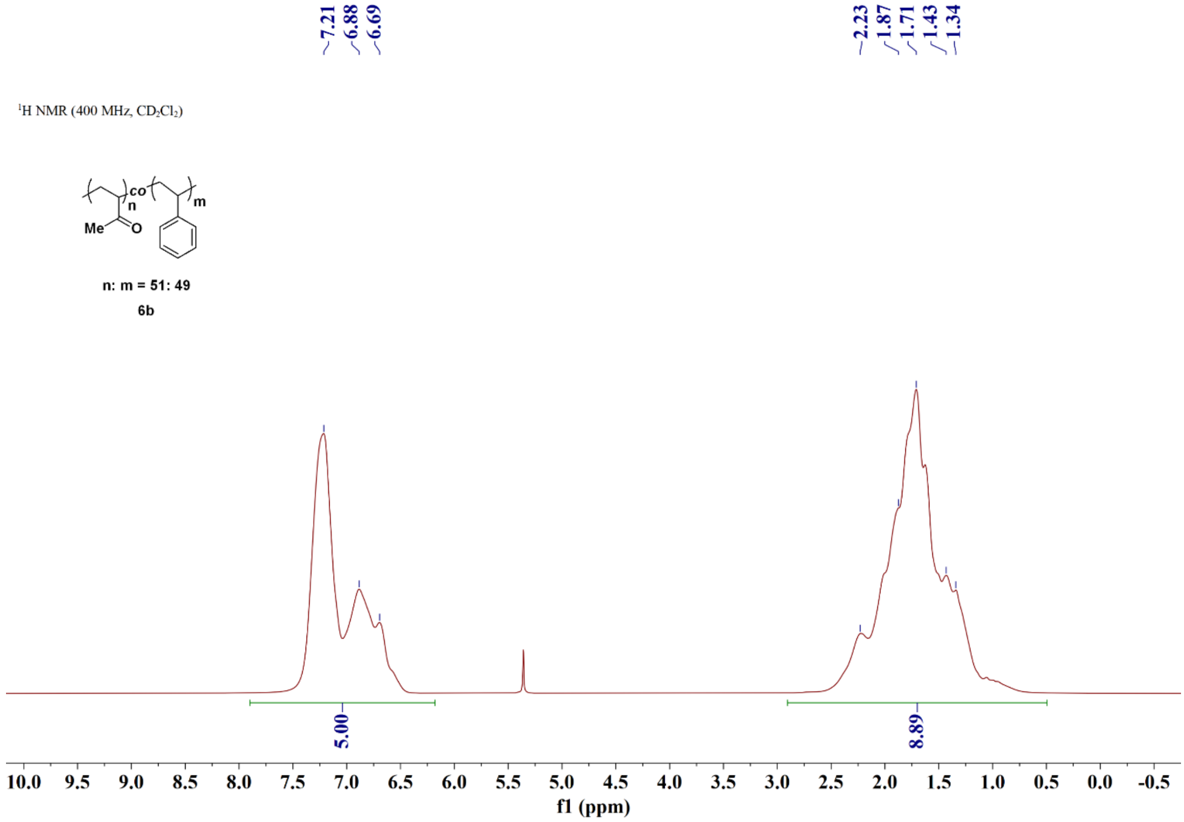


Figure S83. ^{1}H NMR spectrum of PMVK-*co*-PS (51/49) **6b**.

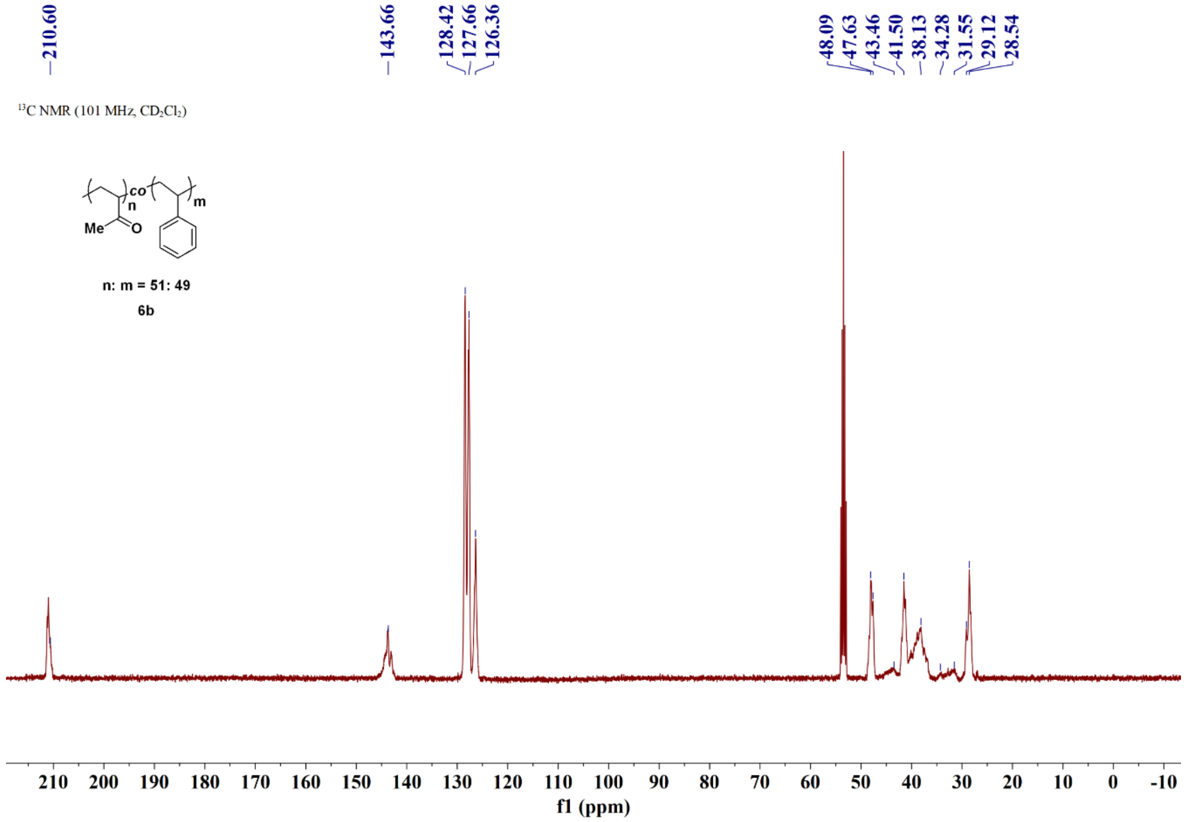


Figure S84. ^{13}C NMR spectrum of PMVK-*co*-PS (51/49) **6b**.

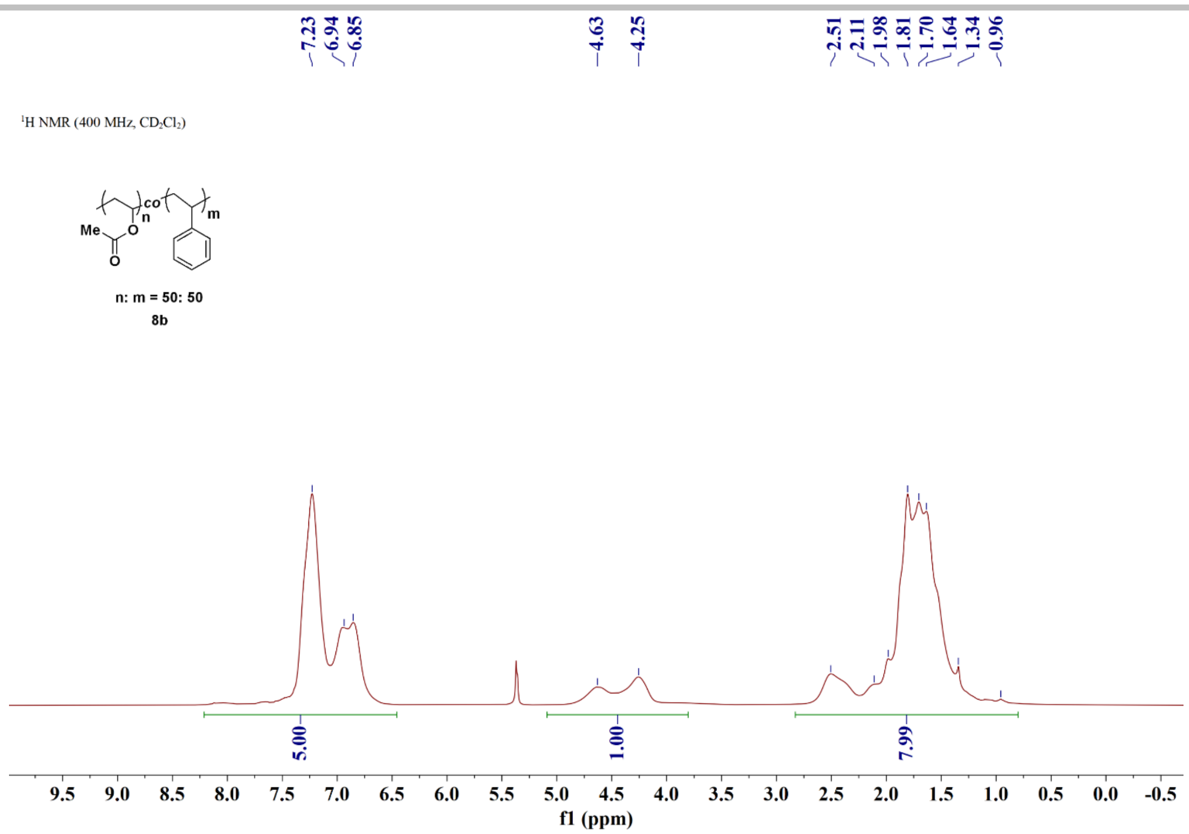


Figure S85. ^{1}H NMR spectrum of PVAc-*co*-PS (50/50) **8b**.

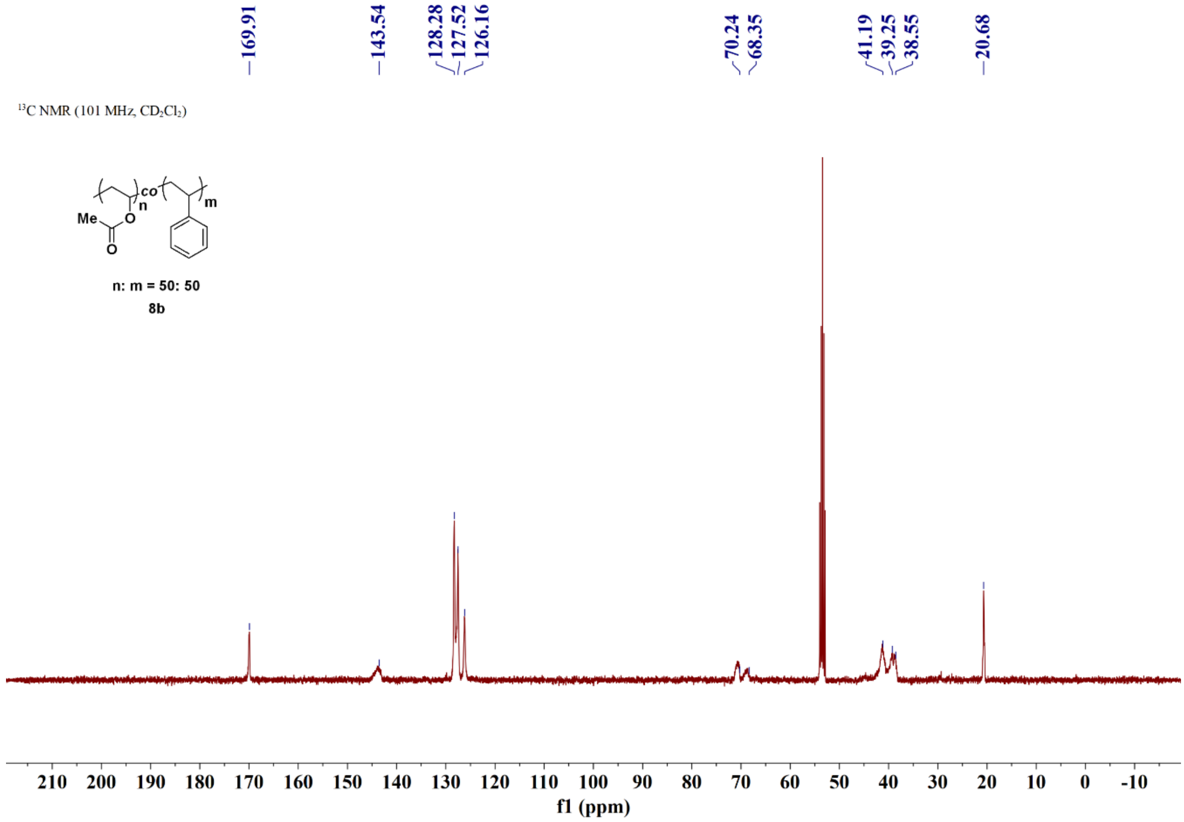


Figure S86. ^{13}C NMR spectrum of PVAc-*co*-PS (50/50) **8b**.

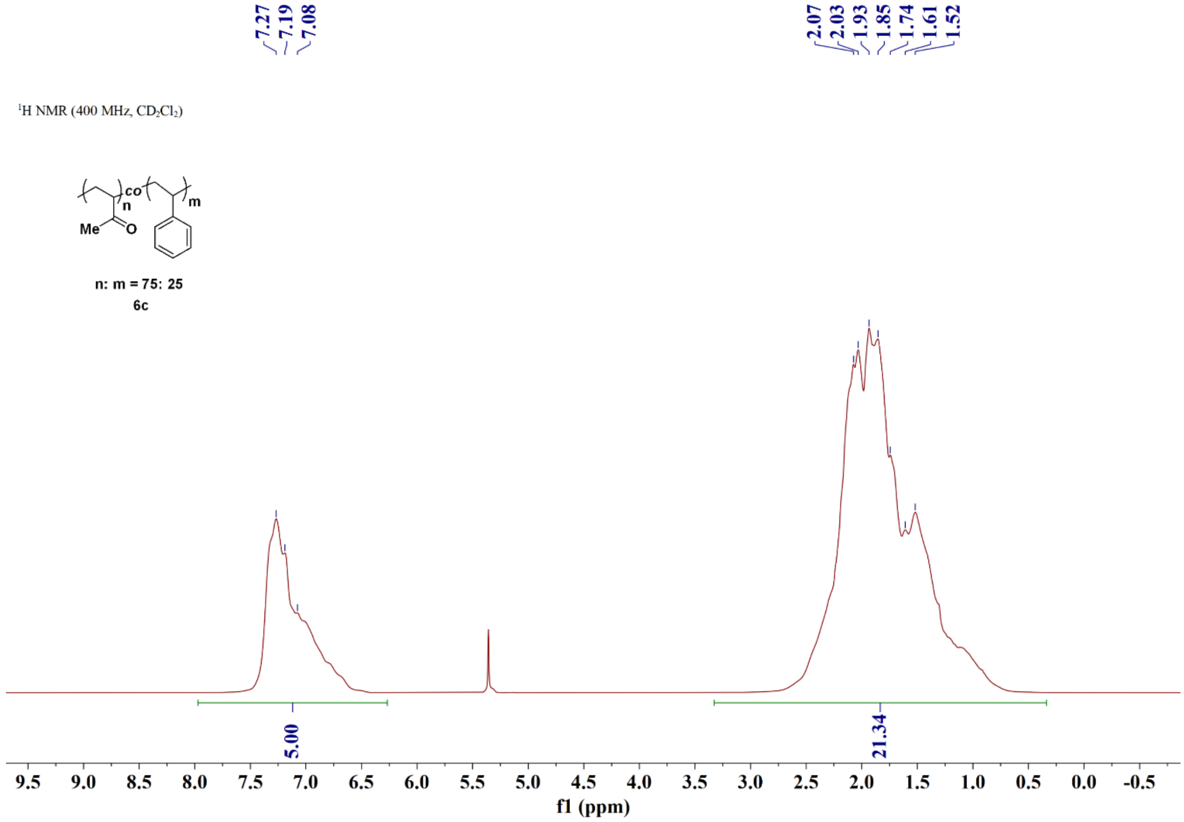


Figure S87. ^{1}H NMR spectrum of PMVK-*co*-PS (75/25) **6c**.

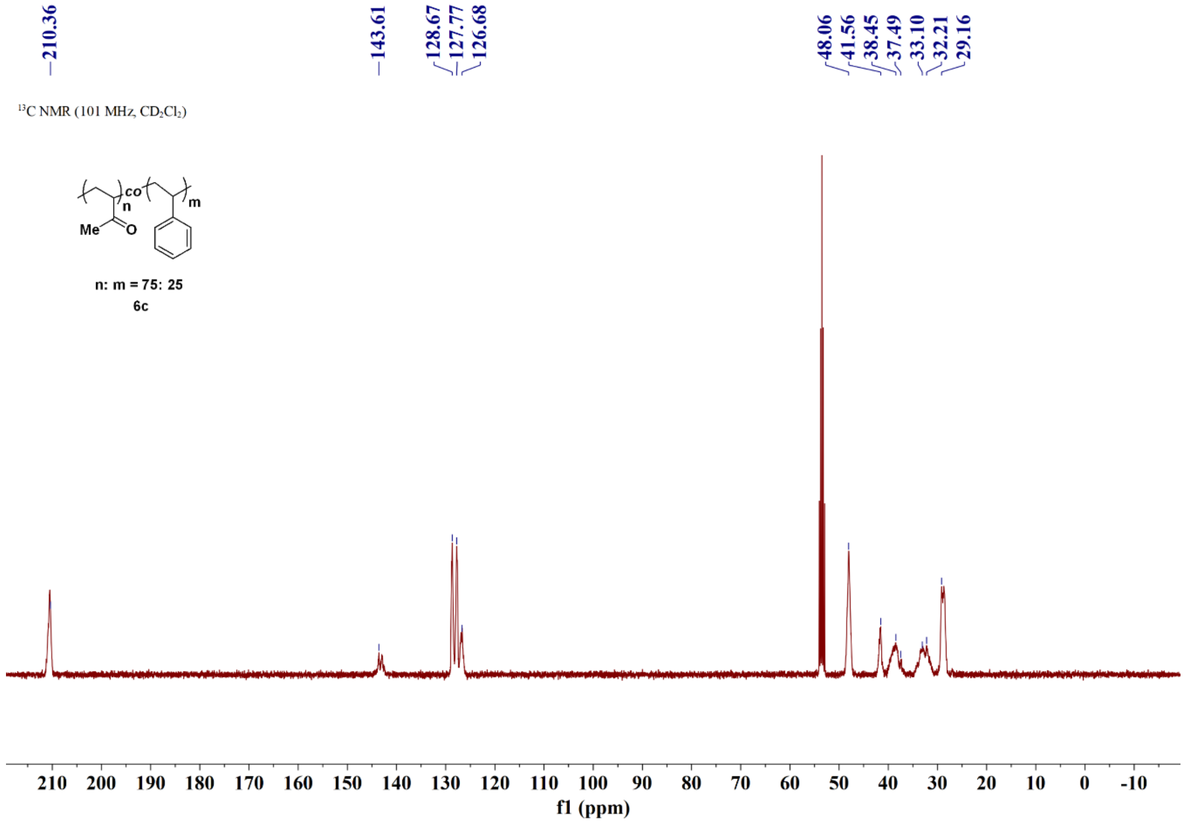


Figure S88. ^{13}C NMR spectrum of PMVK-*co*-PS (75/25) **6c**.

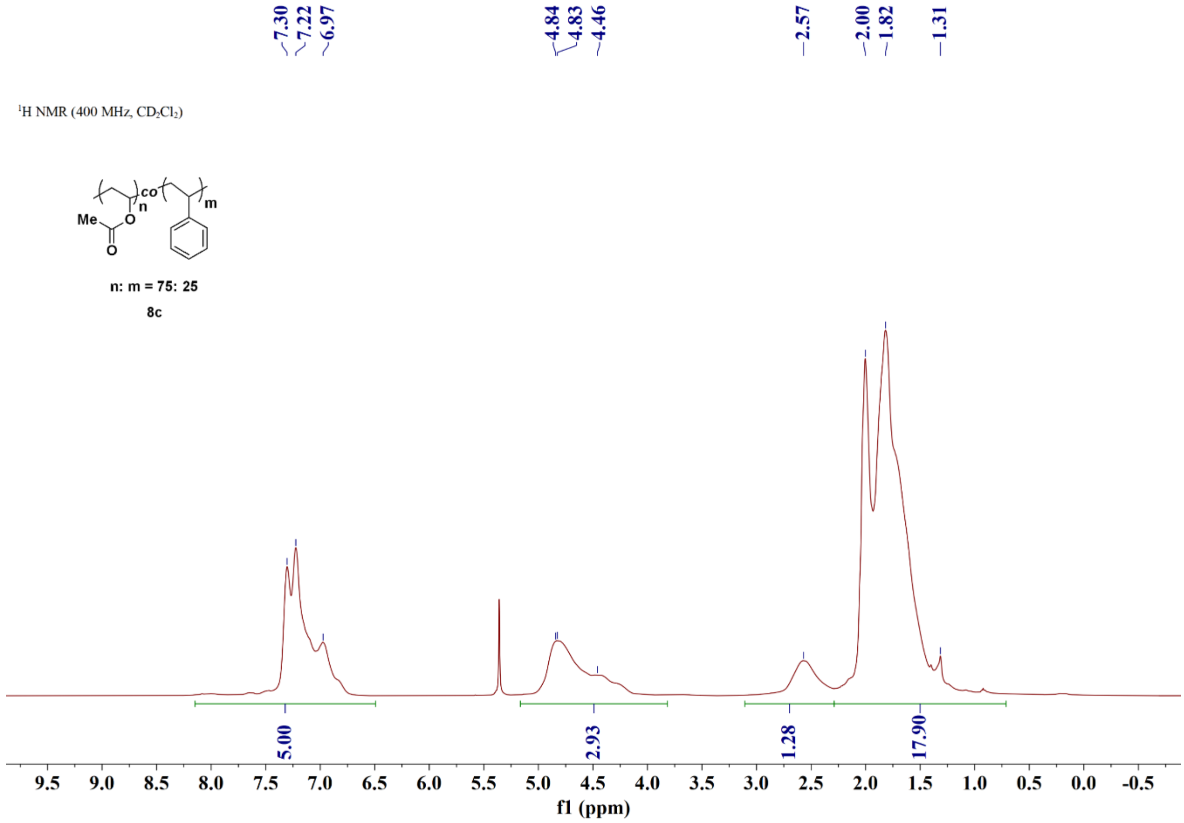


Figure S89. ^{1}H NMR spectrum of PVAc-*co*-PS (75/25) **8c**.

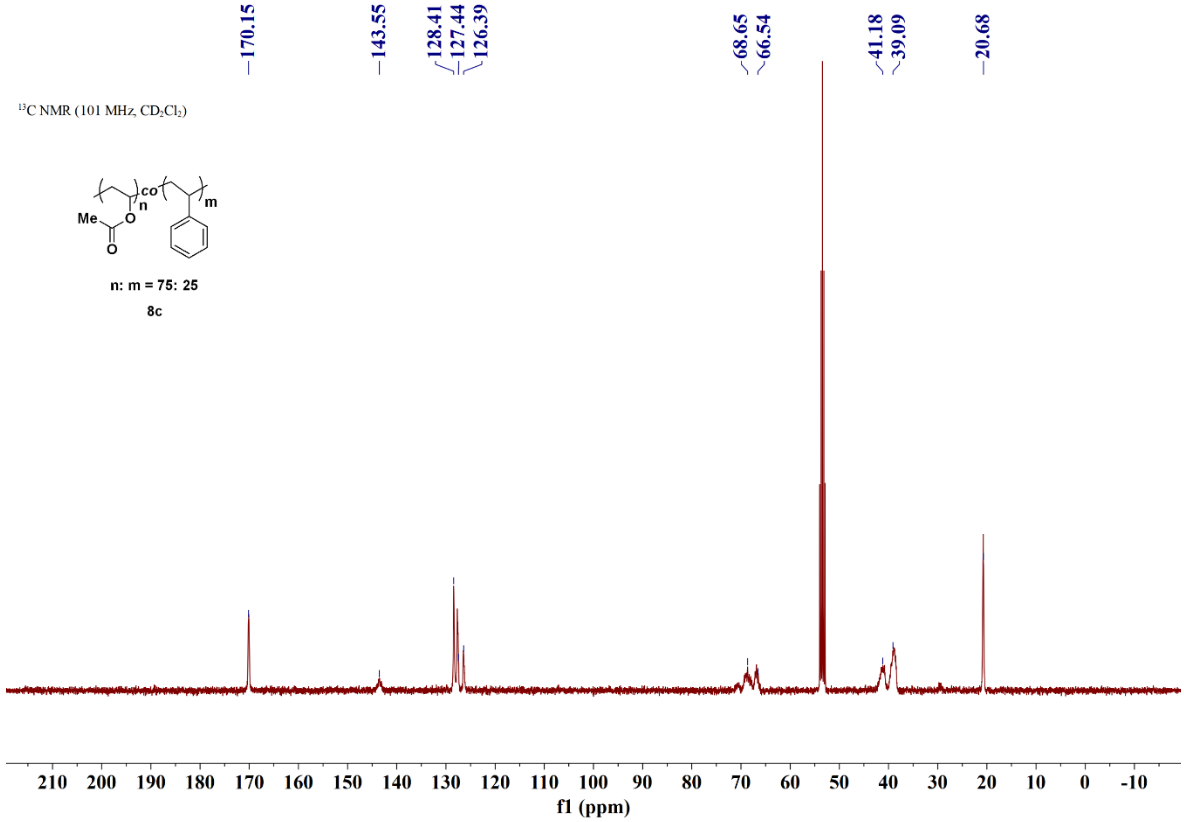


Figure S90. ^{13}C NMR spectrum of PVAc-*co*-PS (75/25) **8c**.

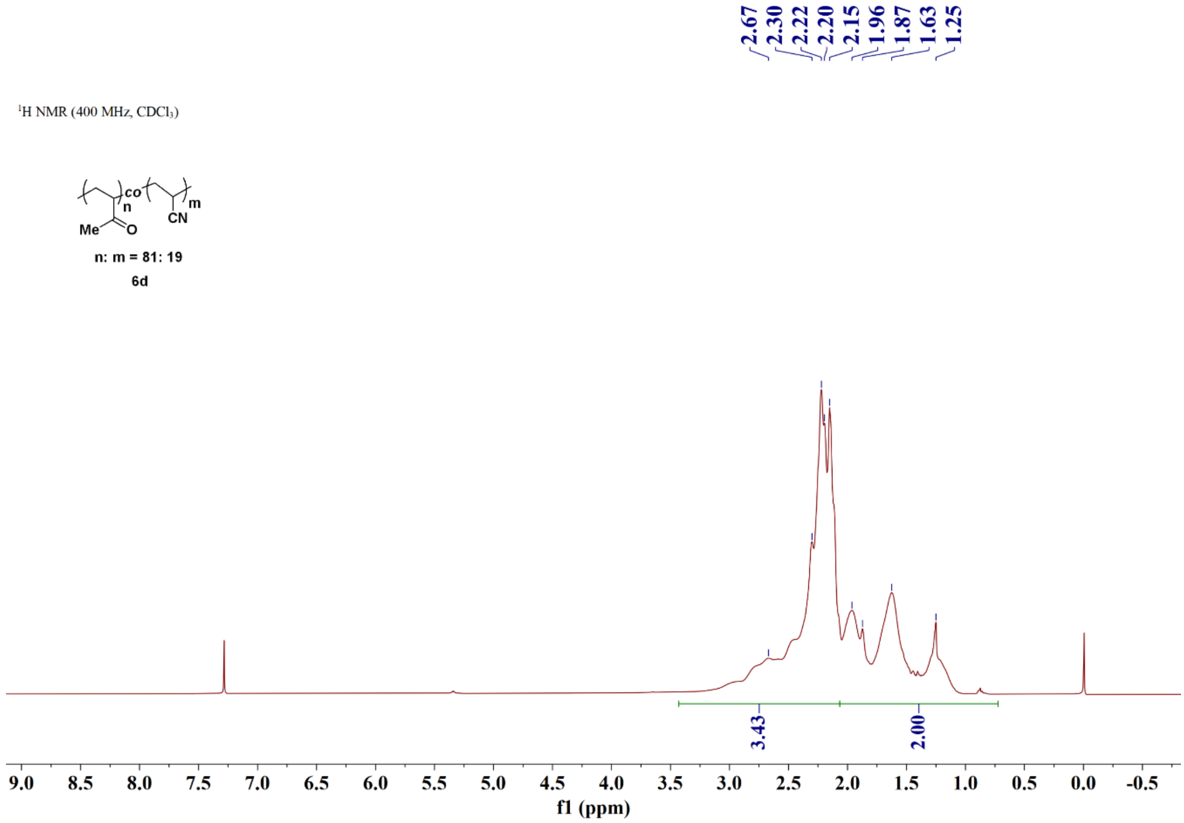


Figure S91. ^{1}H NMR spectrum of PMVK-*co*-PAN (81/19) **6d**.

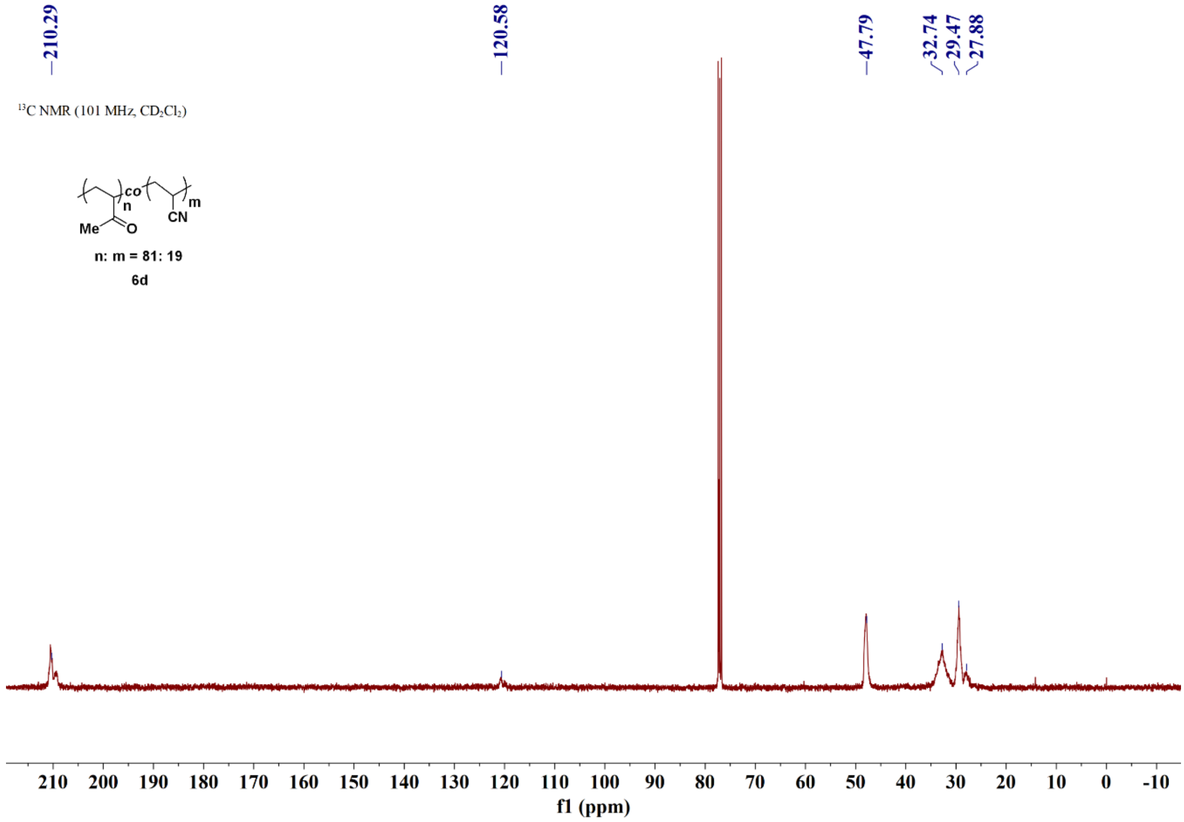


Figure S92. ^{13}C NMR spectrum of PMVK-*co*-PAN (81/19) **6d**.

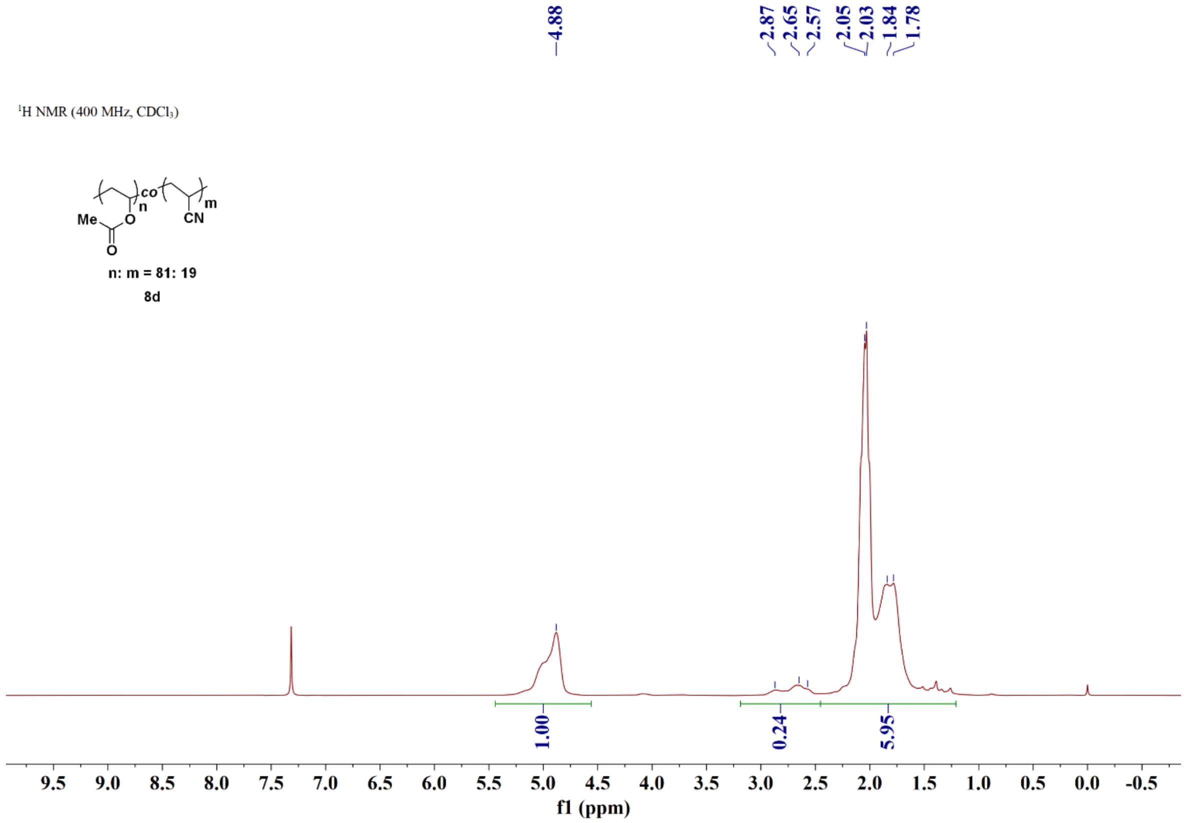


Figure S93. ^{1}H NMR spectrum of PVAc-*co*-PAN (81/19) **8d**.

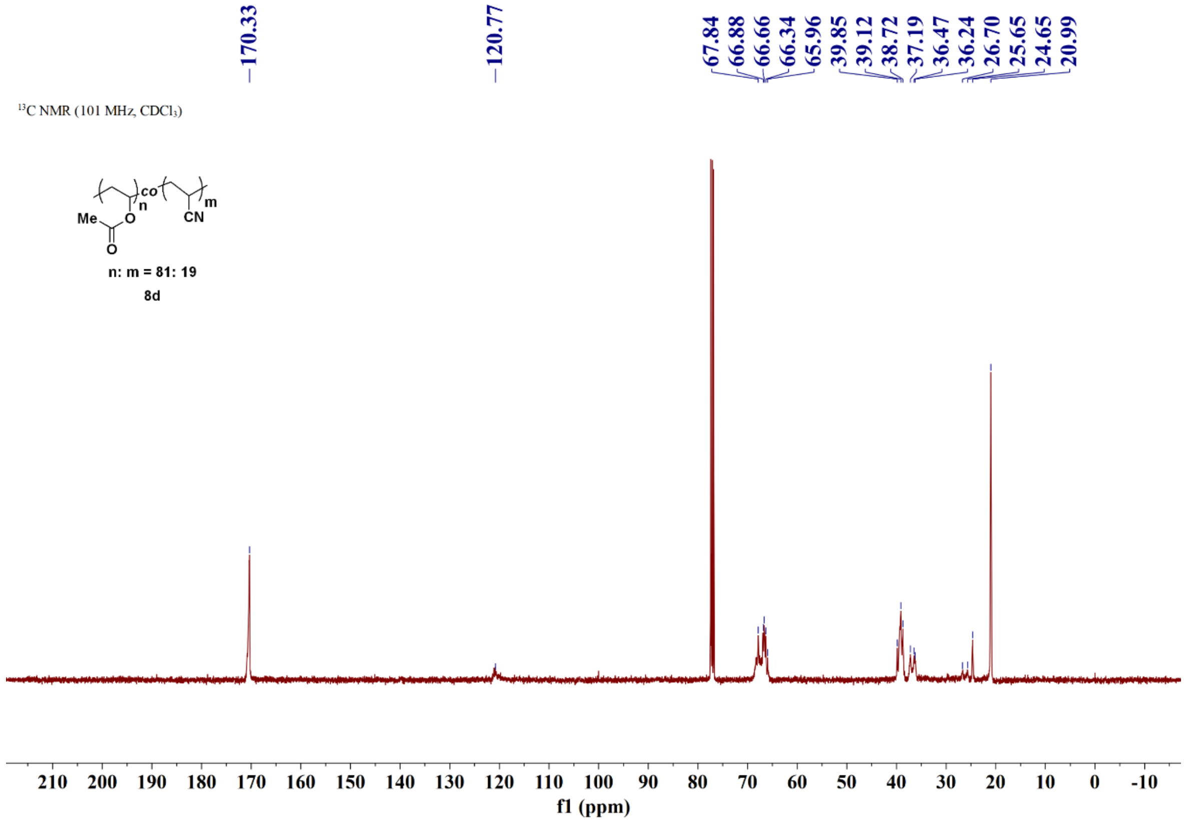


Figure S94. ^{13}C NMR spectrum of PVAc-*co*-PAN (81/19) **8d**.

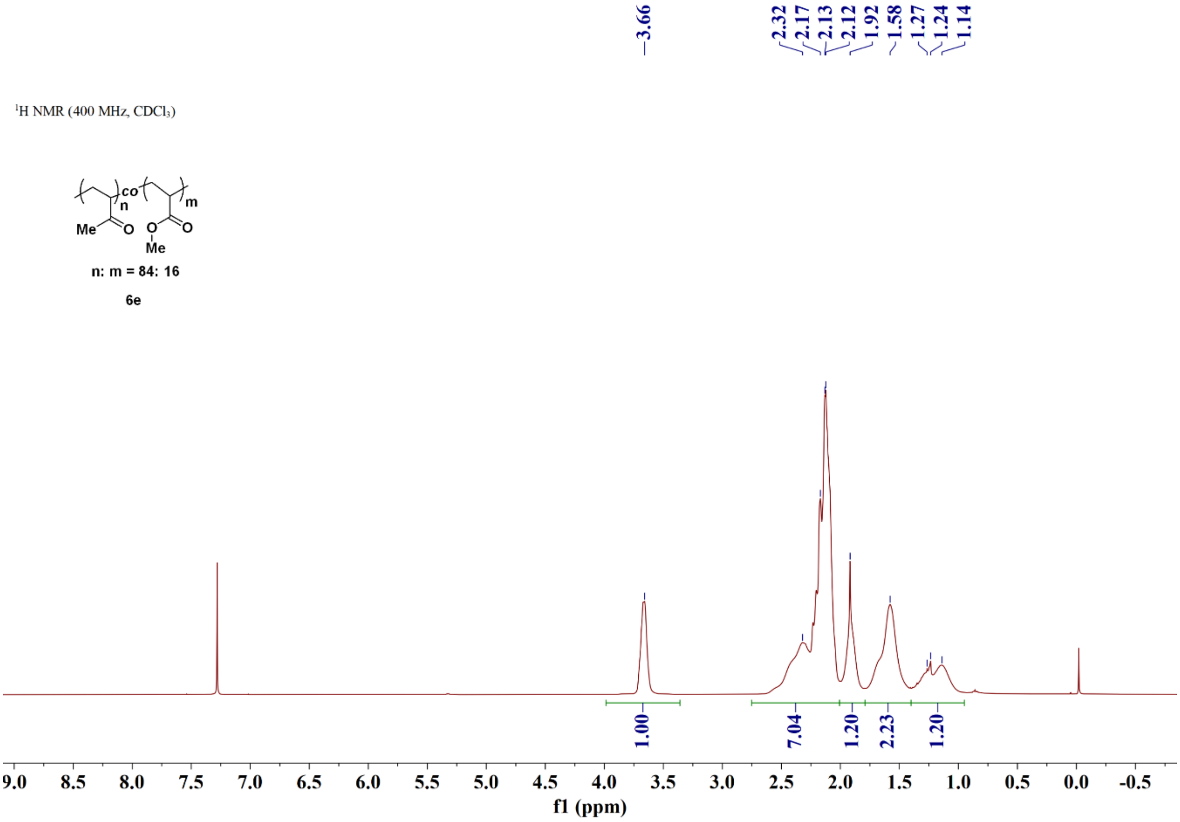


Figure S95. ^{1}H NMR spectrum of PMVK-*co*-PMA (83/17) **6e**.

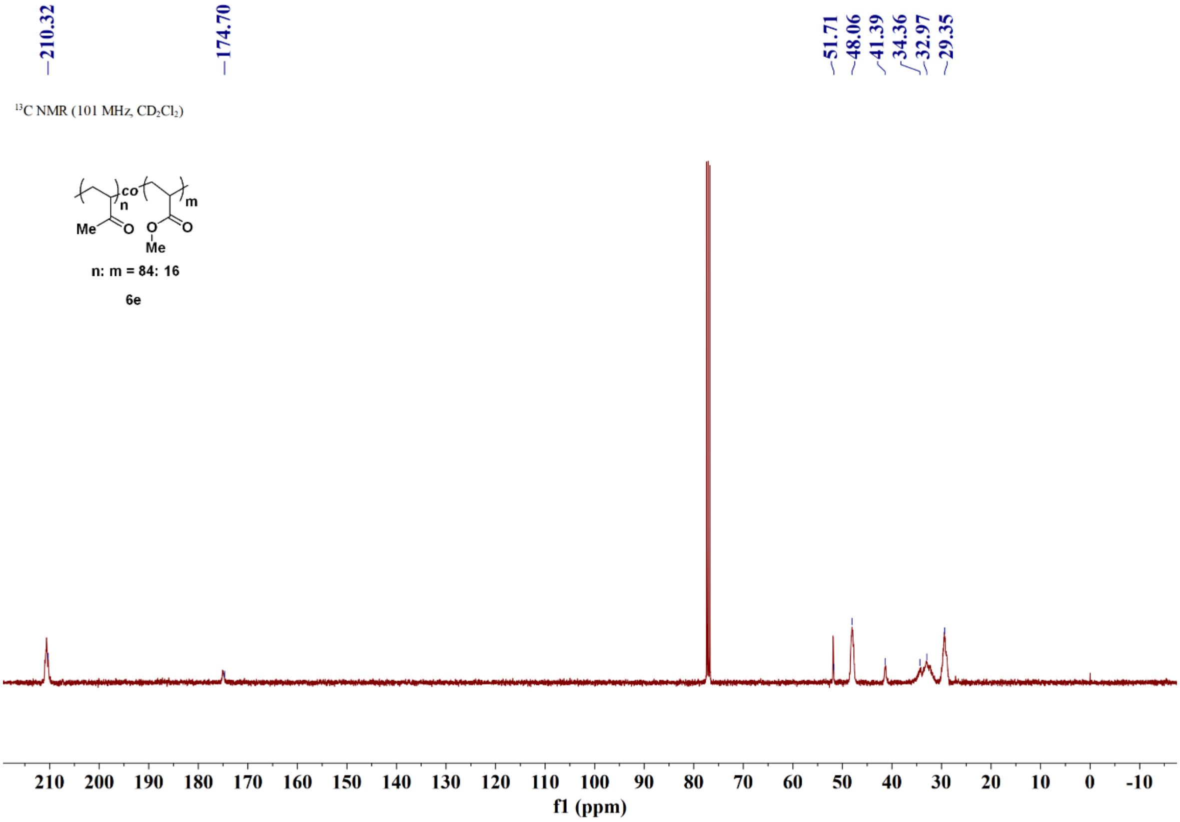


Figure S96. ^{13}C NMR spectrum of PMVK-*co*-PMA (83/17) **6e**.

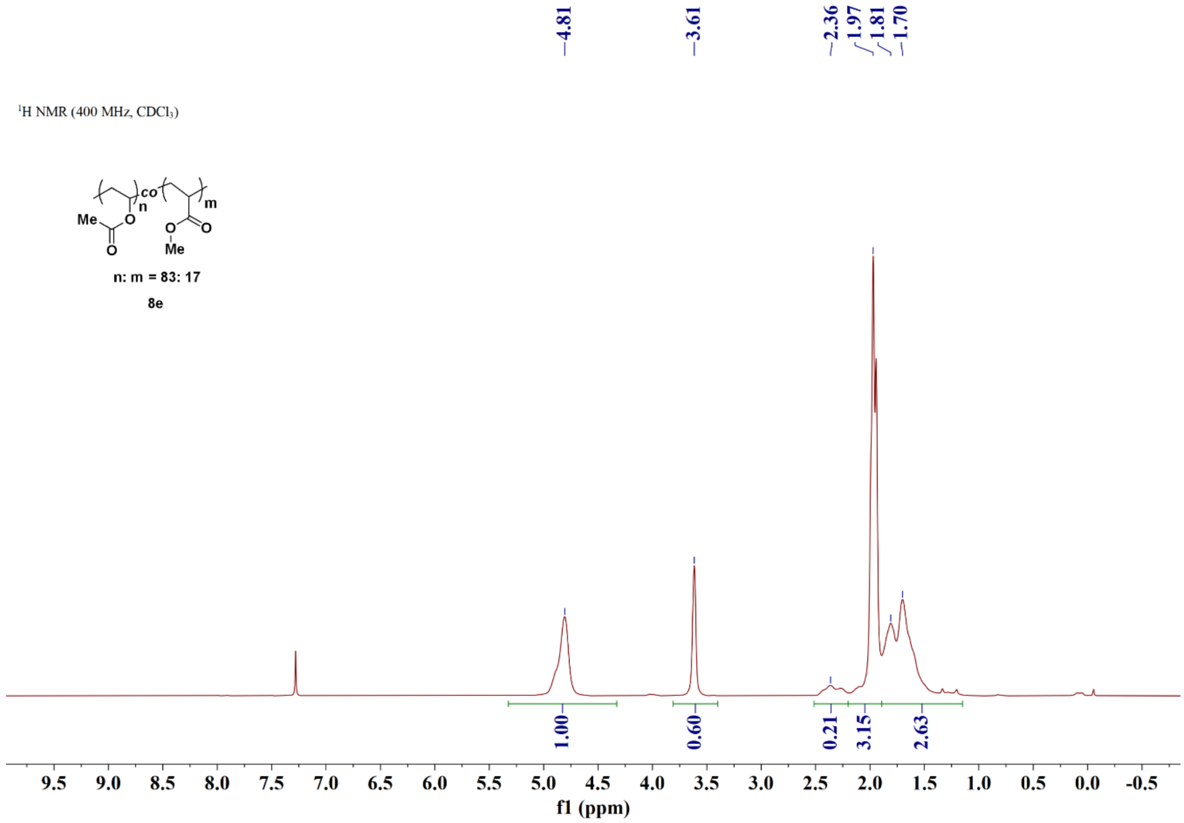


Figure S97. ^{1}H NMR spectrum of PVAc-*co*-PMA (83/17) **8e**.

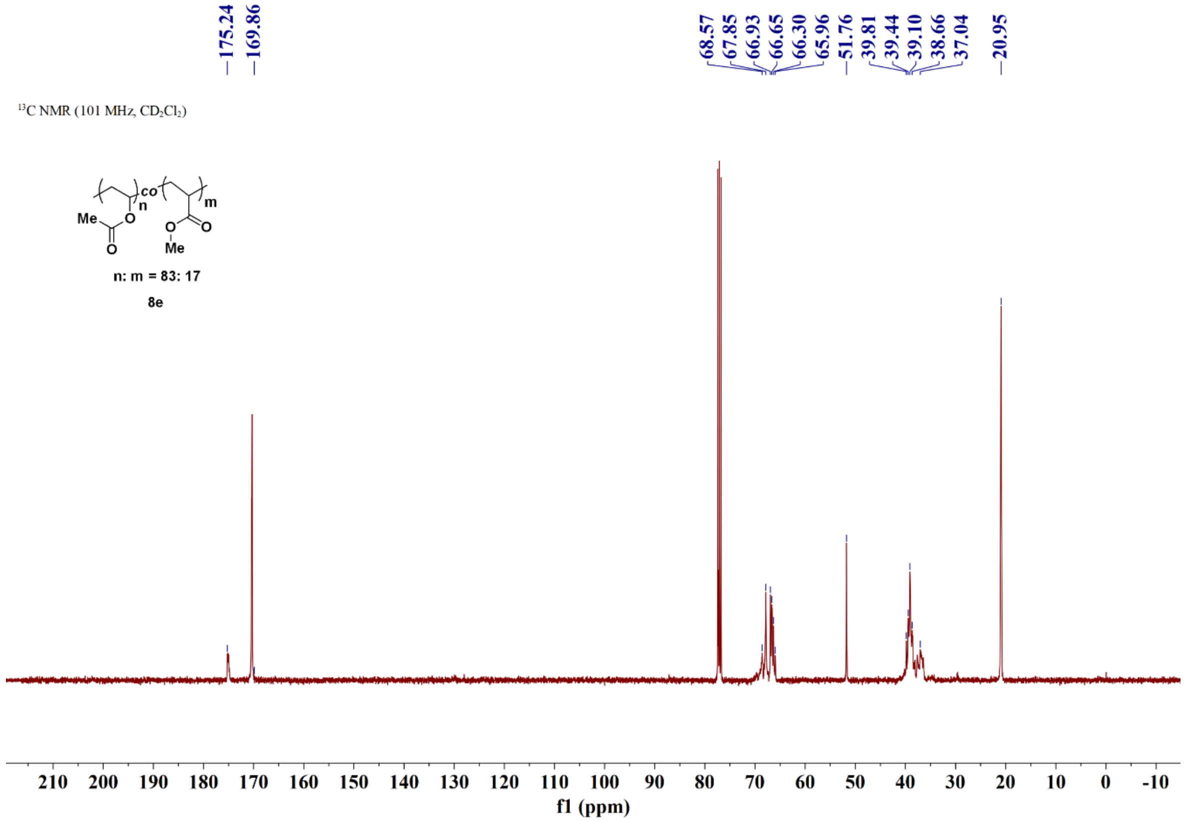


Figure S98. ^{13}C NMR spectrum of PVAc-*co*-PMA (83/17) **8e**.

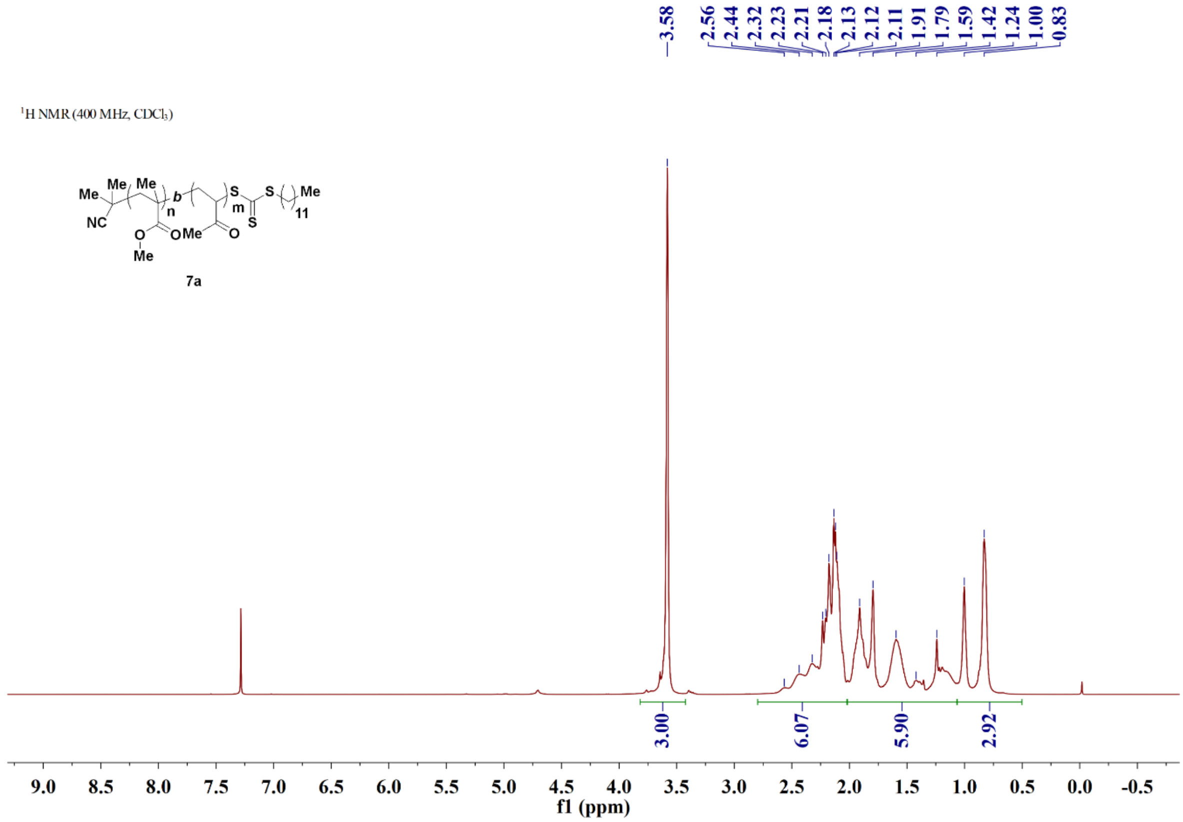


Figure S99. ^{1}H NMR spectrum of PMMA-*b*-PMVK diblock copolymer **7a**.

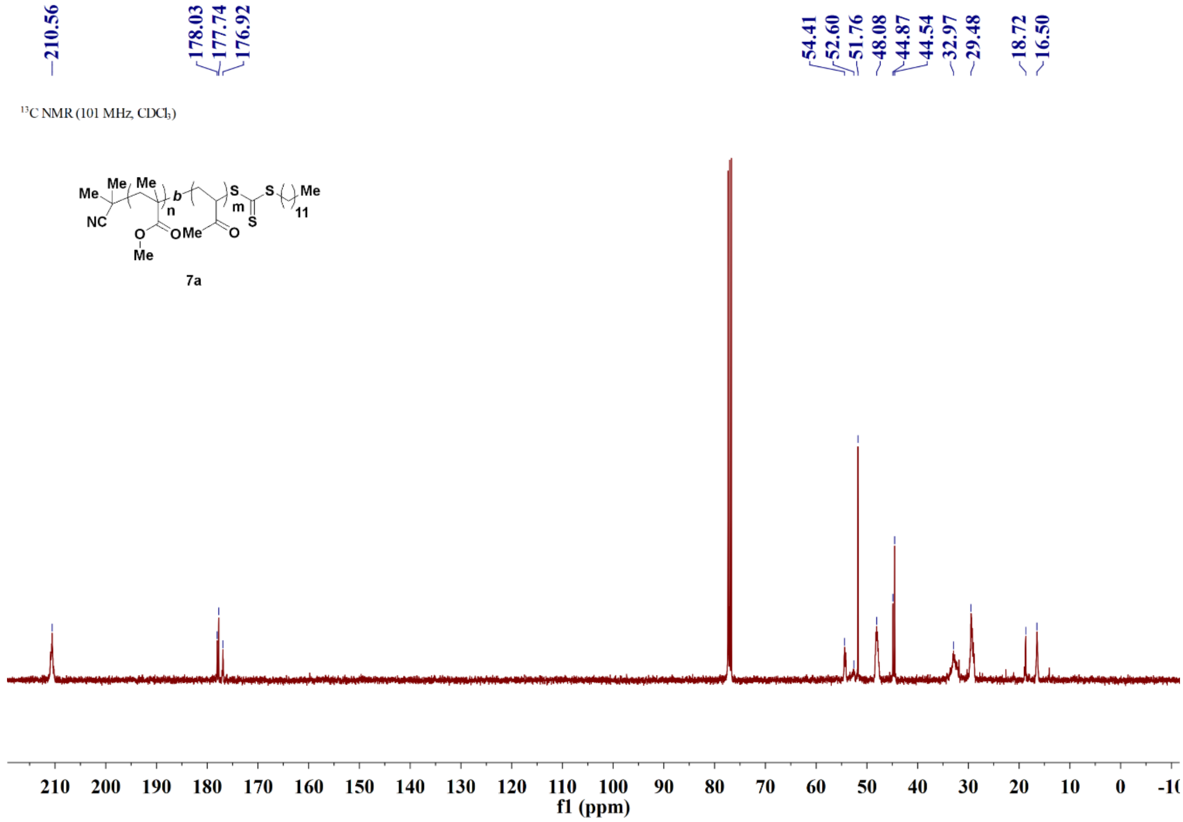


Figure S100. ^{13}C NMR spectrum of PMMA-*b*-PMVK diblock copolymer **7a**.

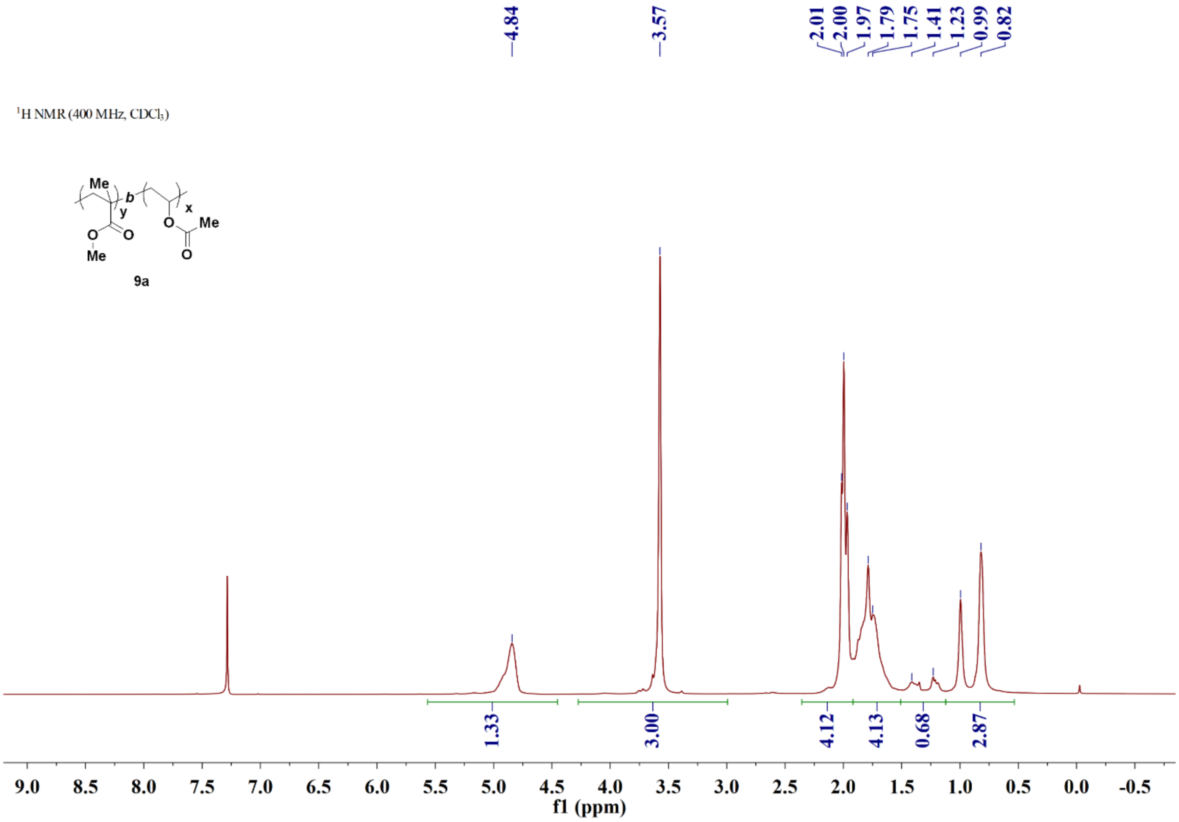


Figure S101. ^{1}H NMR spectrum of PMMA-*b*-PVAc diblock copolymer **9a**.

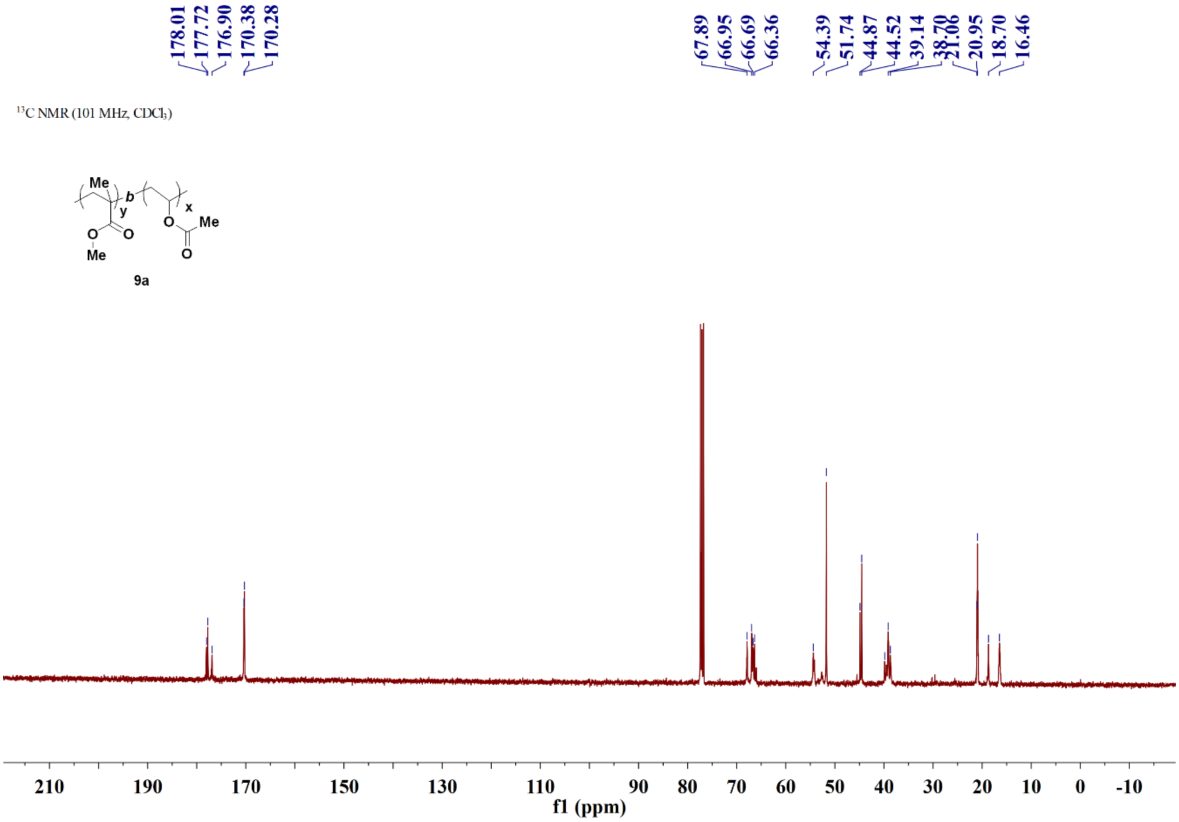


Figure S102. ^{13}C NMR spectrum of PMMA-*b*-PVAc diblock copolymer **9a**.

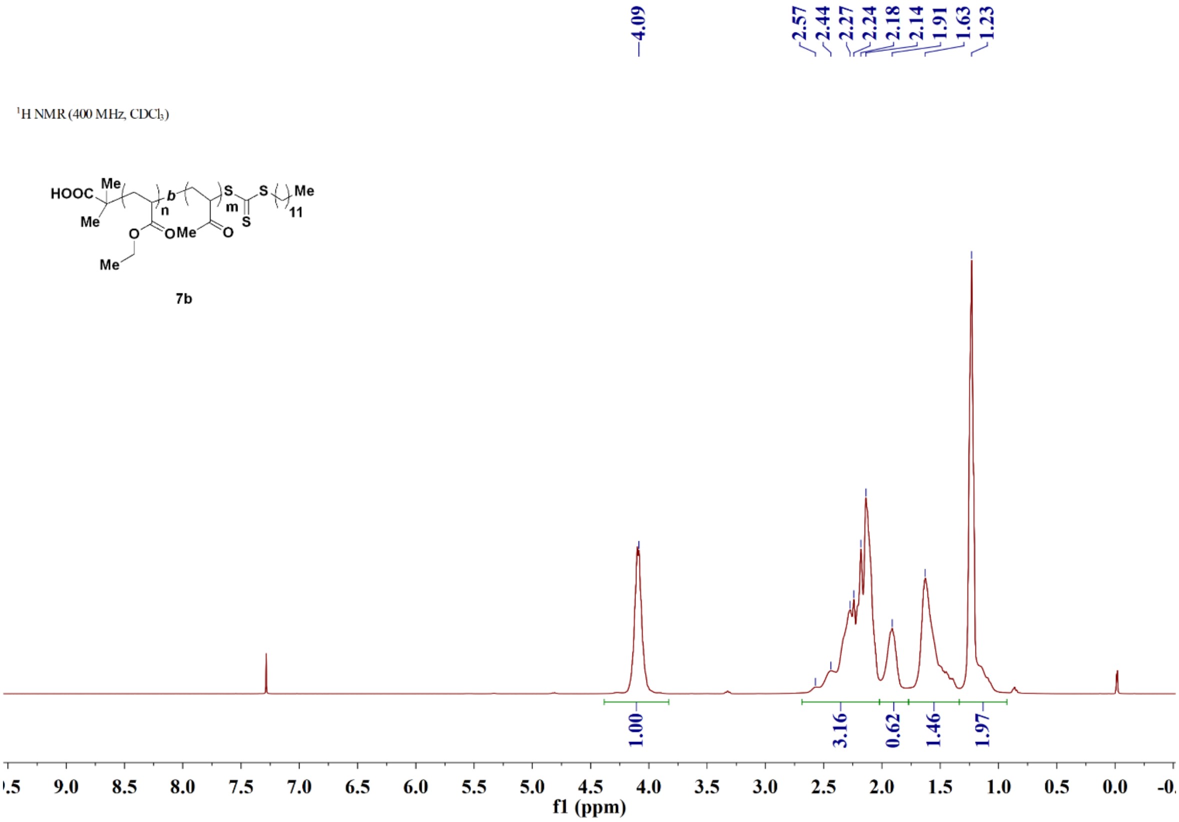


Figure S103. ^{1}H NMR spectrum of PEA-*b*-PMVK diblock copolymer **7b**.

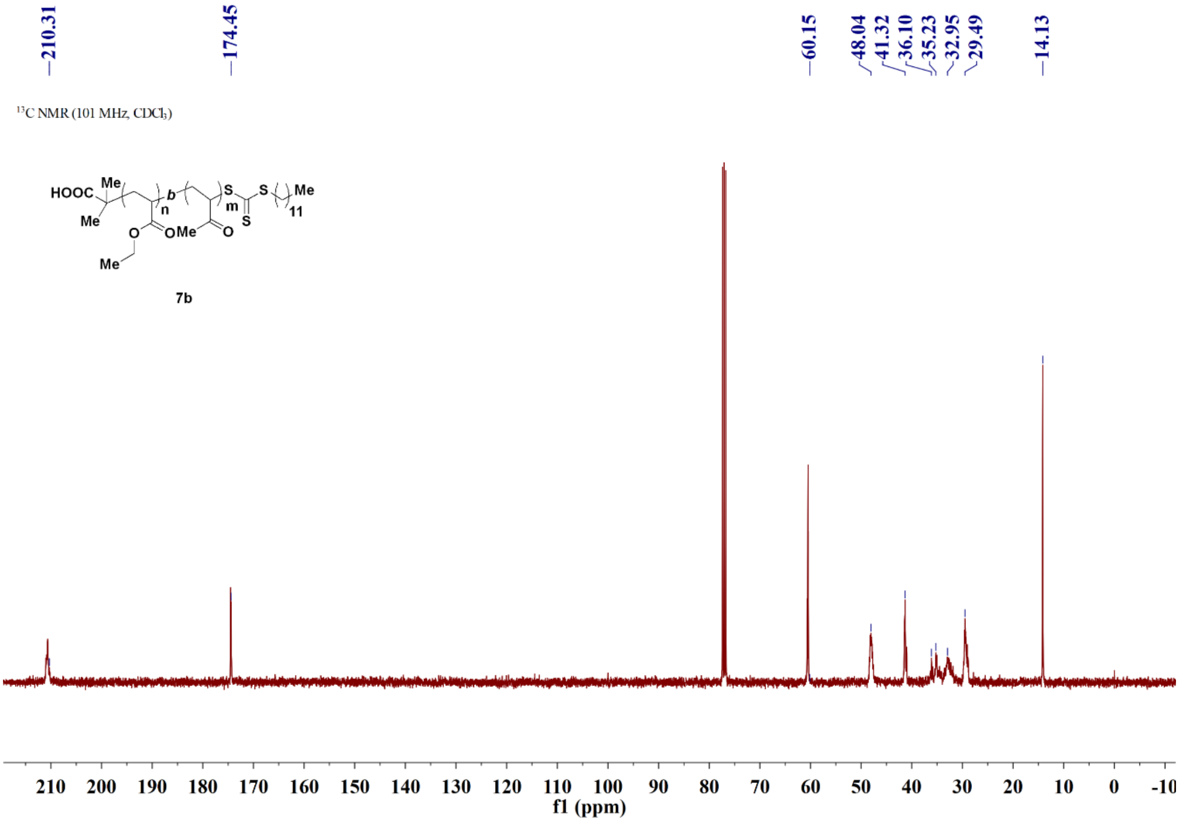


Figure S104. ^{13}C NMR spectrum of PEA-*b*-PMVK diblock copolymer **7b**.

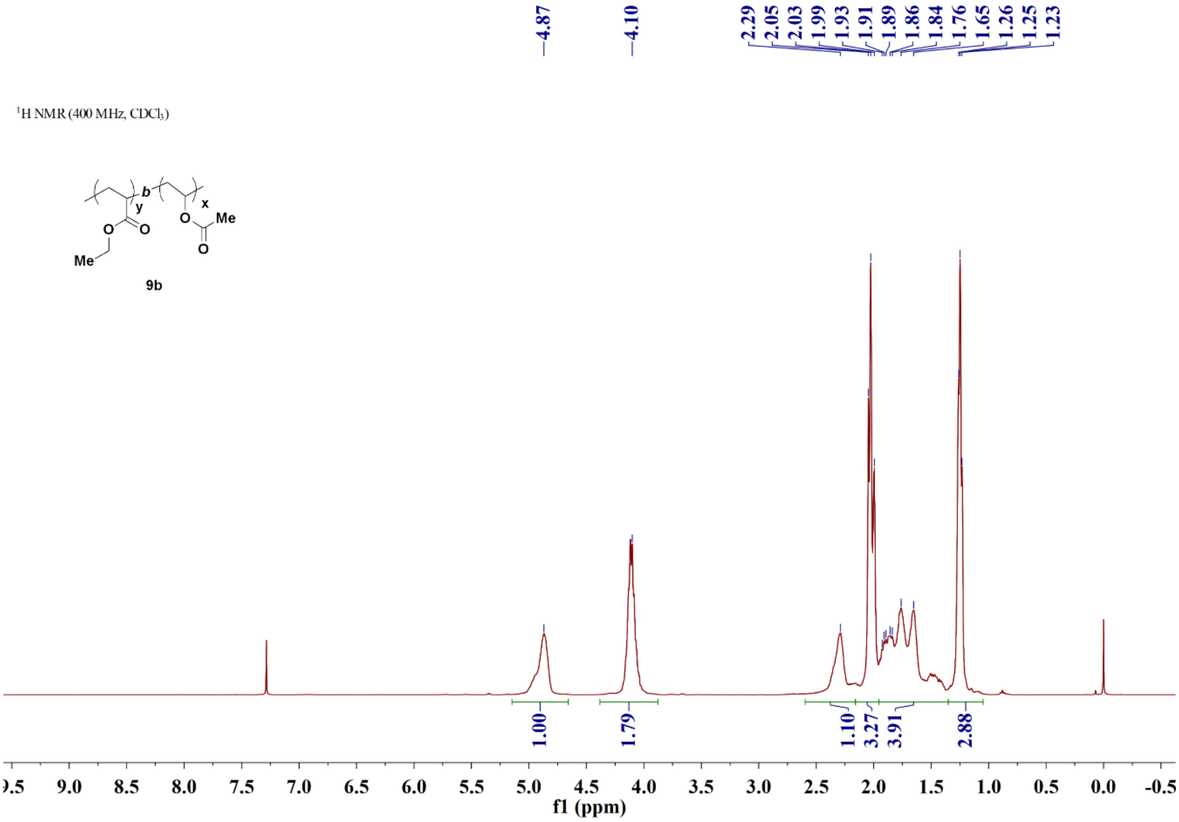


Figure S105. ^{1}H NMR spectrum of PEA-*b*-PVAc diblock copolymer **9b**.

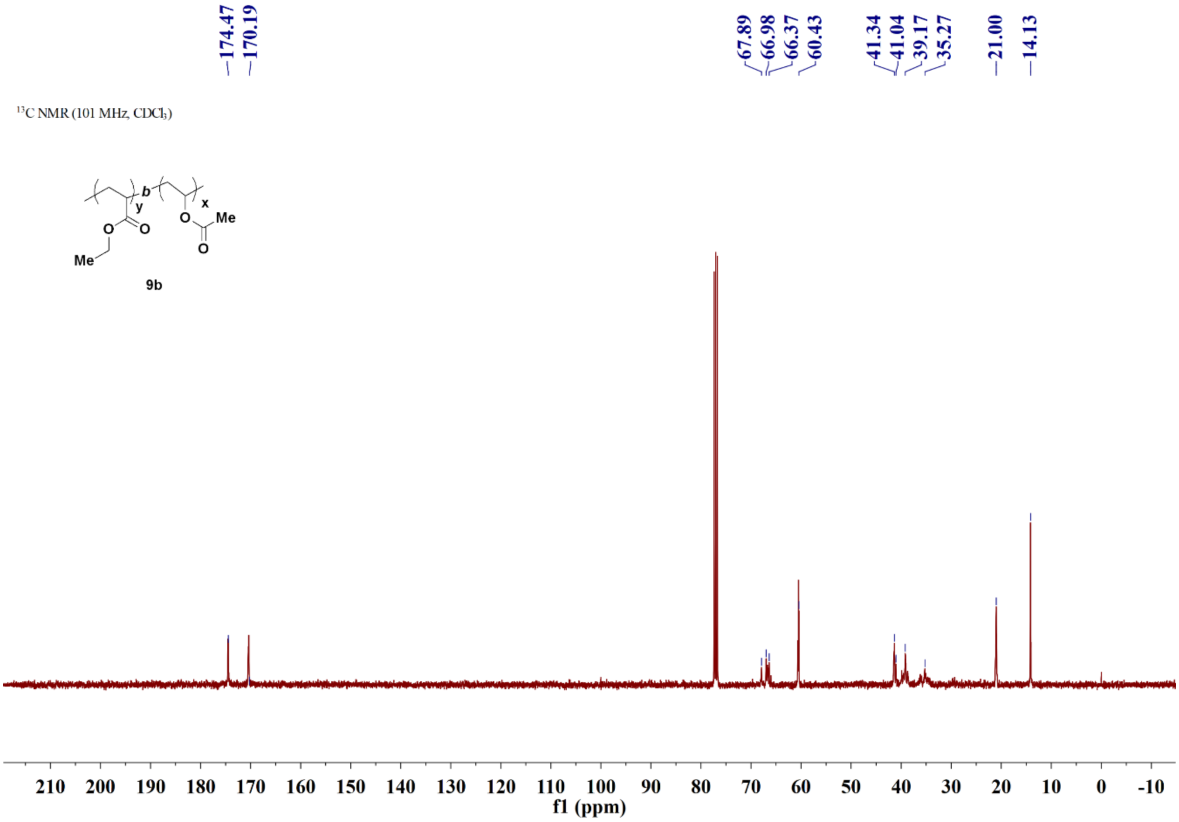


Figure S106. ^{13}C NMR spectrum of PEA-*b*-PVAc diblock copolymer **9b**.

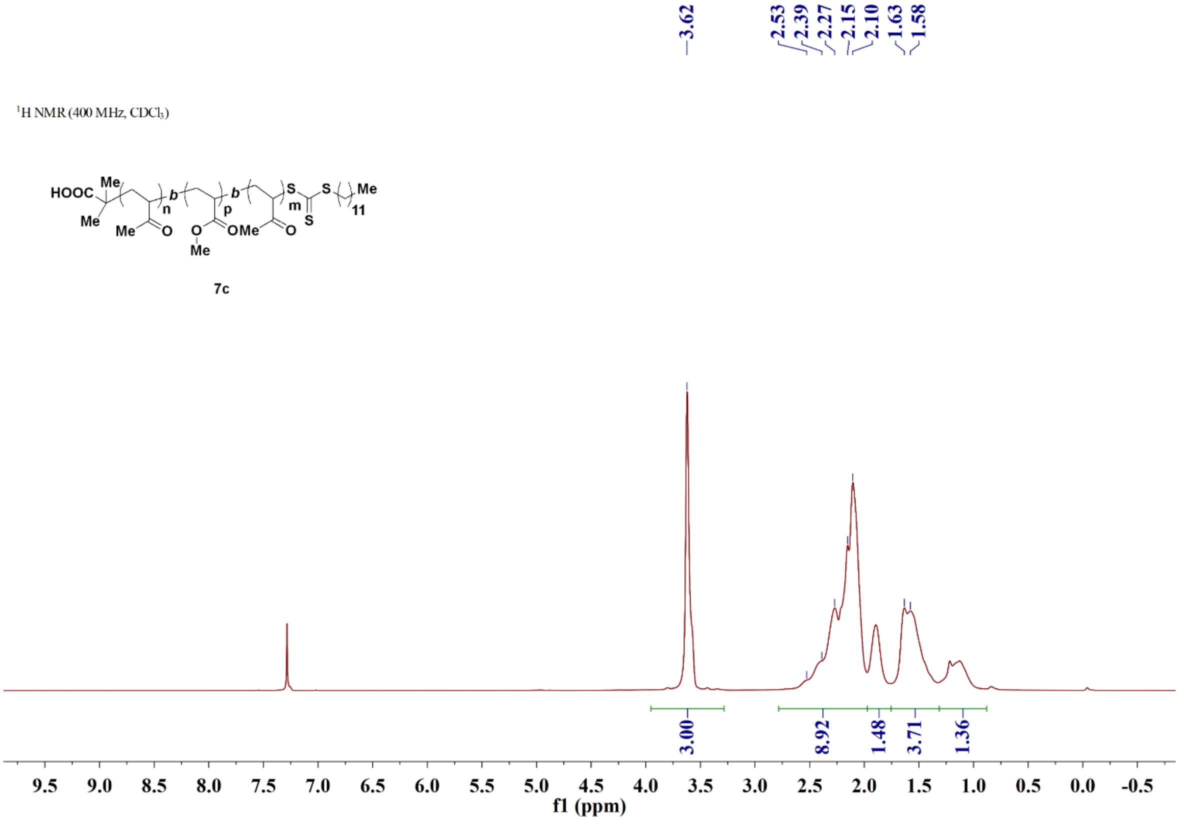


Figure S107. ^{1}H NMR spectrum of PMVK-*b*-PMA-*b*-PMVK triblock copolymer **7c**.

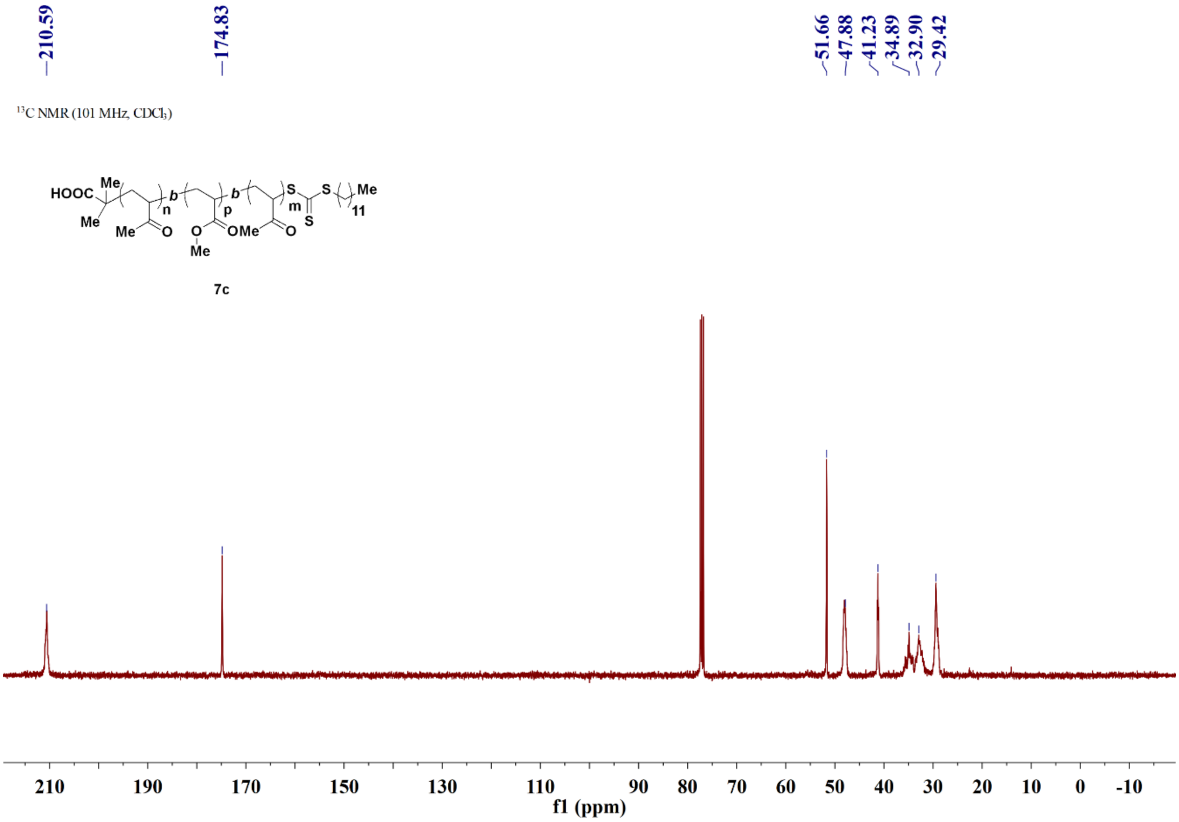


Figure S108. ^{13}C NMR spectrum of PMVK-*b*-PMA-*b*-PMVK triblock copolymer **7c**.

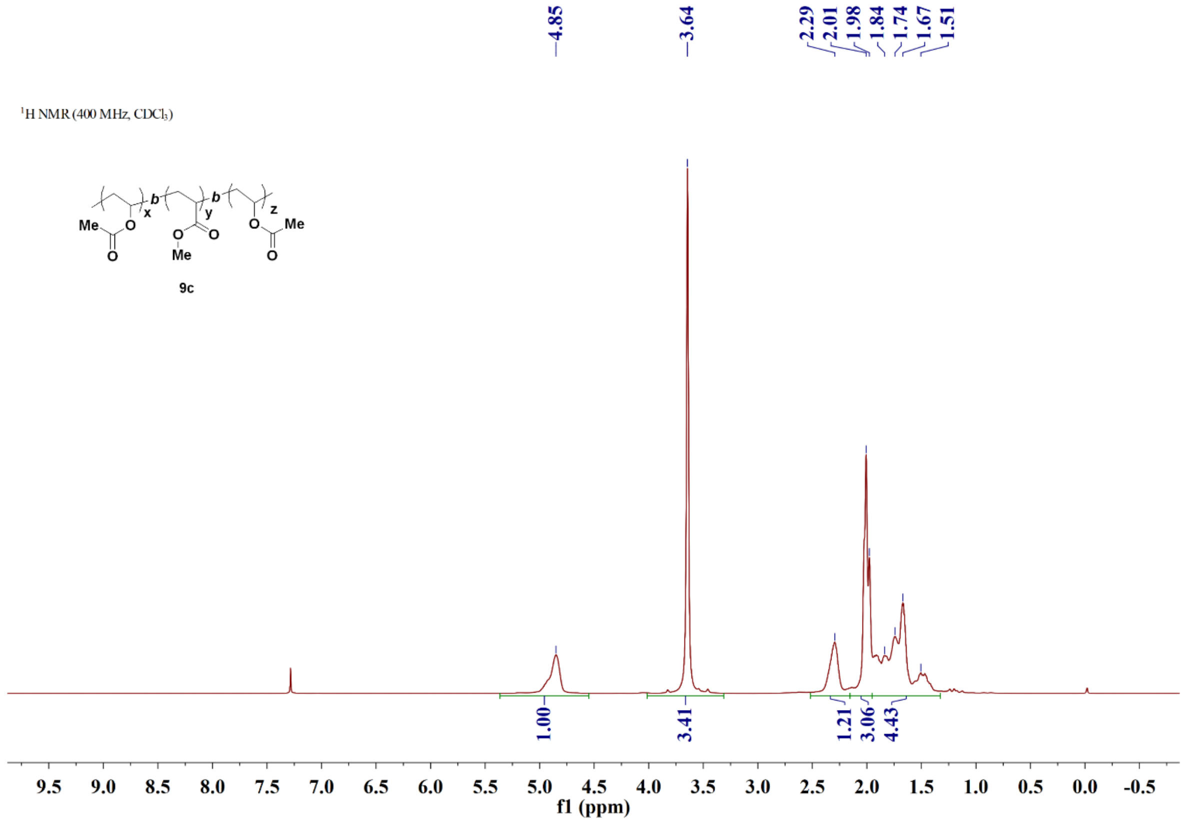


Figure S109. ^{1}H NMR spectrum of PVAc-*b*-PMA-*b*-PVAc triblock copolymer **9c**.

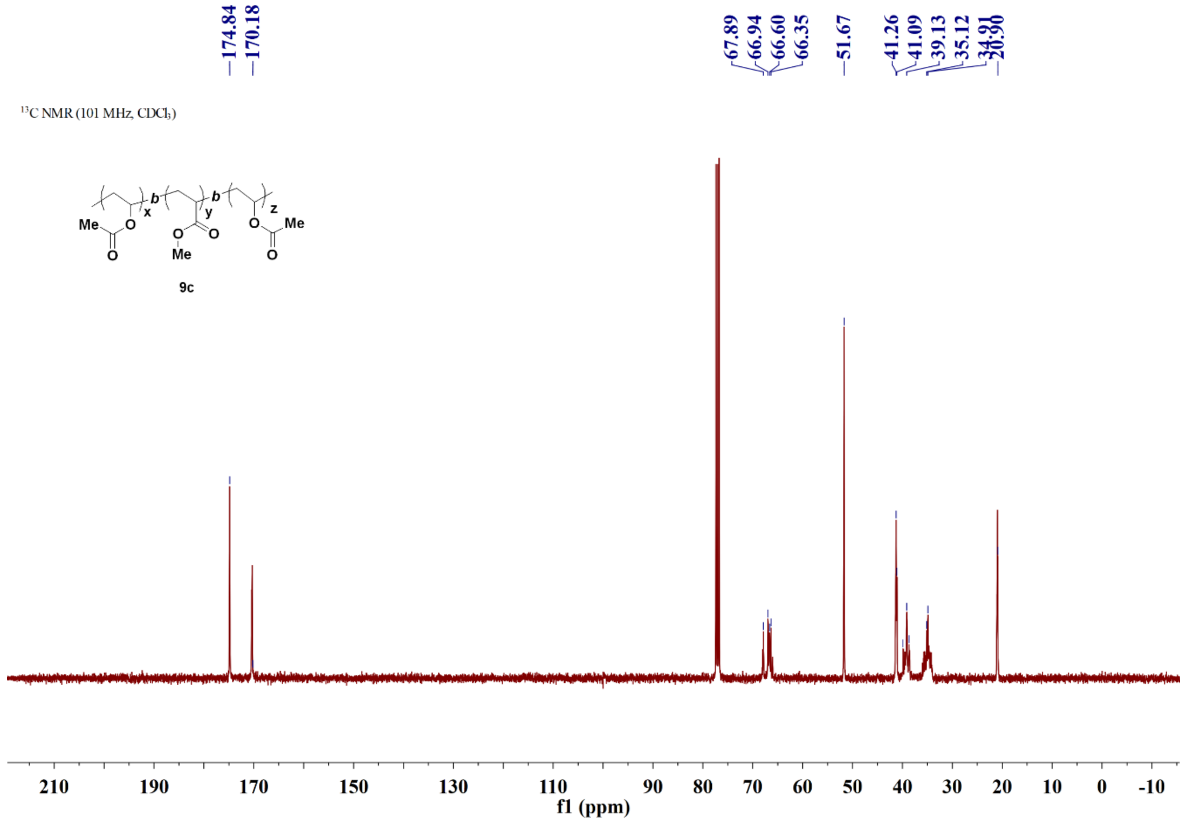


Figure S110. ^{13}C NMR spectrum of PVAc-*b*-PMA-*b*-PVAc triblock copolymer **9c**.

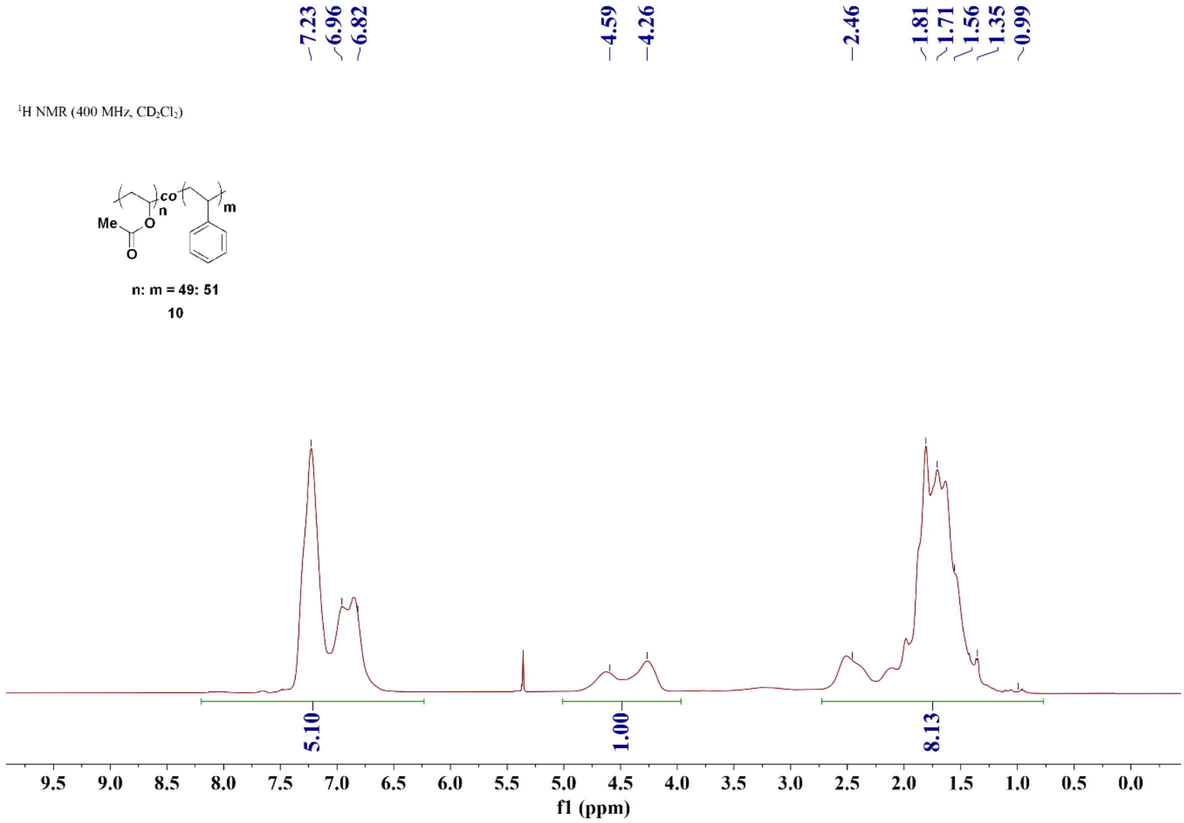


Figure S111. ^{1}H NMR spectrum of PVAc-*co*-PS (49/51) **10**.

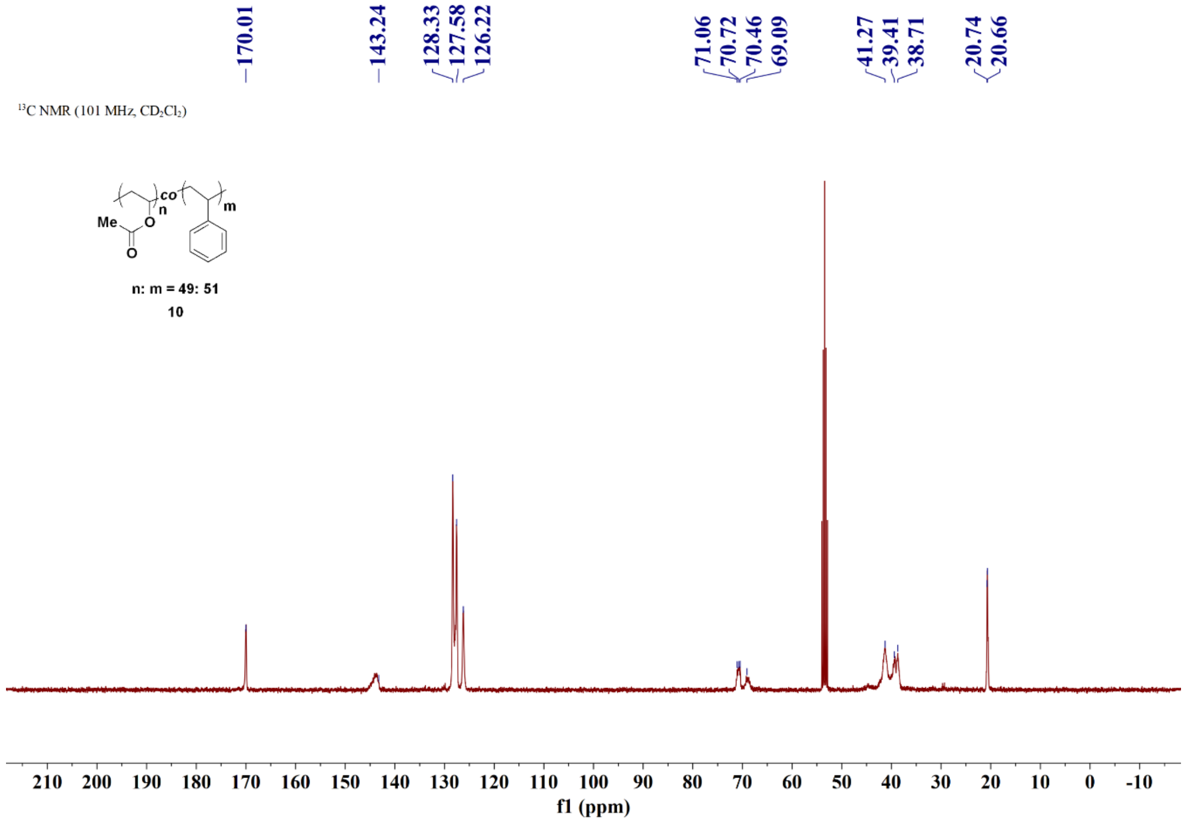


Figure S112. ^{13}C NMR spectrum of PVAc-*co*-PS (49/51) **10**.