SUPPLEMENTARY INFORMATION

A NEW APPROACH FOR MODULAR POLYMER-POLYMER CONJUGATIONS *VIA* HECK COUPLING

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KEYWORDS : Heck reaction, cross-coupling, polymer-polymer conjugation, block copolymer, ADMET

Materials

Chloroform, dichloromethane and triethylamine were distilled over CaH_2. ε-Caprolactone (ε-CL) was distilled from CaH_2 and stored over molecular sieve in a glove box. Dioxane was destilled over sodium lumps. Benzoic acid (99.5 %, Sigma Aldrich), 10-undecen-1-ol (98 %, Aldrich), hexyl acrylate (99 %, Aldrich), lauryl acrylate (90%, Sigma-Aldrich) N,N'-dicyclohexylcarbodiimide (DCC, 99%, Acros), 4-(dimethylamino)pyridine (DMAP, 99% Acros), succinic anhydride (≥99%, Sigma-Aldrich), $Pd(OAc)_2$, tetrabutylammonium-chloride (TBA-Cl, 95%, Acros), 2-bromoethanol (95 %, Sigma-Aldrich,), 4-iodophenol (99 %, Sigma-Aldrich), toluene (extra dry, water < 30 ppm, Acros Organics), poly(ethylene glycol) methyl ether (M_n=1000 g×mol^{-1}, 2000 g×mol^{-1}, 5000 g×mol^{-1}, Sigma-Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 99 %, Sigma Aldrich), acryloyl chloride (97 %, Sigma-Aldrich), ethyl vinyl ether (99 %, Sigma-Aldrich) were used as received. 2-(4-Iodophenoxy) ethanol[1] and monomer **3**[2] were synthesized according to published procedures.

Characterization

^{1}H-NMR measurements were performed on a Bruker Advance spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. All samples were dissolved in $CDCl_3$ and the chemical shifts δ are reported in ppm relative to TMS.

Determination of molecular weights was performed on two SEC Systems

System A: A Polymer Laboratories PL-SEC 50 Plus system having an auto injector, a guard column (PLgel Mixed C, 50×7.5 mm) followed by three linear columns (PLgel Mixed C, 300×7.5 mm, 5 µm bead-size) and a differential refractive index detector, operating in THF at 40°C, with a flow rate of 1 mL×min^{-1}. The GPC system was calibrated with poly(methyl methacrylate) standards (Polymer Standards Service (PSS), Mainz, Germany) ranging from 700 to 2×10^6 Da (The molecular weight distributions were determined relative to PMMA .[3]

System B: A Shimadzu SEC System LC-20 A equipped with a SIL-20A auto sampler, PLgel 5 mm MIXED-D column and a RID-10A refractive index detector in THF (flow rate 1 mL×min^{-1}) at 50 °C. The molecular weight distributions were determined relative to PMMA standards (Polymer Standards Service, M_p 1100–981000 Da).

FAB (Fast-Atom-Bombardement)-mass spectra and high resolution mass spectra (HRMS) FAB were measured on a Finnigan MAT 95.

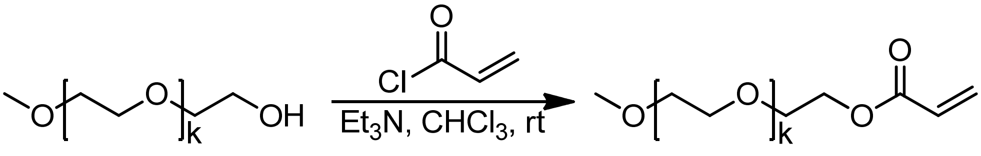
SEC/ESI-MS spectra were recorded on a LXQ mass spectrometer (Thermo Fisher Scientific, San Jose, CA) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode. The instrument was calibrated in the m/z range 195-1822 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA), and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 4.5 kV, a dimensionless sweep gas flow rate of 2, and a dimensionless sheath gas flow rate of 12 were applied. The capillary voltage, the tube lens offset voltage, and the capillary temperature was set to 60 V, 110 V, and 275°C, respectively. The LXQ was coupled to a Series 1200 HPLC-system (Agilent, Santa Clara, CA) consisting of a solvent degasser (G1322A), a binary pump (G1312A), and a high-performance autosampler (G1367B), followed by a thermostated column compartment (G1316A). Separation was performed on two mixed bed size exclusion chromatography columns (Polymer Laboratories, Mesopore 2504.6 mm, particle diameter 3 µm) with precolumn (Mesopore 50-4.6 mm) operating at 30°C. THF at a flow rate of 0.30 mL min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to an RI-detector (G1362A with SS420x A/D) in a setup described previously, 0.27 mL×min^{-1} of the eluent was directed through the RI detector, and 30 µL×min^{-1} was infused into the electrospray source after post column addition of a 100 µM solution of sodium iodide in methanol at 20 µL×min^{-1} by a micro flow HPLC syringe pump (Teledyne ISCO, Model 100DM). 20 µL of a polymer solution with a concentration of ~3 mg×mL^{-1} was injected onto the HPLC system. (This description is similar to a recent publication and was taken from there).[3]

Differential scanning calorimetry (DSC) experiments were carried out on a DSC821e (Mettler Toledo) calorimeter, under nitrogen atmosphere, at a heating rate of 10 °C x min-1 up to a temperature of 150 °C, and using a sample mass of approximately 5 mg. Data from

second heating scans are reported. The melting temperature, *Tm*, is recorded as the minimum (endothermic transitions are represented downwards) of the endothermic melting peak.
Atomic absorption spectroscopy (AAS) was measured on a HITACHI Z-6100 instrument. For isolation of palladium residues, the polymers were dissolved in a small amount of THF followed by acid digestion.

Experimental Part

Synthesis of PEG-Acrylate (P1-3)

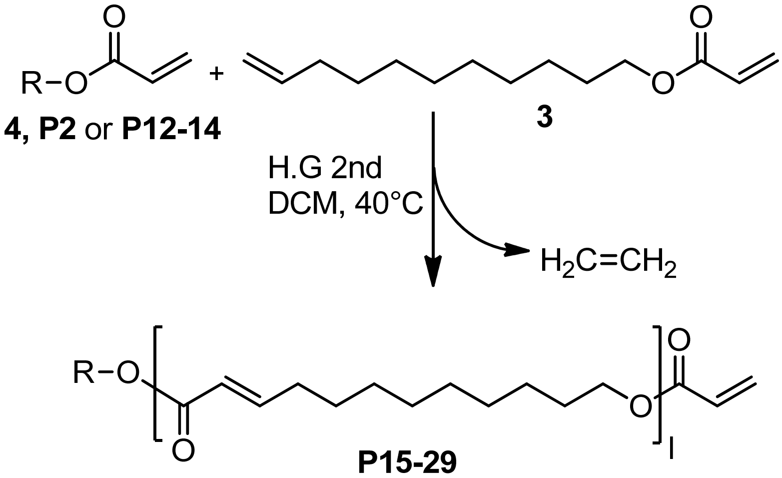


P1-3

Poly(ethylene glycol) methyl ether acrylate (1.0 eq.) was weighed in a round bottom flask and set under argon atmosphere. Then, $CHCl_3$ (final concentration 3×10^{-4} mol L^{-1}) was added and the reaction mixture was stirred for 5 minutes. Subsequently, acryloyl chloride (2.0 eq.) and after further 5 minutes Et_3N (2.5 eq.) was added. The mixture was stirred for about 16h at room temperature. The solvent was then removed under reduced pressure and the residue was quickly filtered through a short column (silica gel, ethyl acetate) to remove the ammonium salts. After concentration of the solution the polymers were then precipitated into cold diethyl ether.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ / ppm: 6.42 (dd, *J* = 17.4, 1.5 Hz, 1H, -CH=C*H*$_2$), 6.14 (dd, *J* = 17.4, 10.3 Hz, 1H, -C*H*=CH$_2$), 5.83 (dd, *J* = 10.3, 1.5 Hz, 1H, -CH=C*H*$_2$), 4.32-4.29 (m, 2H, -O-CH$_2$-C*H*$_2$-OCO-), 3.75-3.71 (m, 2H, -O-C*H*$_2$-CH$_2$-OCO-), 3.67-3.59 (m, PEG backbone), 3.36 (s, 3H, -OCH$_3$).

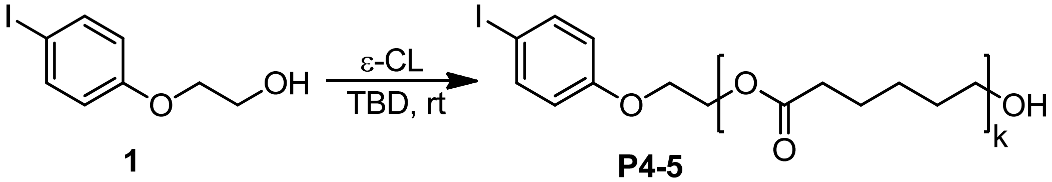
General procedure for ADMET polymerisations



P15-29

Monomer **3** and the selected chain-stopper **(4, P2, P12-14)** were weighed in a supelco conical vial. Then, DCM (final concentration 1.23×10^{-7} mol L^{-1}) was added and the vial was closed with a screw cap comprising a rubber septa. After 5 minutes at a temperature of 40°C, the required amount of ruthenium-catalyst (Hoveyda-Grubbs 2nd generation) (1.0 mol % to **3**) in DCM (150 µL) was added and a needle was inserted in the rubber septa. After 24h the reaction was quenched by adding ethyl-vinyl ether (9 eq. to catalyst) and THF (ca. 2 mL) to the cooled reaction mixture. The ADMET polymers were isolated by precipitation into cold pentane. The molecular weights were determined by SEC analysis (Table 2, Table S1).

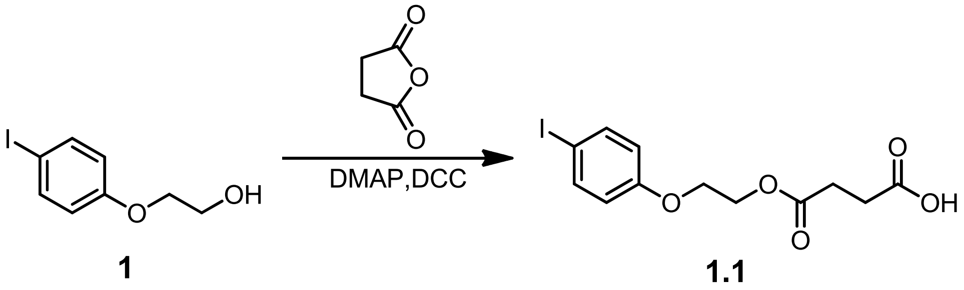
Synthesis of aryliodide functional poly(ε-caprolactone) (P4-5)



To 2-(4-iodophenoxy) ethanol (0.185 g, 0.710 mmol) in toluene (4 mL), TBD (6.10 mg, 4.38·10-2 mmol) and ε-CL (1.00 g, 8.77 mmol) was added. The reaction mixture was stirred for 1h 50 min at 25°C and quenched by addition of benzoic acid (31 mg, 0.253 mmol). The reaction was performed in a glove box under argon atmosphere. The polymer was obtained by precipitation into cold hexane:diethyl ether (1:1).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ / ppm: 7.57-7.52 (m, 2H, Ar), 6.70-6.65 (m, 2H, Ar), 4.42-4.38 (m, 2H, Ar-O-CH_2-C*H*$_2$-OCO-), 4.13-4.10 (m, 2H, Ar-O-C*H*$_2$-CH_2-OCO-), 4.04 (t, *J* = 6.5 Hz, -CH_2-OC(O)-), 3.63 (t, *J* = 6.3 Hz, 2H, -C*H*$_2$-OH), 2.35 (t, *J* = 7.4 Hz, 2H, Ar-O-CH_2-CH_2-OC(O)-C*H*$_2$-), 2.29 (t, *J* = 7.5 Hz, -OC(O)-CH_2-), 1.69-1.55 (m, CH_2), 1.41-1.31 (m, CH_2).

Synthesis 4-(2-(4-iodophenoxy)ethoxy)-4-oxobutanoic acid (1.1)

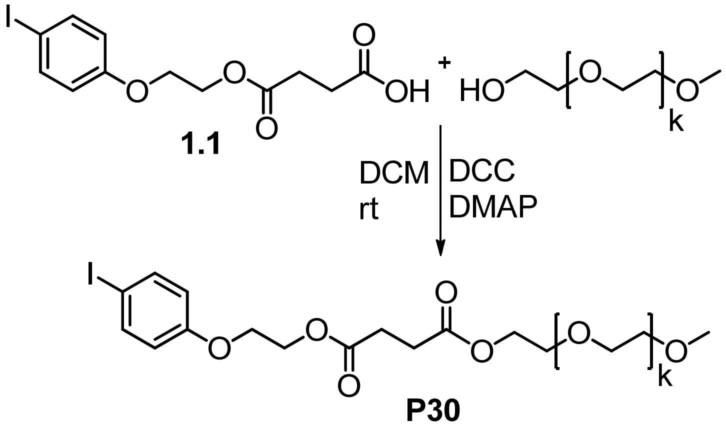


To a stirred solution of 2-(4-iodophenoxy) ethanol (1.0 g, 3.8 mmol) in dry dioxane (25 mL), Et_3N (2.65 mL, 19 mmol) and 4-(dimethylamino)-pyridine (DMAP) (0.695 g, 5.7 mmol) was added. Then, succinic anhydride (1.52 g, 15 mmol) was added and the reaction mixture was stirred at 40°C for 24h. Subsequently, the reaction mixture was poured into ice-cold water and was extracted with DCM (2x20 mL). The combined organic layers were washed with 1M HCl and dried over $NaSO_4$. Purification by recrystallization from ethanol provided the title compound as a white solid (0.97 g, 70 %)

^{1}H-NMR ($CDCl_3$, 300 MHz) δ / ppm: 10.67 (broad, 1H, -C(O)OH), 7.61-7.49 (m, 2H, Ar), 6.73-6.61 (m, 2H, Ar), 4.47-4.43 (m, 2H, Ar-O-CH_2-C*H*$_2$-OCO-), 4.15-4.11 (m, 2H, Ar-O-C*H*$_2$-CH_2-OCO-), 2.71-2.64 (m, 4H, -OC(O)-C*H*$_2$-C*H*$_2$-C(O)OH).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 177.81 (-C(O)OH), 172.24 (-C(O)O-), 158.54 (C_{Ar}-O-), 138.62 (C_{Ar}), 117.22 (C_{Ar}), 83.55 (C_{Ar}-I), 66.12 (C_{Ar}-O-*C*H$_2$-CH_2-O-), 63.12 (C_{Ar}-O-CH_2-*C*H$_2$-O-), 28.99 (-OC(O)-*C*H$_2$-*C*H$_2$-C(O)OH).
HRMS (FAB) of $C_{12}H_{13}IO_5$ $[M+H]^+$ calc. 364.9886 found 364.9888

Synthesis of aryliodide functional poly(ethylene glycol) methyl ether (P30)



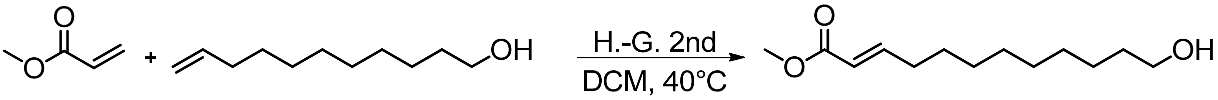
1.1

P30

Poly(ethylene glycol) methyl ether (M_n=2000 g mol^{-1}; 1 g, 0.50 mmol) was dissolved in dry DCM (5 mL). Then, compound **1.1** (0.7 g, 2.0 mmol) and 4-(dimethylamino)-pyridine) (62 mg, 0.50 mmol) was added. After 5 minutes dicyclohexylcarbodiimide (DCC) (0.83 g, 4.0 mmol) in DCM (3 mL) was added and the reaction mixture was stirred for 16h at room temperature. The reaction mixture was then filtered and concentrated. The residue was dissolved in DCM and washed with sat. aq. sodium hydrogen carbonate. The combined organic layers were dried over Na_2SO_4 and the polymer was obtained by precipitation into ice-cold diethyl ether.

^{1}H-NMR (CDCl$_3$, 300 MHz) δ / ppm: 7.57-7.52 (m, 2H, Ar), 6.70-6.65 (m, 2H, Ar), 4.45-4.41 (m, Ar-O-CH$_2$-C*H*$_2$-OCO-), 4.24-4.20 (m, -OC(O)-C*H*$_2$-CH$_2$-O-PEG), 4.13-4.11 (m, Ar-O-C*H*$_2$-CH$_2$-OCO-), 3.76-3.55 (m, PEG backbone and -OC(O)-CH$_2$-C*H*$_2$-O-PEG), 3.37 (s, 3H, -OCH$_3$), 2.66 (s, 4H, -OC(O)-C*H*$_2$-C*H*$_2$-C(O)OH).

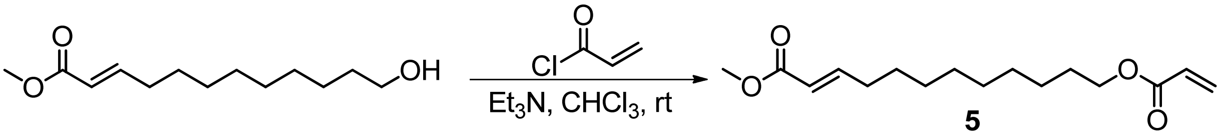
Synthesis of (*E*)-methyl-12-hydroxydodec-2-enoate



Undecenol (0.17 g, 1.00 mmol) and methyl acrylate (0.86 g, 10 mmol) were weighed in a supelco conical vial. Then the vial was closed with a screw cap comprising a rubber septum. After 5 minutes at a temperature of 40°C, the required amount of ruthenium-catalyst (Hoveyda-Grubbs 2nd generation) (5.0 mol % to undecenol) in DCM (150 µL) was added and a needle was inserted in the rubber septum. After 24h the reaction was quenched by adding ethyl-vinyl ether (9 eq. to catalyst) to the cooled reaction mixture. Purification by flash chromatography [hexane:ethyl acetate (10:1)] provided the desired product (0.2 g, 90 %).

^{1}H-NMR (CDCl$_3$, 300 MHz) δ / ppm: 6.96 (dt, J = 15.6, 7.0 Hz, 1H, -OC(O)-CH=C*H*-), 5.81 (dt, J = 15.6, 1.6 Hz, 1H, -OC(O)-C*H*=CH-), 3.72 (s, 3H, -OCH$_3$), 3.63 (t, J = 6.6 Hz, 2H, -C*H*$_2$-OH), 2.19 (qd, J = 7.2, 1.5 Hz, 2H, -OC(O)-CH=CH-C*H*$_2$-), 1.60-1.50 (m, 2H, -C*H*$_2$-CH$_2$-OH), 1.48-1.39 (m, 2H, -C*H*$_2$-CH$_2$-CH$_2$-OH), 1.39-1.21 (m, 10H, CH$_2$).
^{13}C-NMR (CDCl$_3$, 75 MHz) δ / ppm: 167.27 (-O*C*(O)-CH=CH-), 149.85 (-OC(O)-CH=*C*H-), 120.83 (-OC(O)-*C*H=CH-), 62.84 (-*C*H$_2$-OH), 51.38 (-OCH$_3$), 32.76 (-CH=CH-*C*H$_2$-), 32.20 (-*C*H$_2$-CH$_2$-OH), 29.47 (CH$_2$), 29.39 (CH$_2$), 29.30 (CH$_2$), 29.09 (CH$_2$), 28.00 (-*C*H$_2$), 25.76 (CH2).
HRMS (FAB) of $C_{13}H_{24}O_3$ [M+H]$^+$ calc. 229.1804 found 229.1806

Synthesis of (*E*)-methyl 12-(acryloyloxy)dodec-2-enoate



(E)-methyl-12-hydroxydodec-2-enoate (0.1 g, 0.44 mmol) was weighed in a round bottom flask and set under argon atmosphere. Then $CHCl_3$ (5 mL) was added and the reaction mixture was stirred for 5 minutes. Subsequently, acryloyl chloride (0.08 g, 0.88 mmol) and after further 5 minutes Et_3N (0.11 g, 1.1 mmol) was added. The mixture was stirred for about 16h at room temperature. The solvent was then removed under reduced pressure and the residue was quickly filtrated through a short column (silica gel, ethyl acetate) to remove the ammonium salts. The crude product was purified by flash chromatography (hexane:ethyl acetate (15:1). The product was obtained as a colorless oil (0.1 g, 80 %).

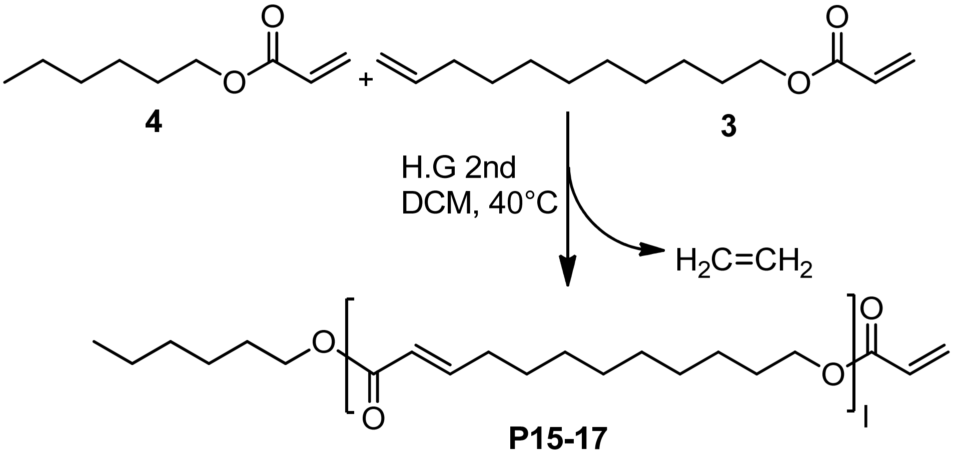
^{1}H-NMR ($CDCl_3$, 300 MHz) δ / ppm: 6.96 (dt, *J* = 15.5, 7.0 Hz, 1H, -OC(O)-CH=C*H*-), 6.39 (dd, *J* = 17.3, 1.4 Hz, 1H, -CH=CH_2), 6.11 (dd, *J* = 17.3, 10.4 Hz, 1H, -C*H*=CH_2), 5.84-5.77 (m, 2H, -CH=CH_2 and -OC(O)-C*H*=CH-), 4.14 (t, *J* = 6.7 Hz, 2H, -CH_2-OC(O)-), 3.71 (s, 3H, -OCH_3), 2.18 (q, *J* = 7.2 Hz, 2H, -OC(O)-CH=CH-CH_2-), 1.70-1.60 (m, 2H, -CH_2-CH_2-OC(O)-), 1.48-1.38 (m, 2H, -CH_2-CH_2-CH_2-OC(O)-), 1.38-1.21 (m, 10H, CH_2).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ / ppm: 167.29 (-O*C*(O)-CH=CH-), 166.44 (-O*C*(O)-CH=CH_2), 149.86 (-OC(O)-CH=*C*H-), 130.54 (-OC(O)-CH=*C*H_2), 128.94 (-OC(O)-*C*H=CH_2), 120.99 (-OC(O)-*C*H=CH-), 64.79 (-*C*H_2-OC(O)-), 51.49 (-OCH_3), 32.40 (-CH=CH-*C*H_2-), 29.49 (CH_2), 29.41 (CH_2), 29.32 (CH_2), 29.21 (CH_2), 28.73 (CH_2), 28.12 (-*C*H_2-CH_2-OC(O)-), 26.03 (-*C*H_2-CH_2-CH_2-OC(O)-).
HRMS (FAB) of $C_{16}H_{26}O_4$ $[M+H]^+$ calc. 283.1909 found 283.1911

General procedure for Heck coupling reactions (Jeffery's condition)

$Pd(OAc)_2$ (5 mol %), $NaHCO_3$ (0.5 eq.) and tetrabutylammoniumchloride (TBA-Cl) (2.5 eq.) were weighted in a round bottom flask. Subsequently, the acrylic-substrate (1 eq.) (**P1-3**) or (**P16, P19** or **P22**) and the aryliodide functional substrate (**P4-5** or **P30**) (1 eq.) were added. After addition of DMF (~2 mL) the reaction mixture was stirred for 48 h at 30°C, under an argon atmosphere. To the reaction mixture, DCM (4mL) was added and the crude product was washed with water (1x10 mL) and sat. aq. sodium hydrogen carbonate (1x10 mL). The product was isolated by precipitation in pentane:diethyl ether 1:1 (PEG polymers)

Analytic Results of ADMET Polymers



Scheme S1: ADMET polymerisation of monomer **3** in presence of a hexyl acrylate chain-stopper **4**. ADMET polymerisations were performed at 40°C, 1 mol% of 2nd Hoveyda-Grubbs catalyst (relative to **3**) and a small amount of DCM (150 µL). Polymers of varying molecular weights were synthesized using different amounts of monomer **3** relatively to the chain-stopper.

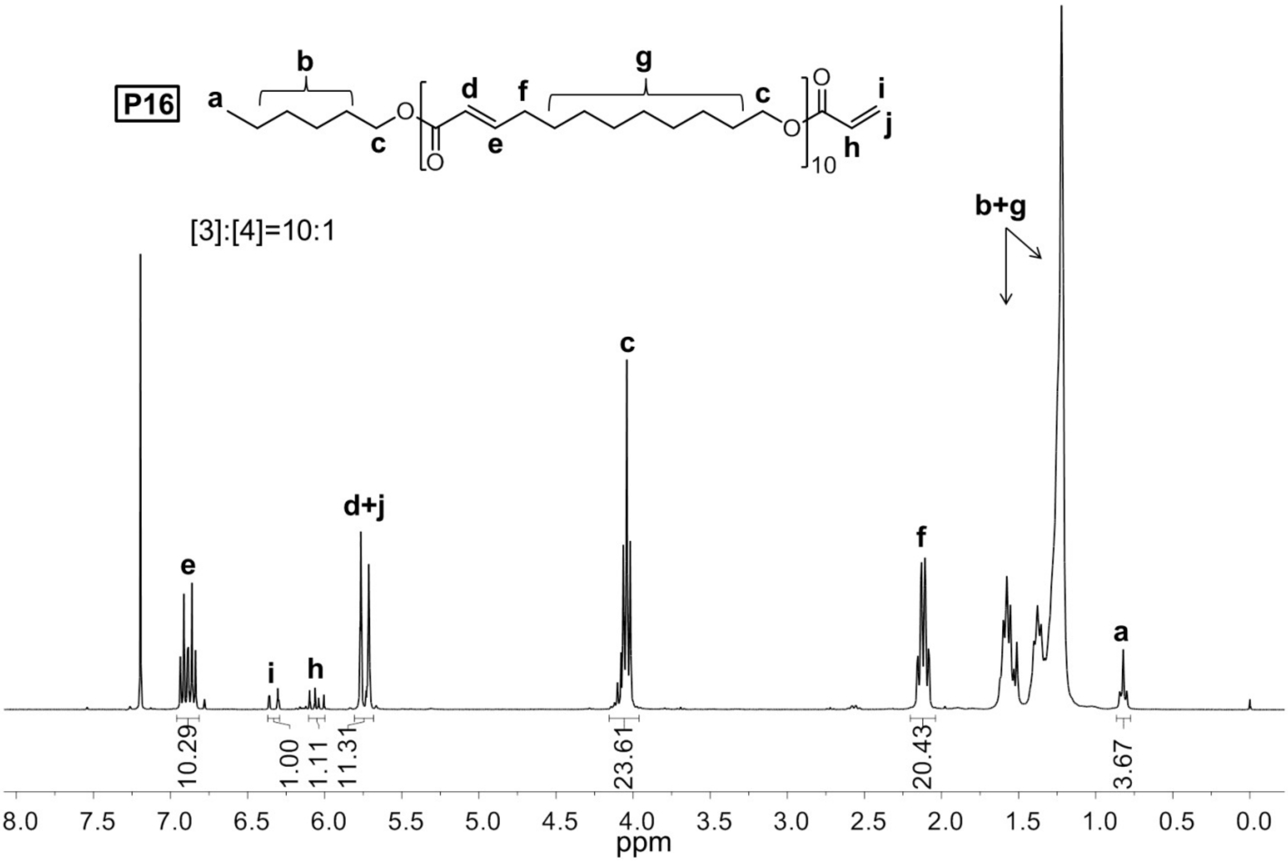


Figure S1: ^{1}H-NMR of the ADMET polymerisation of monomer **3** in presence of a hexyl acrylate chain-stopper (**4**) ([3]:[4]=10:1).

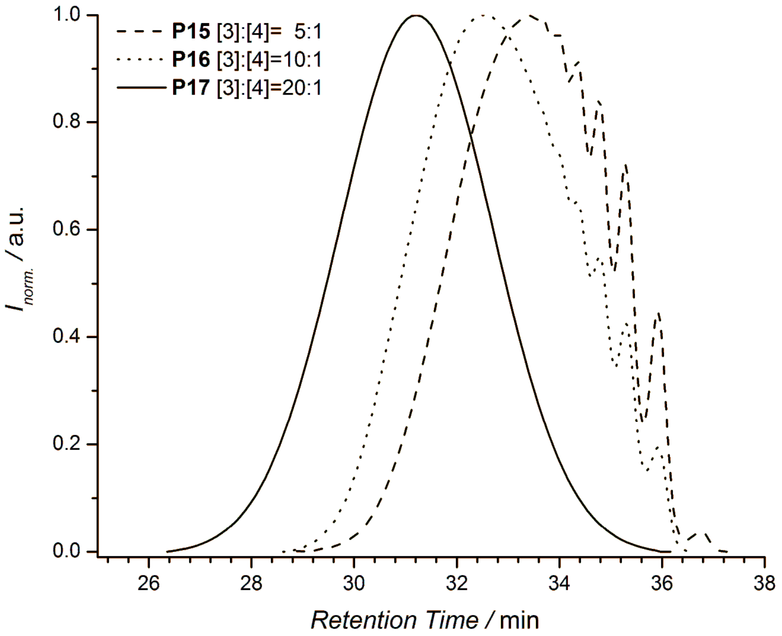
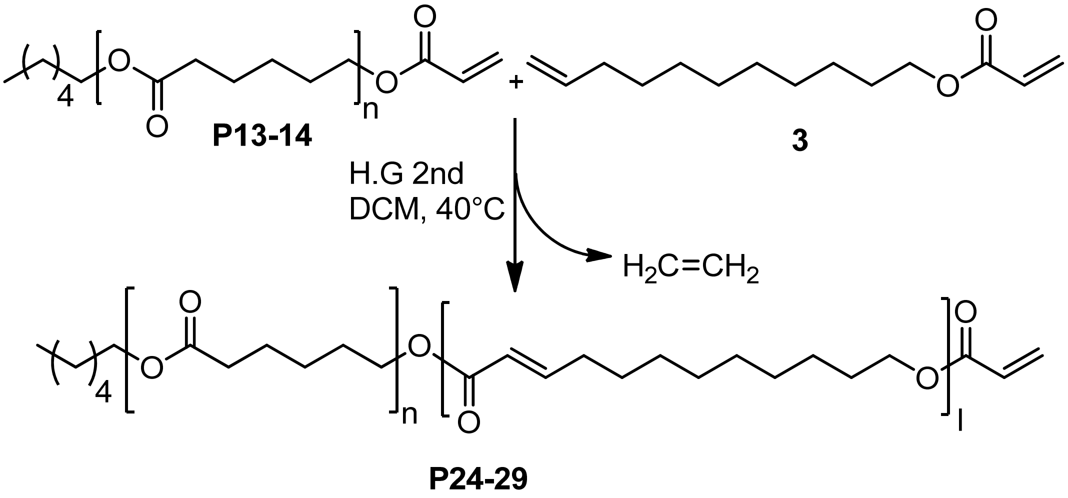


Figure S2: SEC traces of the ADMET homopolymers using hexyl acrylate (**4**) as chain-stopper Polymers of varying molecular weights were synthesized using different amounts of monomer **3** relatively to the chain-stopper. ADMET polymerisations were performed at 40°C using the Hoveyda-Grubbs catalyst 2nd generation (1 mol% to **3**).



Scheme S2: ADMET polymerisation of monomer **3** in presence of an acrylated poly(ε-caprolactone)(**P13** or **P14**) using the Hoveyda-Grubbs 2nd generation catalyst (1 mol% to **3**) and a small amount of dichloromethane (150 µL).

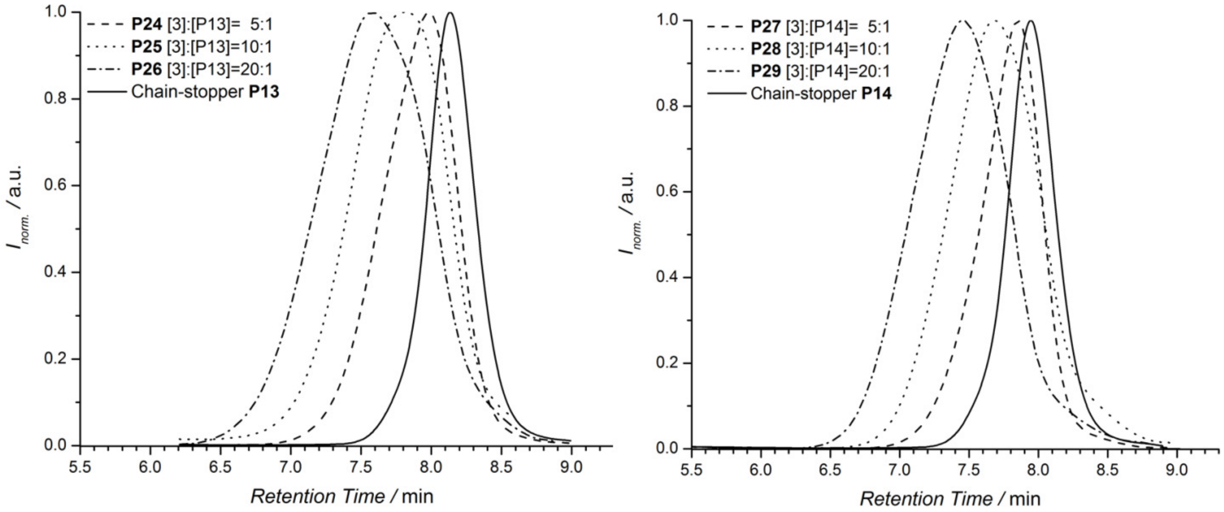


Figure S3: SEC analysis of the ADMET diblock copolymers using an acrylated poly(ε-caprolactone) chain-stopper (**P13** or **P14**)

Table S1: Corresponding molecular weights of the SEC analysis (Figure S3).

Monomer	**Chain-stopper**	**Ratio [3]:[CS]**	**Copolymer**	$M_{n,\mathrm{SEC}}^{(B)}$	$PDI^{(B)}$
3	**P13**	**5:1**	**P24**	**5900**	**1.27**
3	**P13**	**10:1**	**P25**	**6800**	**1.40**
3	**P13**	**20:1**	**P26**	**9200**	**1.58**
3	**P14**	**5:1**	**P27**	**7800**	**1.23**
3	**P14**	**10:1**	**P28**	**9000**	**1.44**
3	**P14**	**20:1**	**P29**	**11400**	**1.49**

^{B} **Measured on SEC system B**

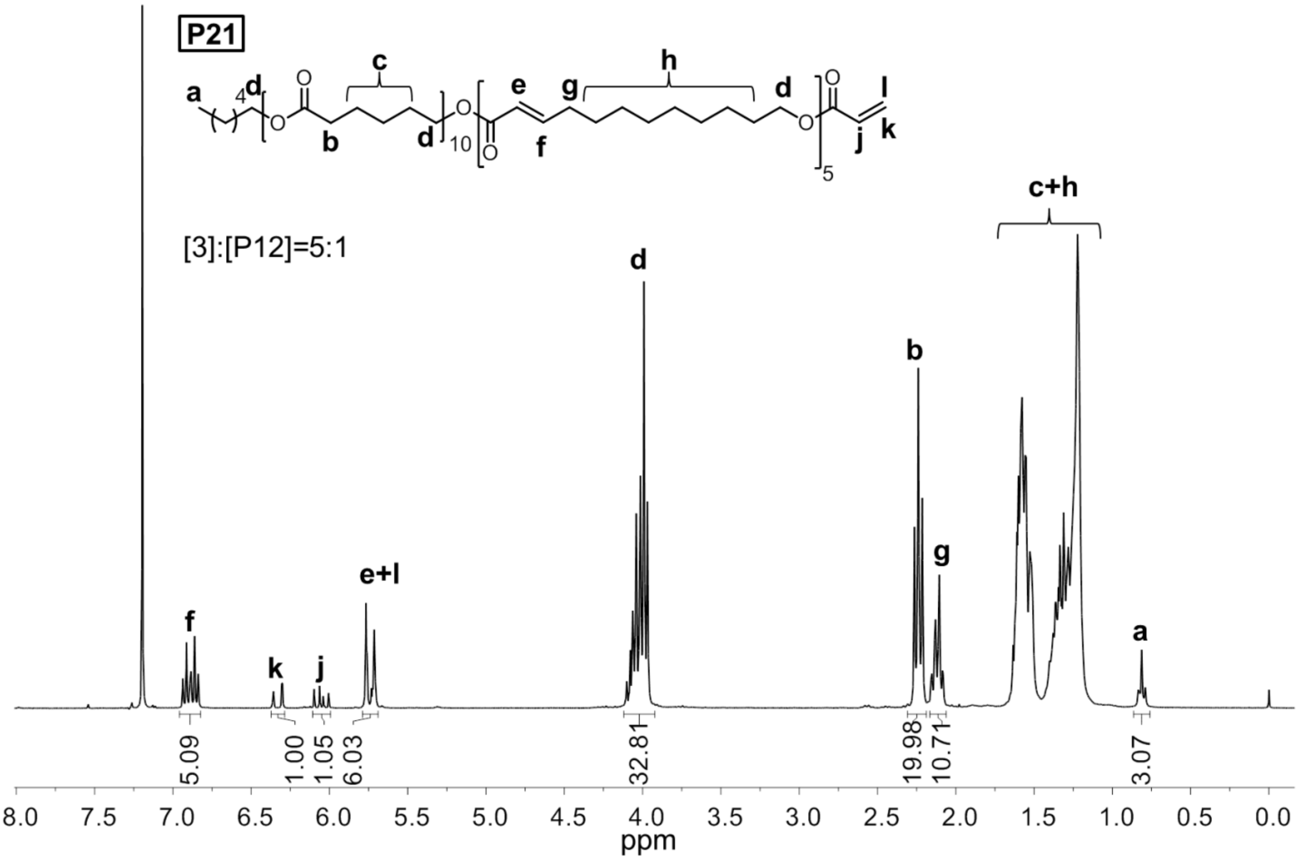
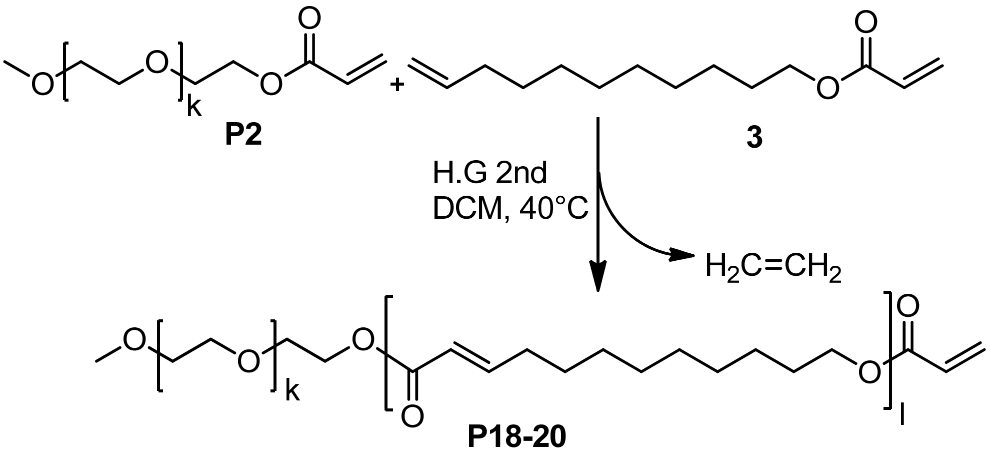


Figure S4: ^{1}H-NMR of the ADMET polymerisation of monomer 3 in presence of an arylated poly(ε-caprolactone) chain-stopper (P12) ([3]:[CS1]=5:1).



Scheme S3: ADMET polymerisation of monomer **3** in presence of an acrylated PEG$_{2000}$ chain-stopper (**P2**) using 1 mol% (relative to 3) of the Hoveyda-Grubbs 2nd generation catalyst.

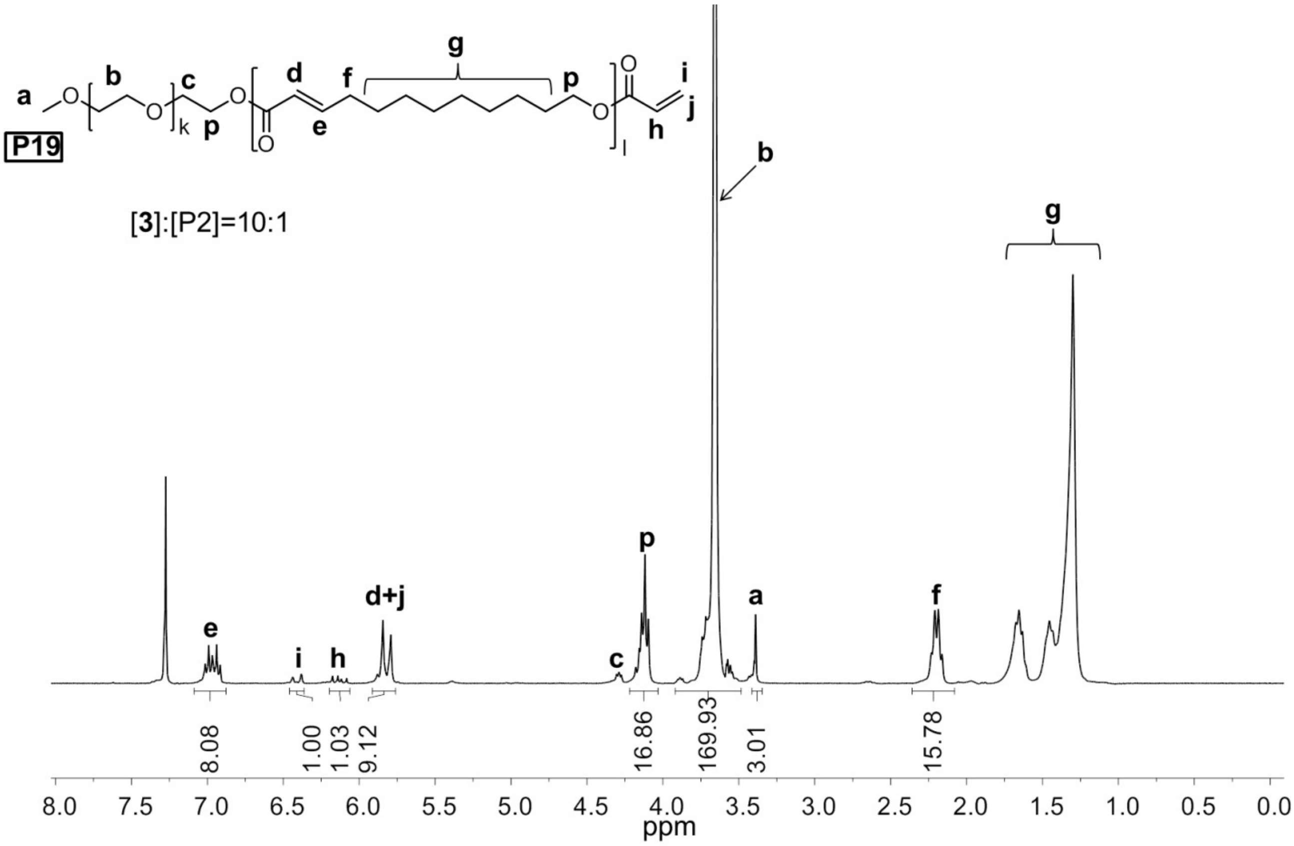


Figure S5: ^{1}H-NMR of the ADMET polymerisation of monomer **3** in presence of a PEG-Acrylate chain-stopper (**P2**) ([3]:[P2]=10:1) to afford diblock copolymer (**P19**).

Analytic Results of Heck Reactions:

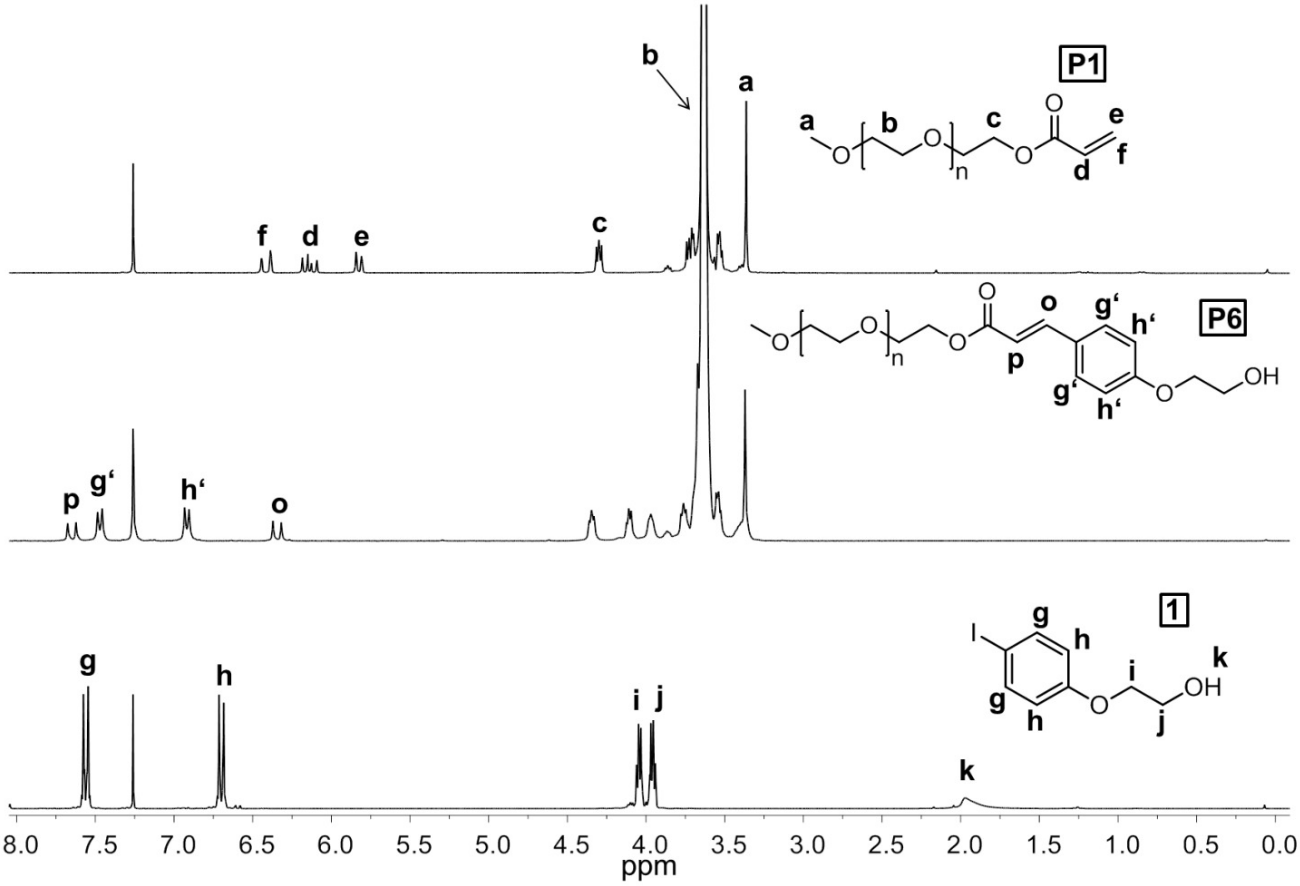


Figure S6: ^{1}H-NMR spectra of 2-(4-iodophenoxy)ethanol (**1**)(bottom), the PEG-Acrylate (**P1**)(top), and the Heck coupling product (**P6**) (middle).

Table S2: Theoretical and experimental *m/z* values for the isotopic distribution of the Heck coupling of **P1** and **1** to afford **P6** (Figure 1) in the *m/z* range between 1030 and 1090.

Ion assignment	formula	*m/z* $^{\text{theo.}}$	*m/z* $^{\text{exp}}$.	Δm/z
[**P1**(n=20)+Na]$^+$	$[C_{46}H_{90}NaO_{23}]^+$	1033.58	1033.83	0.25
[**P1**(n=21)+Na]$^+$	$[C_{48}H_{94}NaO_{24}]^+$	1077.60	1077.83	0.23
[**P6**(n=17)+Na]$^+$	$[C_{48}H_{86}NaO_{22}]^+$	1037.55	1037.83	0.28
[**P6**(n=18)+Na]$^+$	$[C_{50}H_{90}NaO_{23}]^+$	1081.58	1081.83	0.25

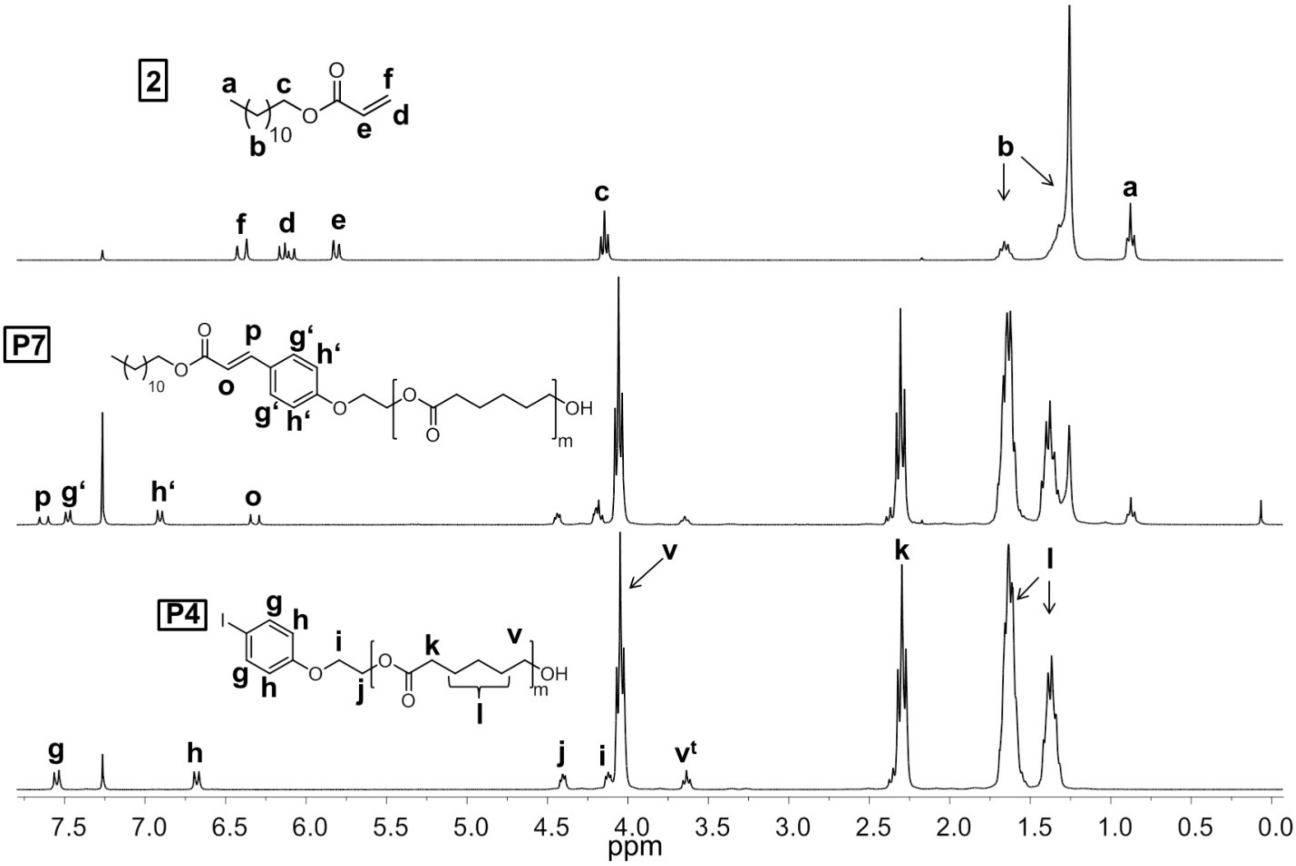


Figure S7: ^{1}H-NMR spectra of 2-(4-iodophenoxy)ethanol (**1**)(bottom), lauryl acrylate (**2**)(top), and the Heck coupling product (**P4**) (middle).

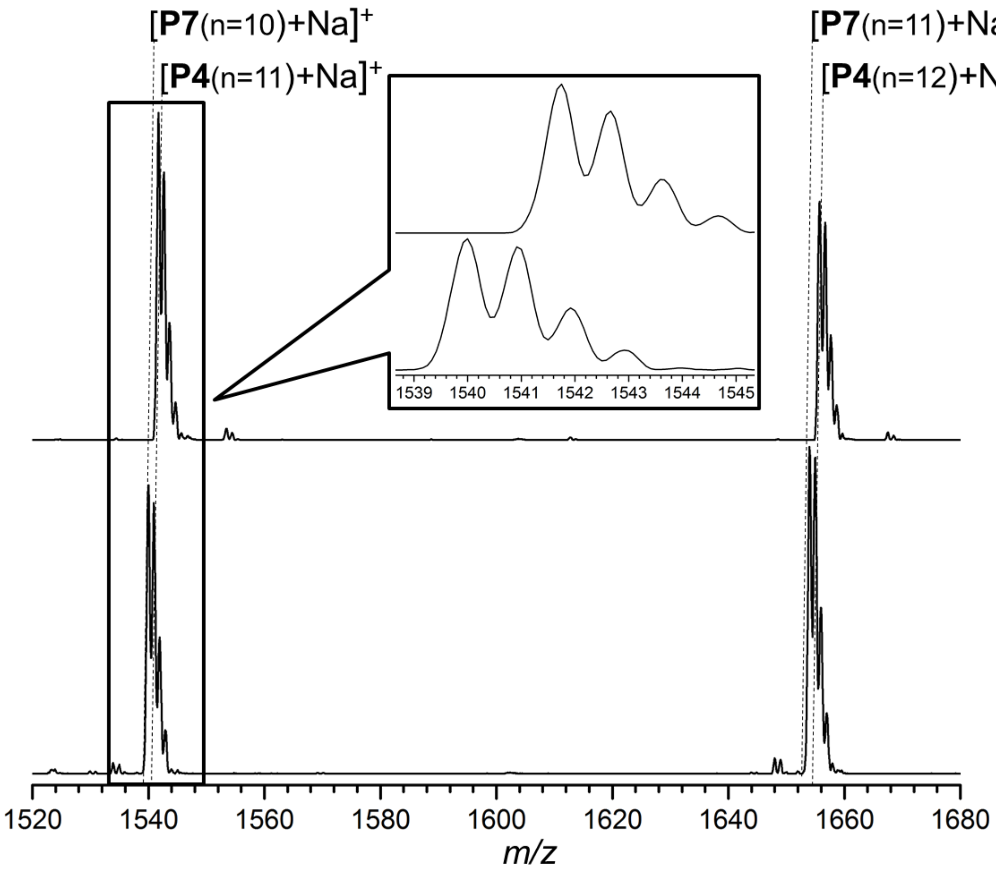
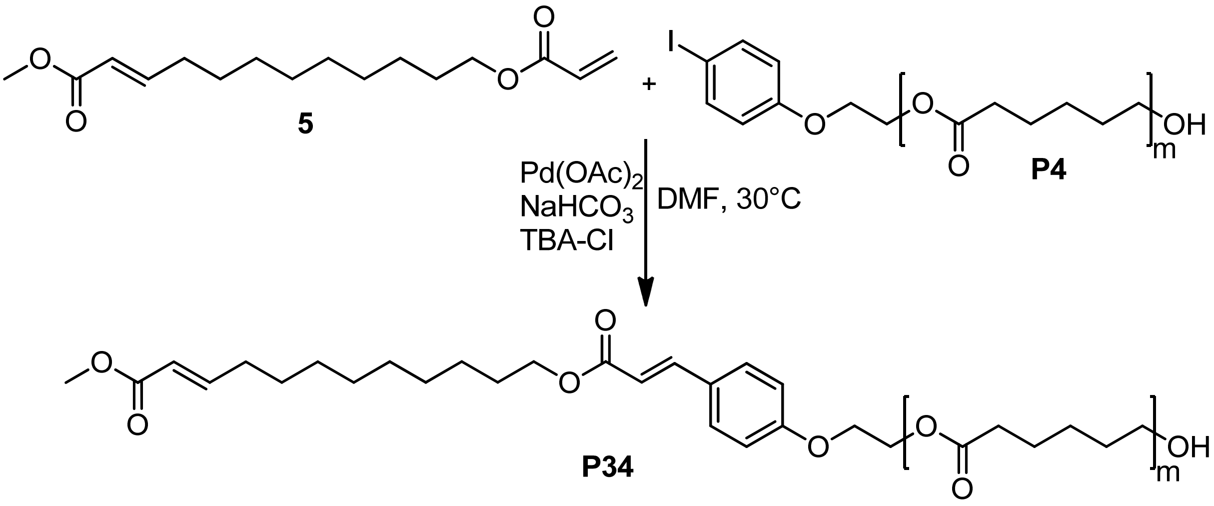


Figure S8: Expanded SEC/ESI-MS spectrum (*m/z* = 1520–1680) of **P4** (top) and **P7** (bottom).

Table S1: Theoretical and experimental *m/z* values for the isotopic distribution of the Heck coupling of **P4** and **2** to afford **P7** (Figure S8) in the *m/z* range between 1520 and 1680.

Ion assignment	formula	*m/z* theo.	*m/z* exp.	Δm/z
[**P4**(n=11)+Na]+	$[C_{74}H_{119}INaO_{24}]^+$	1541.70	1541.75	0.05
[**P4**(n=12)+Na]+	$[C_{80}H_{129}INaO_{26}]^+$	1655.77	1655.75	0.02
[**P7**(n=10)+Na]+	$[C_{83}H_{136}NaO_{24}]^+$	1539.93	1540.00	0.07
[**P7**(n=11)+Na]+	$[C_{89}H_{146}NaO_{26}]^+$	1653.99	1654.00	0.01



Scheme S4: Test reaction of a model compound ((*E*)-methyl 11-(acryloyloxy)undec-2-enoate, **5**) having an acrylate and an internal α,β-unsaturated ester group to study the selectivity of the Heck reaction. The Heck coupling was performed with a 1:1 molar ratio of the end groups using 5 mol% Pd(OAC)$_2$ (relative to the aryliodide functional PCL, **P4**), 0.5 eq NaHCO$_3$ and 1 eq tetrabutylammoniumchloride (TBA-Cl). After 48h the crude reaction mixture was analyzed *via* ^{1}H-NMR (Figure S9).

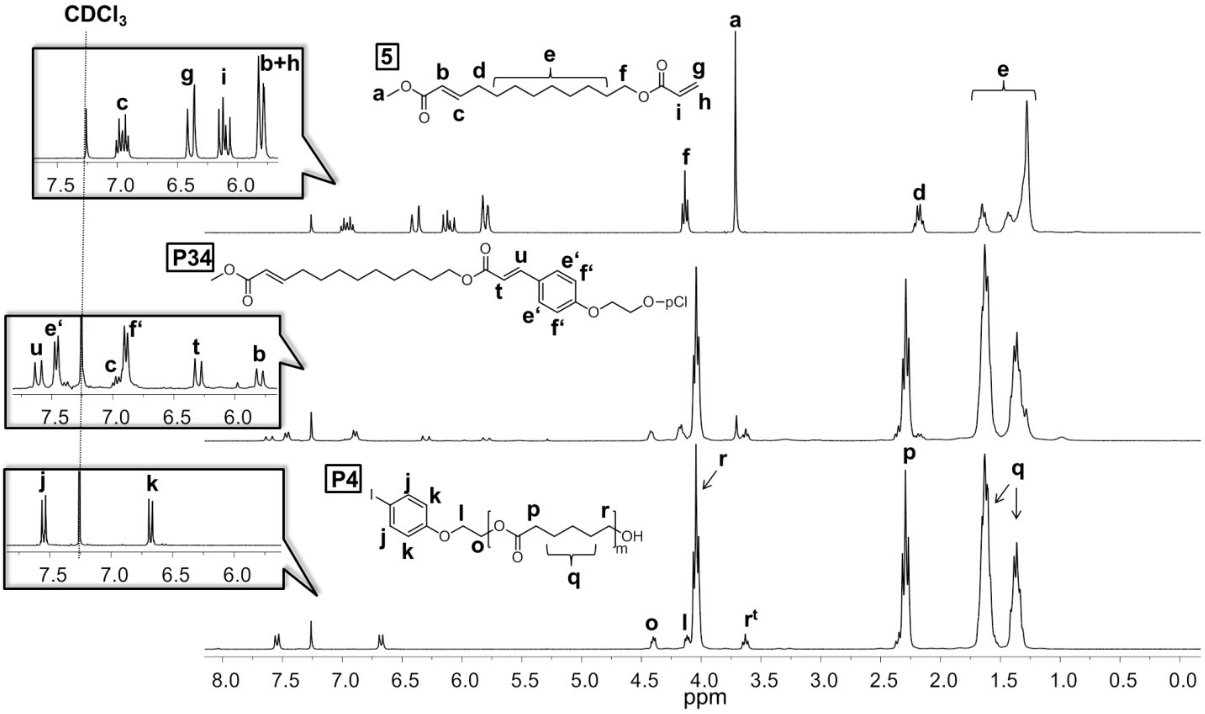
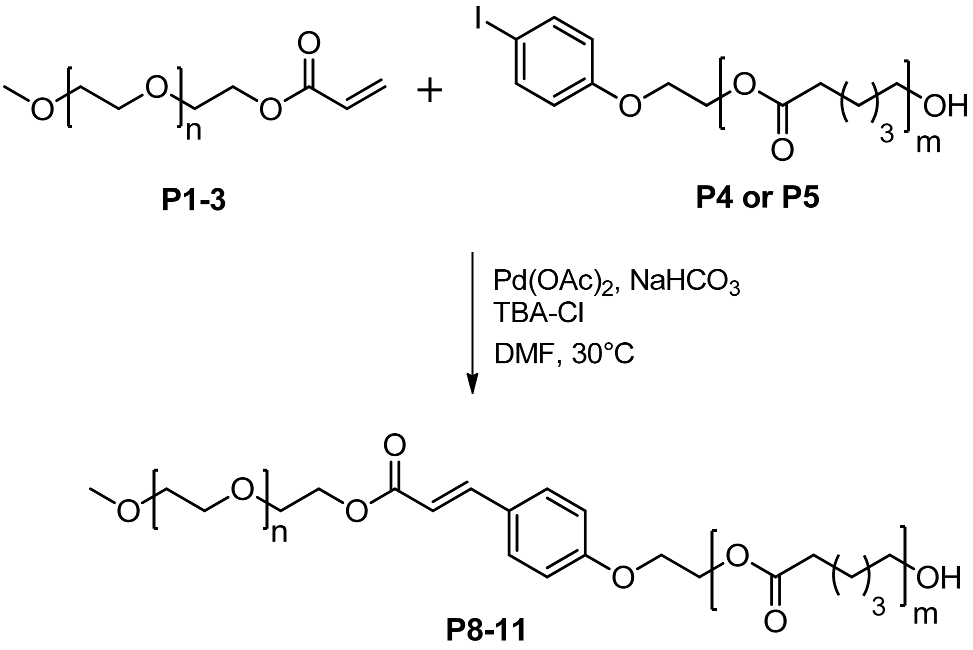


Figure S9: Full scale and expansion of the ^{1}H-NMR spectra of the aryliodide functionalized poly(ε-caprolactone)($M_{n,\mathrm{SEC}}$ = 3400 Da, *PDI*=1.17, **P4**)(bottom), the model compound (**5**)(top), and the Heck coupling product (**P34**) (middle).



Scheme S5: Synthesis of PEG-*b*-PCL copolymers via Heck coupling under Jefferys condition. (30°C, DMF c(**P1-3**)=5 g×L^{-1}, 0.5 eq. $NaHCO_3$, and 5 mol% of $Pd(OAc)_2$). For Heck reactions of **P1** or **P2**, 1eq. tetrabutylammoniumchloride (TBA-Cl) was used. Heck reactions of **P3** were performed without a phase transfer reagent.

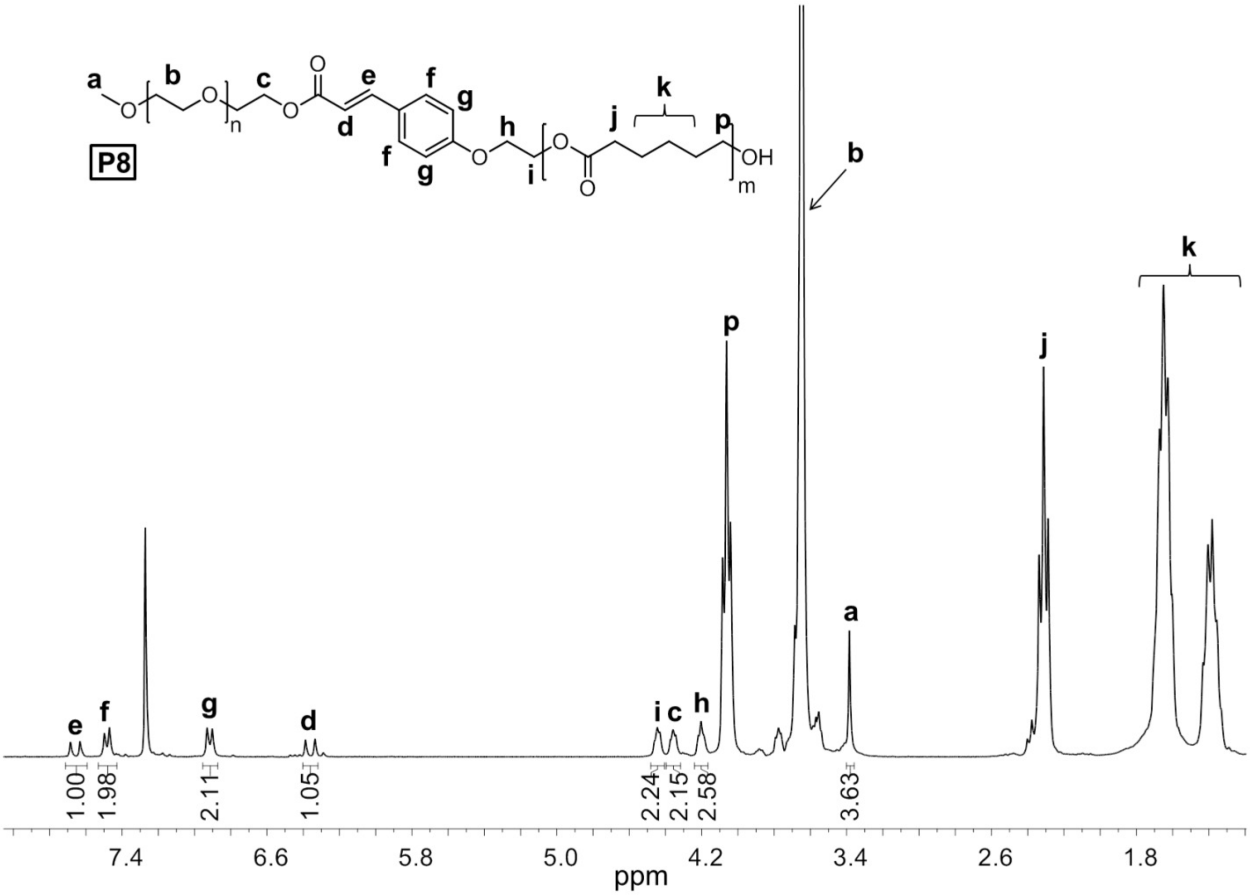


Figure S10: ^{1}H-NMR of the Heck coupling of PEG-Acrylate (**P1**) and aryliodide functional poly(ε-caprolactone) (**P4**) to afford the diblock copolymer (**P8**).

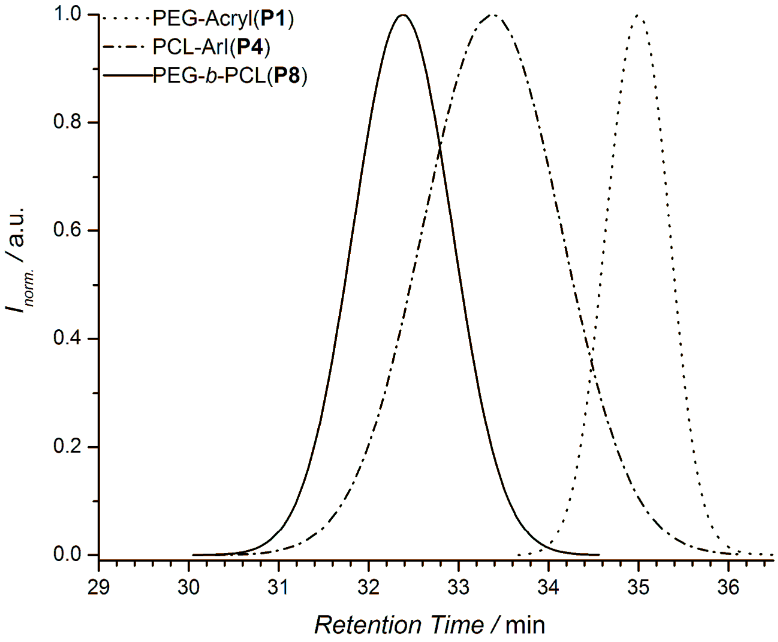


Figure S11: SEC analysis of the Heck coupling of PEG-Acrylate (**P1**, $M_{n,\mathrm{SEC(A)}}$ = 1600 Da, *PDI*=1.03) and aryliodide functional poly(ε-caprolactone) (**P4**, $M_{n,\mathrm{SEC(A)}}$ = 3400 Da, *PDI*=1.17) to afford the diblock copolymer (**P8**, $M_{n,\mathrm{SEC(A)}}$ = 9800 Da, *PDI*=1.18).

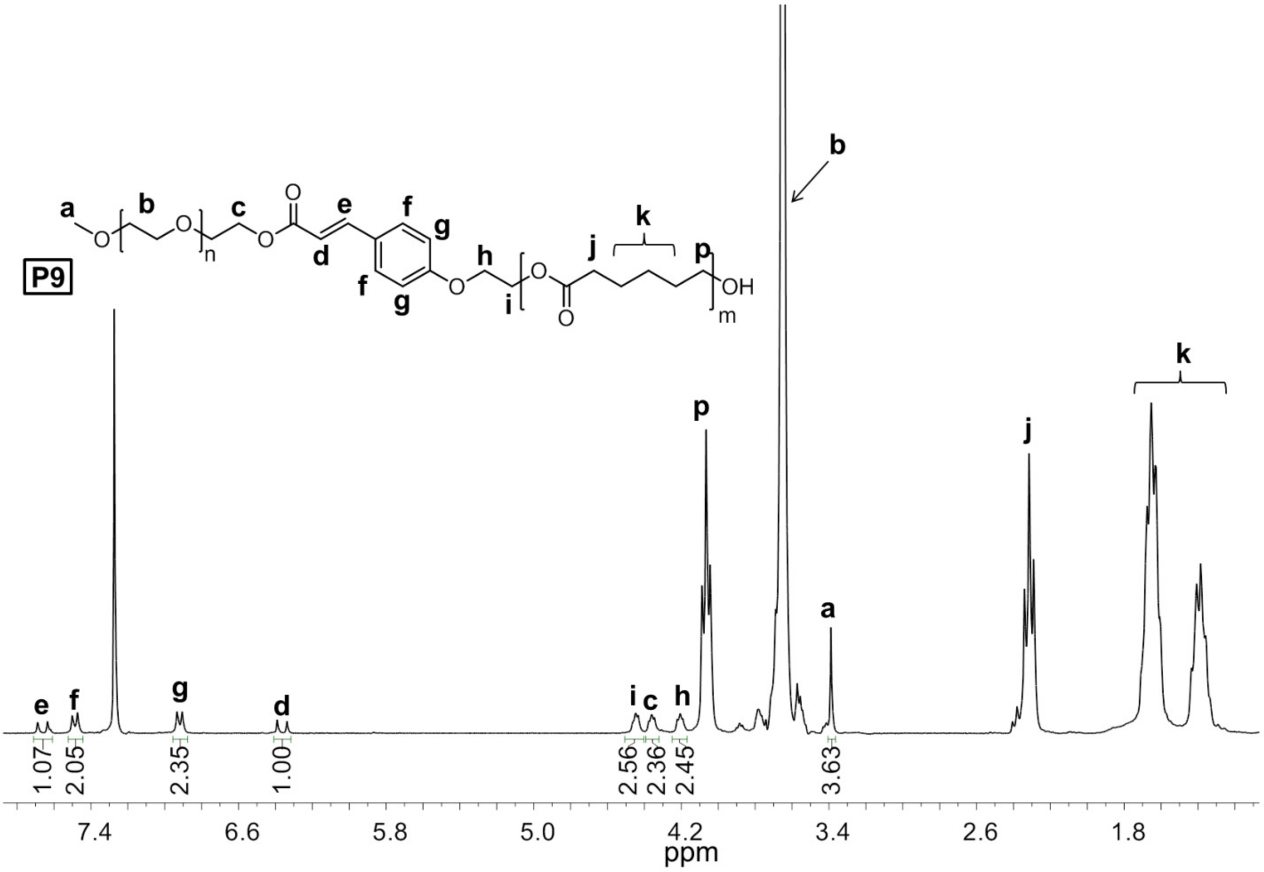


Figure S12: ^{1}H-NMR of the Heck coupling of PEG-Acrylate (P2) and aryliodide functional poly(ε caprolactone) (P4) to afford the diblock copolymer (P9).

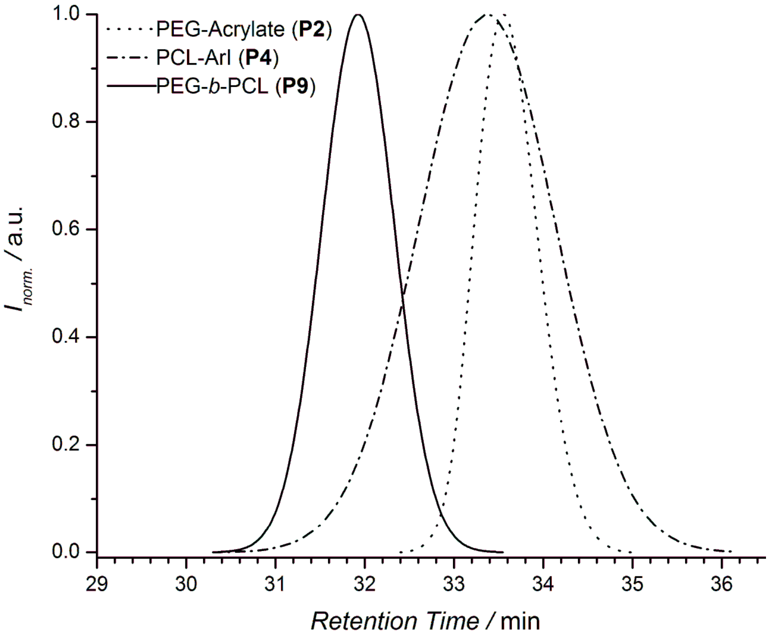


Figure S13: SEC analysis of the Heck coupling of PEG-Acrylate (**P2**, $M_{n,\mathrm{SEC}}$ = 3100 Da, *PDI*=1.03) and aryliodide functional poly(ε-caprolactone) (**P4**, $M_{n,\mathrm{SEC}}$ = 3400 Da, *PDI*=1.17) to afford the diblock copolymer (**P9**, $M_{n,\mathrm{SEC}}$ = 7400 Da, *PDI*=1.08).

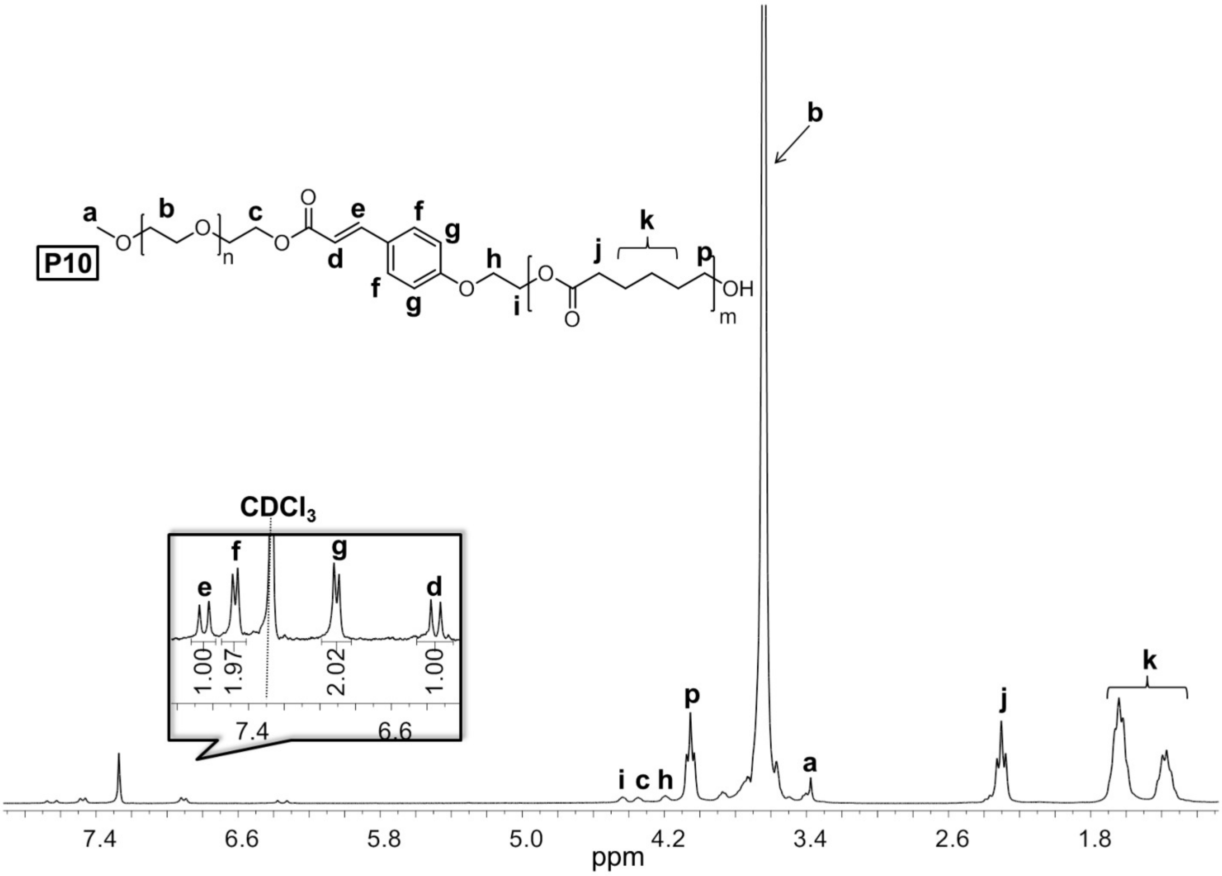


Figure S14: Full scale and expansion of the ^{1}H-NMR spectra of the Heck coupling product of PEG-Acrylate (**P3**) and aryliodide functional poly(ε-caprolactone) (**P4**) to afford the diblock copolymer (**P10**).

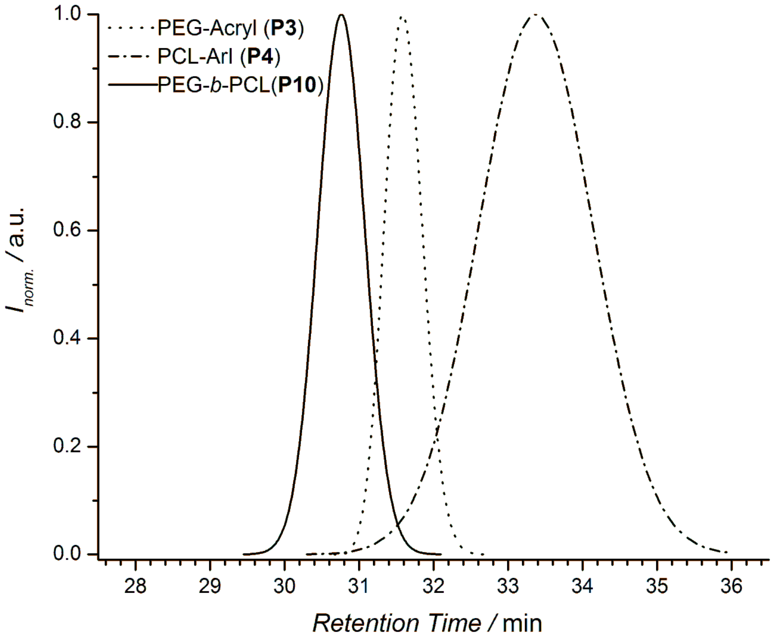


Figure S15: SEC analysis of the Heck coupling of PEG-Acrylate (**P3**, $M_{n,\mathrm{SEC}}$ = 8200 Da, *PDI*=1.02) and aryliodide functional poly(ε-caprolactone) (**P4**, $M_{n,\mathrm{SEC}}$ = 3400 Da, *PDI*=1.17) to afford the diblock copolymer (**P10**, $M_{n,\mathrm{SEC}}$ = 12000 Da, *PDI*=1.12).

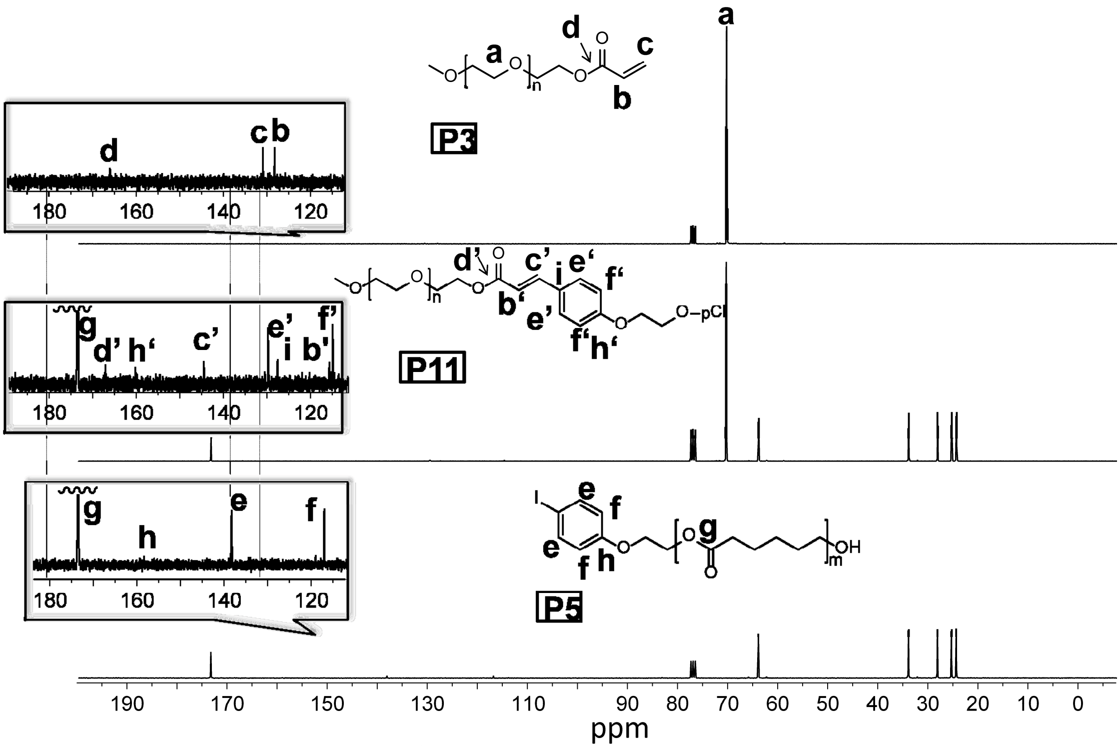
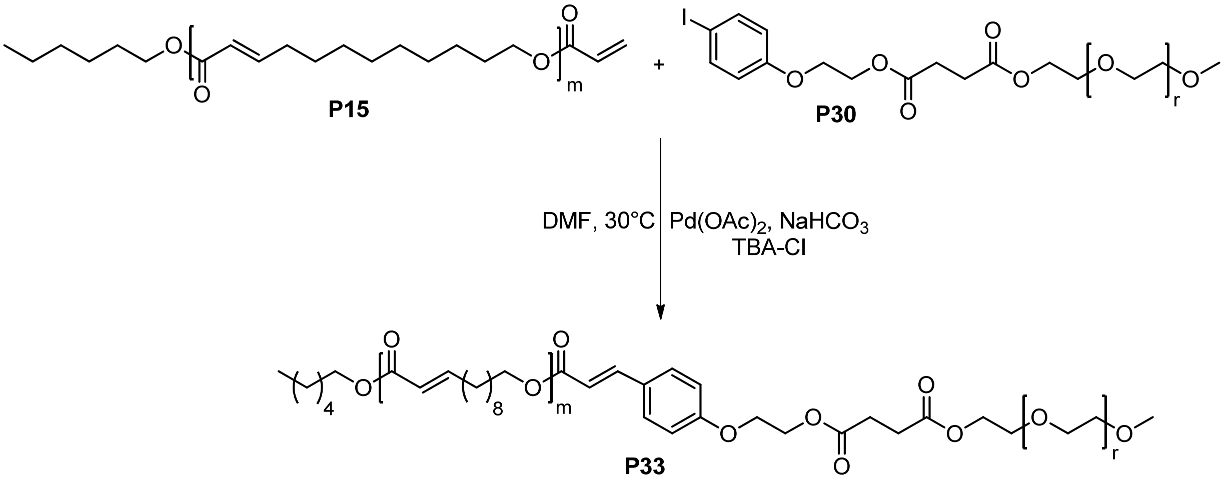


Figure S 16: Full scale and expansions of the ^{13}C-NMR spectra of PEG-Acrylate P3 (top), PCL-ArI P5 (bottom), and their Heck coupling product P11 (middle).



Scheme S6: Synthesis of $(3)_m$-*b*-PEG copolymers *via* Heck coupling under Jefferys condition. (30°C, DMF c(**P15**)=5·g×L^{-1}, 0.5 eq. $NaHCO_3$, 5 mol% of $Pd(OAc)_2$ and 1 eq. tetrabutyl-ammoniumchloride (TBA-Cl)).

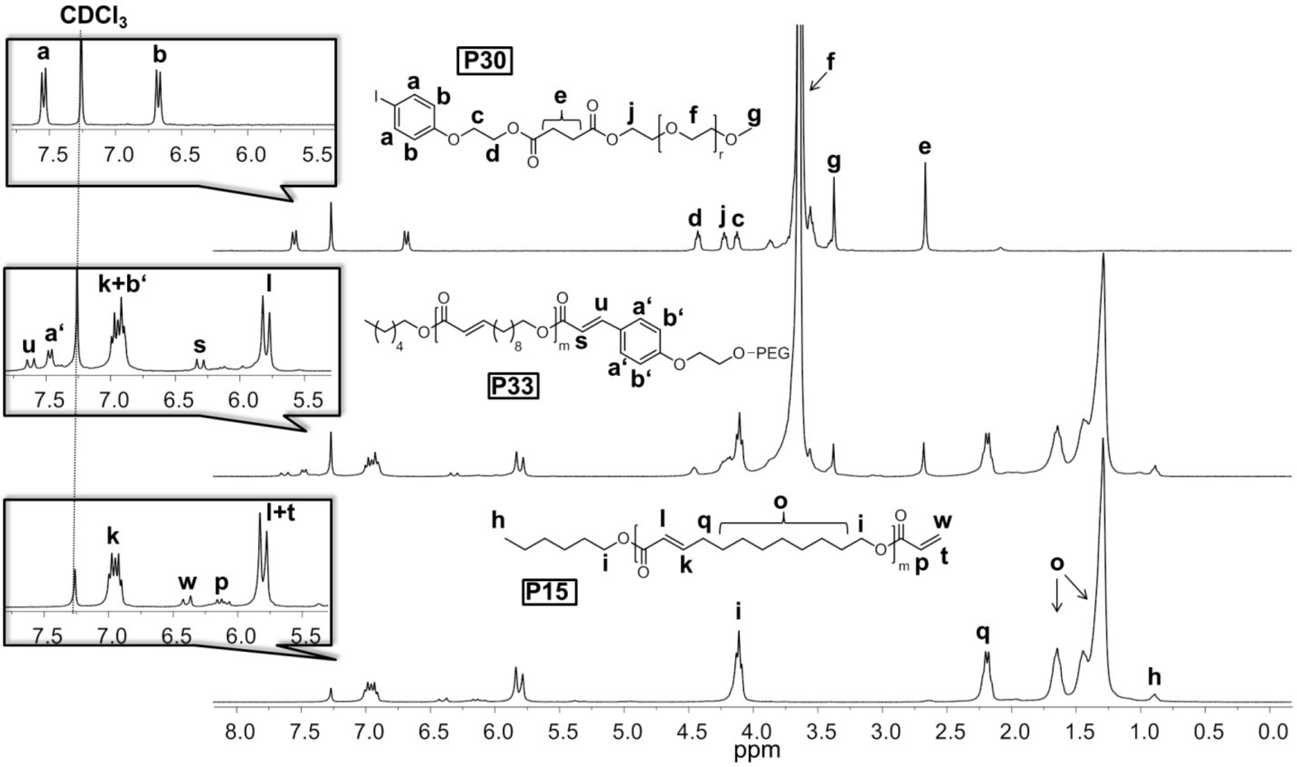


Figure S17: Full scale and expansion of the ^{1}H-NMR spectra of the Heck coupling of ADMET polymer (**P15**) (bottom) and aryliodide functional PEG (**P30**) (top) to afford the diblock copolymer (**P33**) (middel).

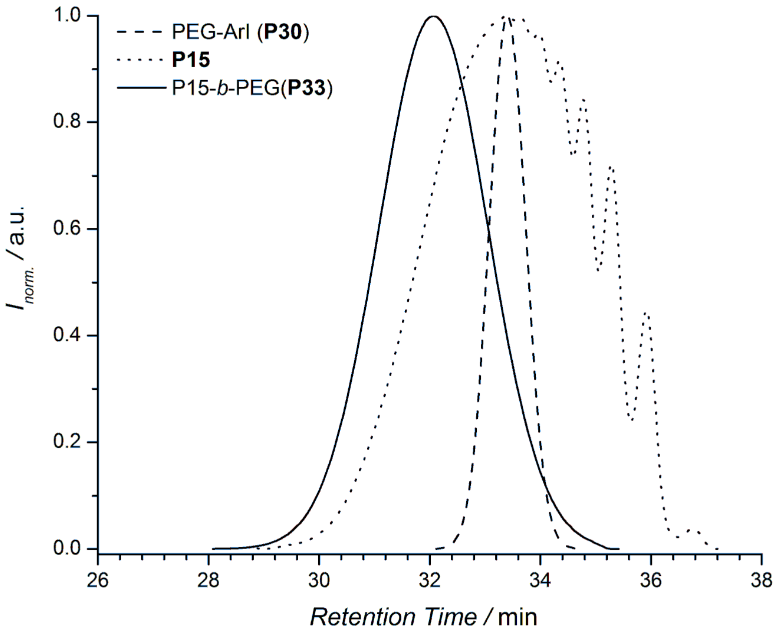
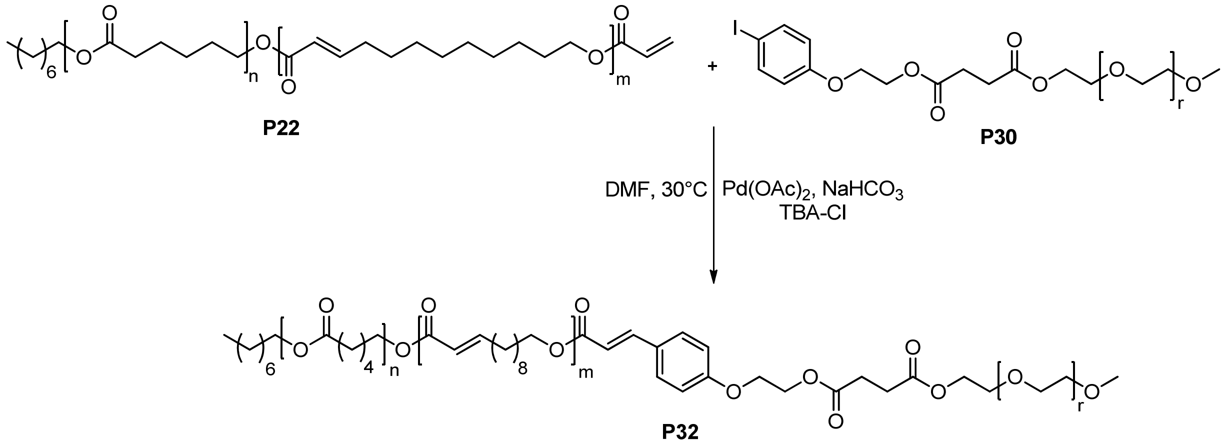


Figure S18: SEC analysis of the Heck coupling of ADMET homopolymer (**P15**, $M_{n,\mathrm{SEC}}$ = 2600 Da, *PDI*=1.56) and aryliodide functional PEG (**P30**, $M_{n,\mathrm{SEC}}$ = 3800 Da, *PDI*=1.03) to afford the diblock copolymer $(3)_m$-*b*-PEG (**P33**, $M_{n,\mathrm{SEC}}$ = 6500 Da, *PDI*=1.33).



Scheme S7: Synthesis of PCL-*b*-$(3)_m$-*b*-PEG triblock copolymers *via* Heck coupling under Jefferys condition. (30°C, DMF c(**P22**)=5·g×L^{-1}, 0.5 eq. NaHCO$_3$, 5 mol% of Pd(OAc)$_2$ and 1 eq. tetrabutyl-ammoniumchloride (TBA-Cl)).

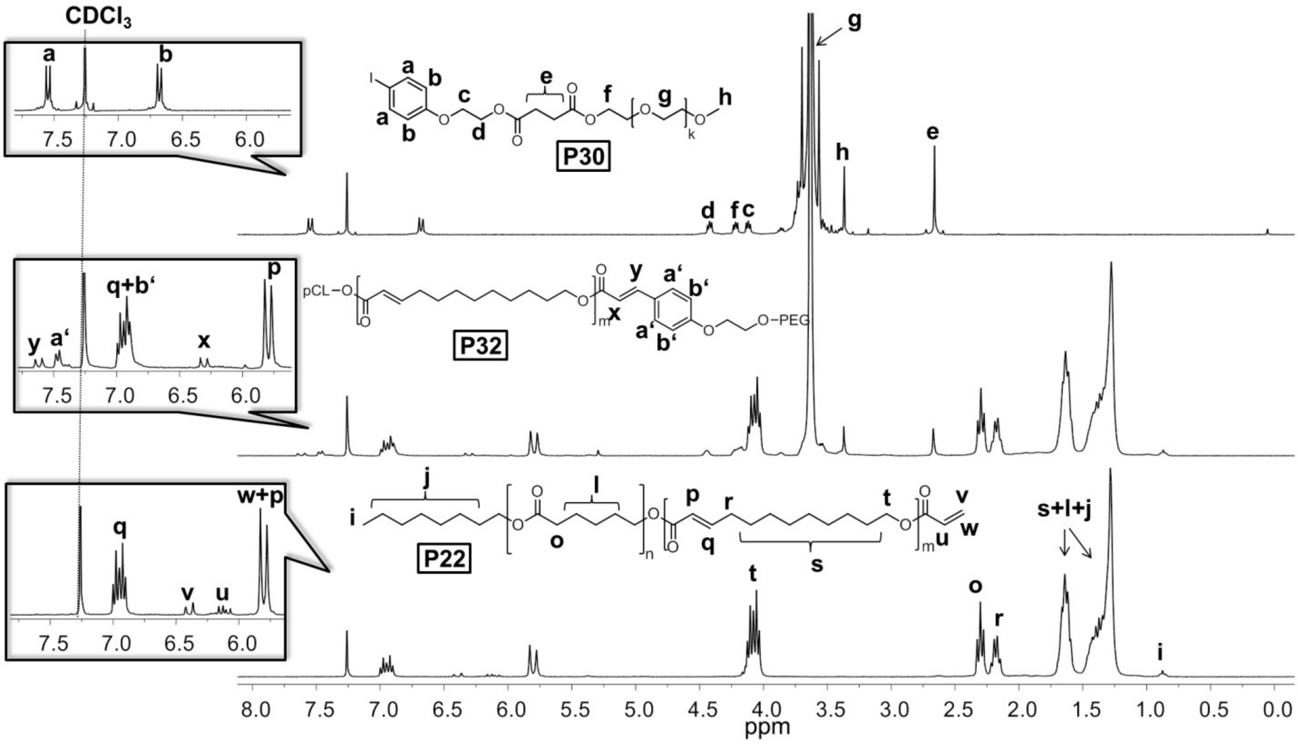


Figure S19: Full scale and expansion of the ^{1}H-NMR spectra of the Heck coupling of ADMET diblock copolymer (PCL-*b*-$(3)_m$,**P22**) (bottom) and aryliodide functional PEG (**P30**) (top) to afford the diblock copolymer (**P32**) (middel).

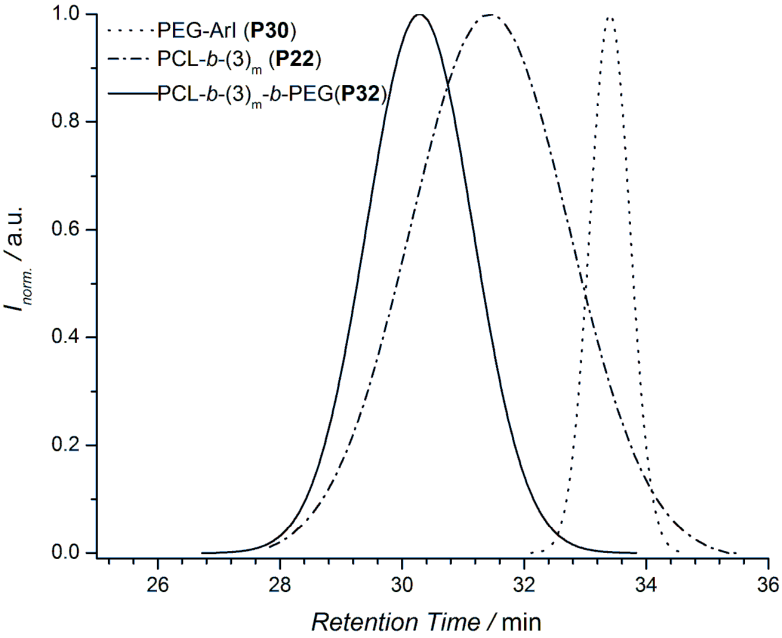


Figure S20: SEC analysis of the Heck coupling of ADMET diblock copolymer PCL-*b*-$(3)_m$ (**P22**, $M_{n,\mathrm{SEC}}$ = 7300 Da, *PDI*=1.41) and aryliodide functional PEG (**P30**, $M_{n,\mathrm{SEC}}$ = 3800 Da, *PDI*=1.03) to afford the triblock copolymer PCL-*b*-$(3)_m$-*b*-PEG (**P32**, $M_{n,\mathrm{SEC}}$ = 11500 Da, *PDI*=1.26).

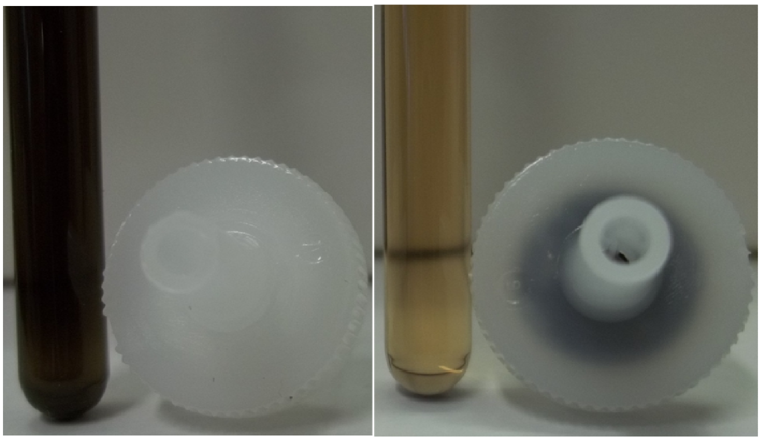


Figure S21: Pictures of reaction mixture before and after the filtration through a syringe microfilter (Rotilabo® pore size: 0.45 µm) to remove the palladium catalyst residues.

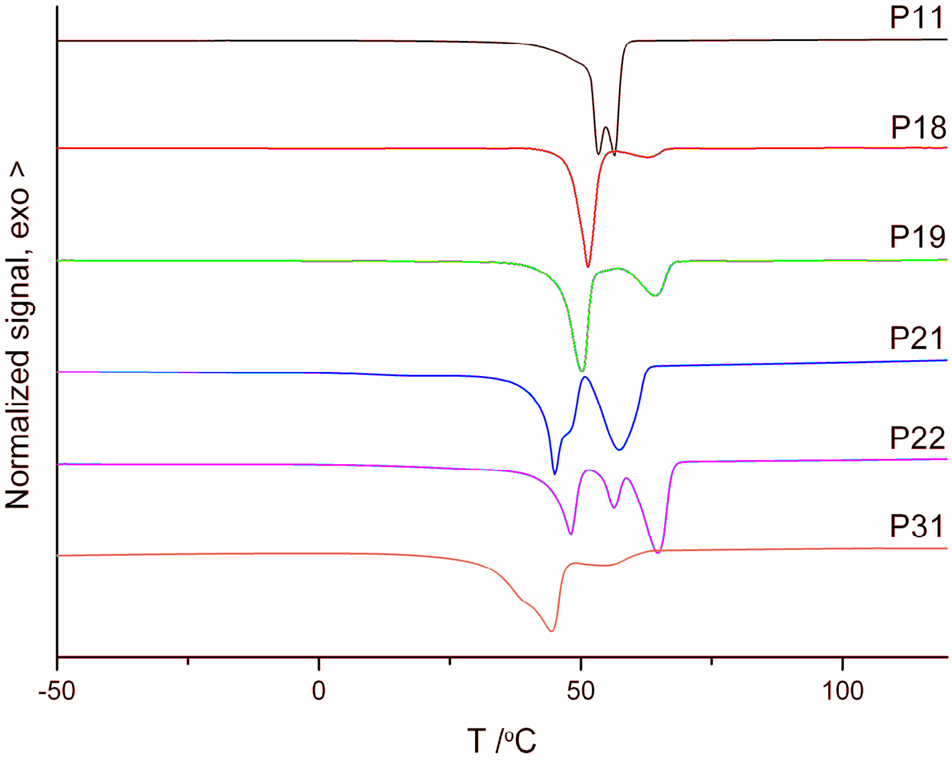


Figure S22: DSC analysis of selected copolymers synthesized via Heck polymer-polymer conjugation. Second heating scans recorded at a heating rate of 10 °C/min are reported. **P11:** PCL-*b*-PEG ($M_{n,\mathrm{SEC}}$ = 17300 Da, *PDI* = 1.12), **P18:** PEG-*b*-(3)$_n$ ($M_{n,\mathrm{SEC}}$ = 5200 Da, *PDI* = 1.19), **P19:** PEG-*b*-(3)$_n$ ($M_{n,\mathrm{SEC}}$ = 7100 Da, *PDI* = 1.36), **P21:** PCL-*b*-(3)$_n$ ($M_{n,\mathrm{SEC}}$ = 4700 Da, *PDI* = 1.26), **P22:** PCL-*b*-(3)$_n$ ($M_{n,\mathrm{SEC}}$ = 6200 Da, *PDI* = 1.33), **P31:** PCL-*b*-(3)$_m$-*b*-PEG ($M_{n,\mathrm{SEC}}$ = 9500 Da, *PDI* = 1.30).

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1. W. Qu, M.-P. Kung, C. Hou, S. Oya and H. F. Kung, *Journal of Medicinal Chemistry*, 2007, **50**, 3380-3387.
2. L. Montero de Espinosa and M. A. R. Meier, *Chemical Communications*, 2011, **47**, 1908-1910.
3. M. Glassner, K. K. Oehlenschlaeger, T. Gruendling and C. Barner-Kowollik, *Macromolecules*, 2011, **44**, 4681-4689.