Preparation of waterborne functional polymers using a bifunctional coupler

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Experimental section:

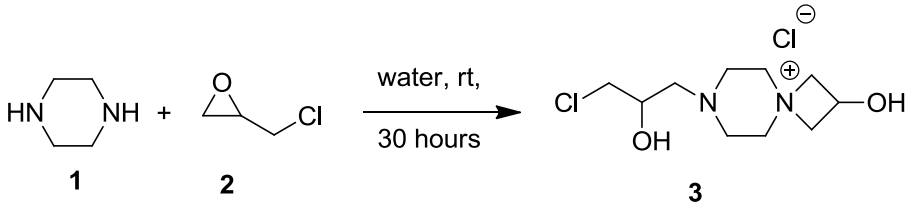
Materials: Hexylamine (99%, Aldrich), decylamine (99%, Aldrich), epichlorohydrin (99%, Merck), piperazine (99+%, Aldrich), 1, 4-diaminobutane (99%, Aldrich), triethylamine (99%, VWR) were used as received. Salt free poly(vinyl amine) was obtained from BASF as aqueous solution. This aqueous solution was freeze dried and the solid poly(vinyl amine) was used as starting material. Distilled water was used as solvent for all the reactions.

Measurements:

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 FT-NMR spectrometer at 400 and 100 MHz, respectively. Deuterium oxide (D_2O), deuterated methanol (CD_3OD) and deuterated dimethyl sulfoxide (DMSO-d_6) were used as solvents. Tetramethylsilane (TMS) was used as an internal standard. All Raman spectra were recorded on a Buker RFS100/s Raman spectrometer, fitted with a Nd: YAG laser (1064nm). The spectral resolution was 4 cm^{-1}. For one spectrum 1000 scans were collected at a laser power of 200mW. Size exclusion chromatography analysis (SEC) were carried out with water (with addition of 0.1 M NaCl, 0.1% TFA, 0.01% NaN_3) as eluting solvent at 30^{o}C with a flow rate of 1 mL/ min using a high pressure liquid chromatography pump (Agilent 1100) and refractive index detector (Wyatt, Optilab DSP). Three columns with PSS Novema gel were applied. The length of each column was 300 mm, the diameter was 8 mm, the diameter of the gel particles were 10 µm and the nominal pore widths were 30, 3000 and 3000 Å. Calibration was achieved using Pullulan standards.

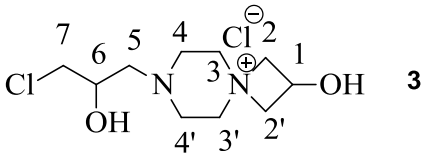
Synthesis:

Preparation of the bifunctional coupler 3:



To a solution of piperazine (**1**) (3.3 g, 0.038 mol) in water (25 mL), epichlorohydrin (**2**) (6 mL, 0.076 mol) was added. The mixture was stirred for 2 days at 25°C. Then water was removed in vacuum. The bifunctional coupler **3** was obtained as a white solid (> 95% purity). Further purification was achieved by extracting the aqueous solution of the coupler with dichloromethane before removal of the water in vacuum.

Yield: > 95%



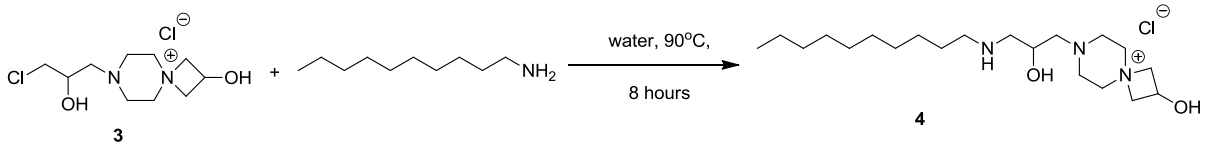
3

^{1}H NMR (DMSO-d^{6}, 400MHz): δ = 6.70 & 5.36 (d, OH), 4.65 (m, H^{1}), 4.49 & 4.17 (m, H^{2}, H$^{2'}$), 3.84 (m, H^{6}), 3.7-3.4 (m, H^{3}, H$^{3'}$, H^{7}), 2.8-2.4 (m, H^{4}, H$^{4'}$, H^{5}) ppm. **^{13}C NMR** (DMSO-d^{6}, 100MHz): δ = 70.25 (C^{2}, C$^{2'}$), 67.83 (C^{6}), 60.58 (C^{3}), 59.59 (C$^{3'}$), 58.84 (C^{5}), 57.72 (C^{1}), 48.33 (C^{7}), 47.88 (C^{4}), 47.54 (C$^{4'}$) ppm.

Elemental analysis ($C_{10}H_{20}Cl_2N_2O_2$): calculated C: 44.29%, H: 7.43%, N: 10.33%, found: C: 44.15%, H: 7.82%, N: 10.35%

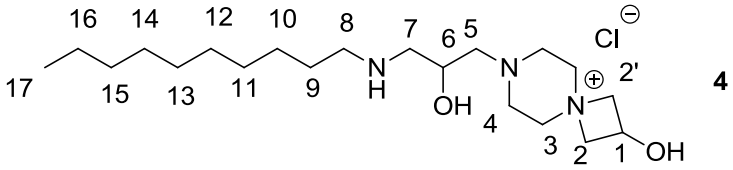
Raman spectrum: 750-650 cm^{-1} (C-Cl bond)

Model reaction of the bifunctional coupler with decyl amine (preparation of the functionalized coupler 4):



To a solution of coupler **3** (1.36 g, 5.00 mmol) in distilled water (5 mL), decyl amine (0.787 g, 5.00 mmol) was added. The solution was stirred for 8 hours at 90°C and then cooled down to room temperature. Removal of water yielded the pure functionalized coupler **4**.

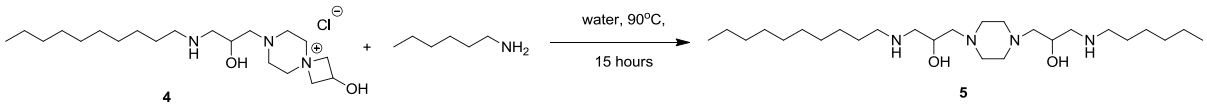
Yield: > 95%



^{1}H NMR (DMSO-d^{6}, 400MHz): δ = 4.63 (m, H^{1}), 4.48 & 4.12 (m, H^{2}, H$^{2'}$), 3.7-3.2 (m, H^{3}, H^{6}), 2.9-2.1 (m, H^{4}, H^{5}, H^{7}, H^{8}), 1.7-1.1 (m, H^{9}, H^{10}, H^{11}, H^{12}, H^{13}, H^{14}, H^{15}, H^{16}), 0.84 (m, H^{17}) ppm. **^{13}C NMR** (DMSO-d^{6}, 100MHz): δ = 69.16 (C^{2}, C$^{2'}$), 64.26 (C^{6}), 60.68 & 59.89 (C^{3}, C$^{3'}$), 58.91 (C^{5}), 57.74 (C^{1}), 53.39 (C^{7}), 47.94-47.59 (C^{4}, C$^{4'}$), 38.67 (C^{8}), 31.25 (C^{9}), 28.87 (C^{10}), 28.81 (C^{11}), 28.65(C^{12}), 28.53 (C^{13}), 26.89 (C^{14}), 25.86 (C^{15}), 22.05(C^{16}), 13.91 (C^{17}) ppm.

Elemental analysis ($C_{20}H_{42}ClN_3O_2$, HCl, ½ H_2O): calculated C: 54.91%, H: 10.14%, N: 9.60%, found: C: 54.96%, H: 10.12%, N: 9.14%

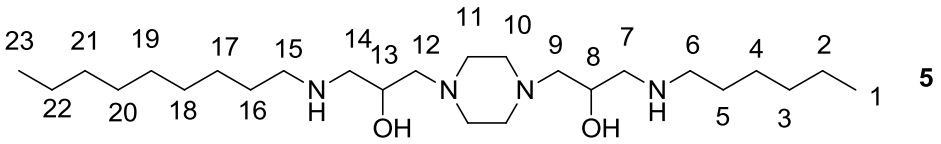
Model reaction of the functionalized coupler with primary amines (preparation of the coupling product 5):



4 5

To a solution of functionalized coupler **4** (1.96 g, 5.00 mmol) in distilled water (5 mL), hexyl amine (0.506 g, 5.00 mmol) was added. The solution was stirred for 15 hours at 90°C and then cooled down to room temperature. Removal of water yielded the coupling product **5**.

Yield: > 90%

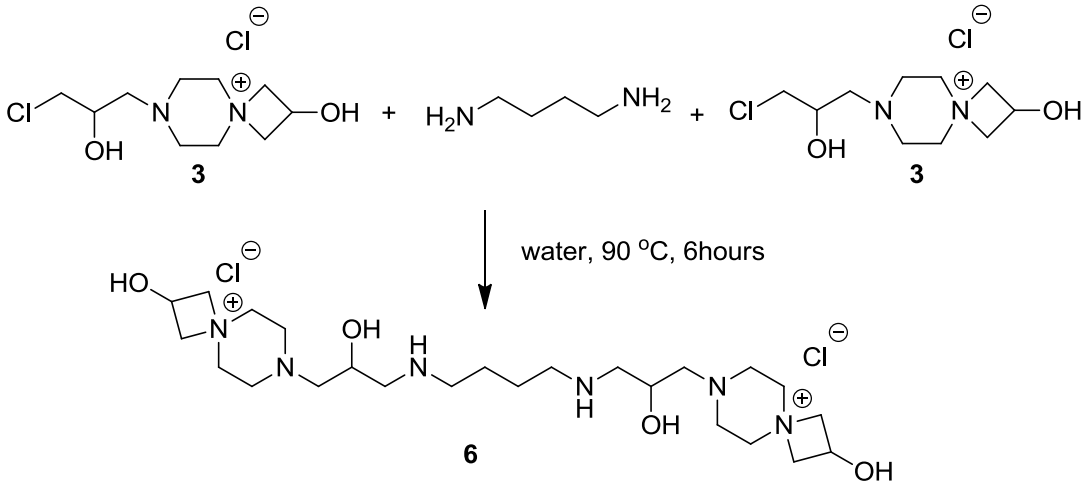


5

^{1}H NMR (DMSO-d^{6}, 400MHz): δ = 3.9 (m, H^{8}, H^{13}), 3-2.4 (m, H^{6}, H^{7}, H^{9}, H^{10}, H^{11}, H^{12}, H^{14}, H^{15}), 1.8-1.2 (m, H^{2}, H^{3}, H^{4}, H^{5}, H^{16}, H^{17}, H^{18}, H^{19}, H^{20}, H^{21}), 0.856 (m, H^{1}, H^{23}) ppm.

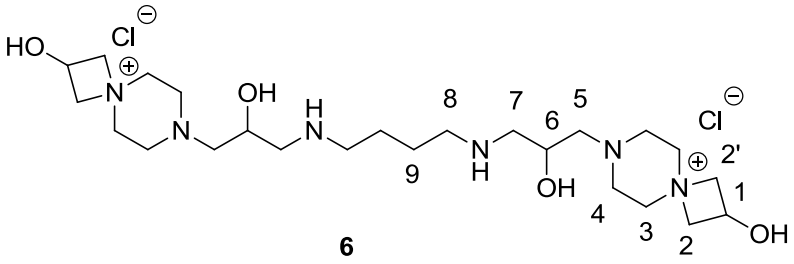
^{13}C NMR (DMSO-d^{6}, 100MHz): δ = 63.61 & 63.38 (C^{8}, C^{13}), 53.26 (C^{9}, C^{12}), 51.49 (C^{7}, C^{14}), 47.12 (C^{10}, C^{11}), 31.26 (C^{16}), 30.7 (C^{5}), 28.5-28.8 (C^{4}, C^{17}), 26.86 (C^{18}), 26.02 (C^{19}), 25.7 (C^{20}), 25.49 (C^{21}), 25.49 (C^{3}), 22.069 (C^{22}), 21.86 (C^{2}), 13.93 (C^{23}), 13.82 (C^{1}) ppm.

Reaction of the bifunctional coupler with 1, 4-diaminobutane 2:1 moler ratio (Selective conversion of one functional group of the coupler, preparation of compound 6):



To a solution of coupler **3** (6.15 g, 22.68 mmol) in distilled water (24 mL), 1, 4-diaminobutane (1.0 g, 11.3 mmol) was added. The solution was stirred for 6 hours at 90^{o}C and then cooled down to room temperature. Removal of water yielded the pure product **6**.

Yield: > 95%

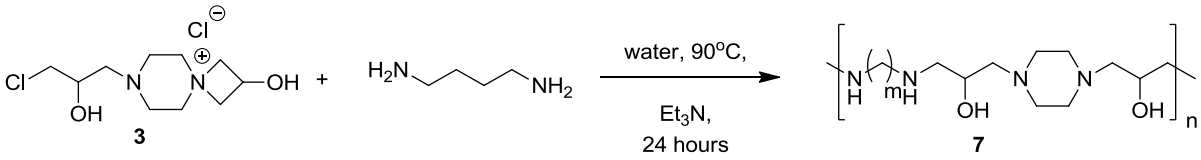


^{1}H NMR (DMSO-d^{6}, 400MHz): δ = 6.64 & 5.62 (OH), 4.66 (m, H^{1}), 4.53 & 4.17 (m, H^{2}, H$^{2'}$), 3.7-3.4 (m, H^{3}, H$^{3'}$, H^{6}), 2.8-2.4 (m, H^{4}, H$^{4'}$, H^{5}, H^{7}), 2.44 (m, H^{8}), 1.7 (m, H^{9}) ppm. **^{13}C NMR** (DMSO-d^{6}, 100MHz): δ = 70.36 (C^{2}, C$^{2'}$), 63.7 (C^{6}), 60.59 (C^{3}), 58.86 (C^{5}), 57.72 (C^{1}), 50.97 (C^{7}), 47.85-47.35 (C^{4}, C$^{4'}$), 37.92 (C^{8}), 23.84 (C^{9}) ppm.

Elemental analysis ($C_{24}H_{50}Cl_2N_6O_4$, 2HCl, 2½ H_2O): calculated C: 42.67%, H: 8.5%, N: 12.44%, found: C: 42.99%, H: 8.9%, N: 12.15%

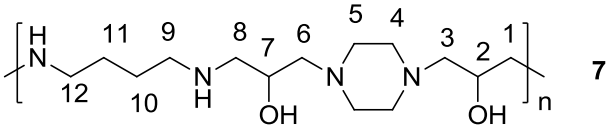
Use of the bifunctional coupler as a monomer to prepare multifunctional polymers via condensation polymerization:

Preparation of copolymers containing secondary hydroxyl groups, secondary and tertiary amine groups in the backbone 7:



3 7

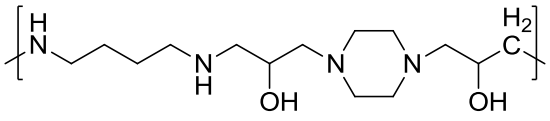
To a solution of bifunctional coupler **3** (1.49 g, 0.0055 mol) in distilled water (10 mL), 1,4-diaminobutane (0.487 g, 0.0055 mol) and triethylamine (0.55 g, 0.0055 mol) was added. The solution was allowed to stir for 24 hours at reflux and then cooled down to room temperature. The polymer **7** was purified by dialysis.



7

^{1}H NMR (D_2O, 400MHz): δ = 4.05 (H^2, H^7), 3.6-3.3 ($H^{chain\ end}$), 3.1-2.2 (H^1, H^3, H^4, H^5, H^6, H^8, H^9, H^{12}), 1.8-1.4 (m, H^{10}, H^{11}) ppm.

Elemental analysis: Calculated considering one repeating unit as following



, 2 HCl, 3 H_2O

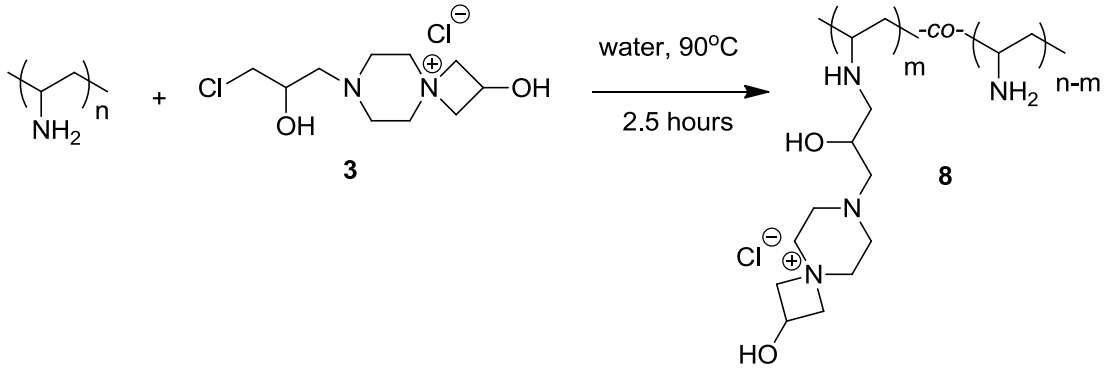
Calculated: C: 40.48%, H: 9.27%, N: 13.55%, found: C: 40.97%, H: 9.92%, N: 12.96%

GPC analysis:

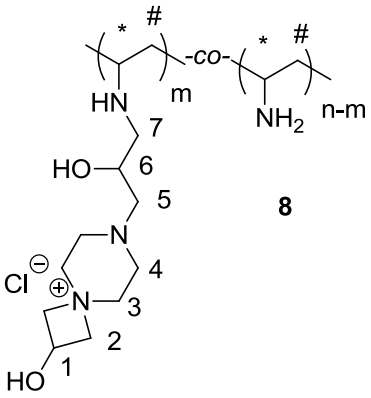
M_n = 1400, M_w = 1600, PDI = 1.1

Preparation of functional polymers:

Preparation of azetidinium functionalized poly(vinyl amine) 8 (procedure for 20% functionalization of the amine groups using the bifunctional coupler 3):



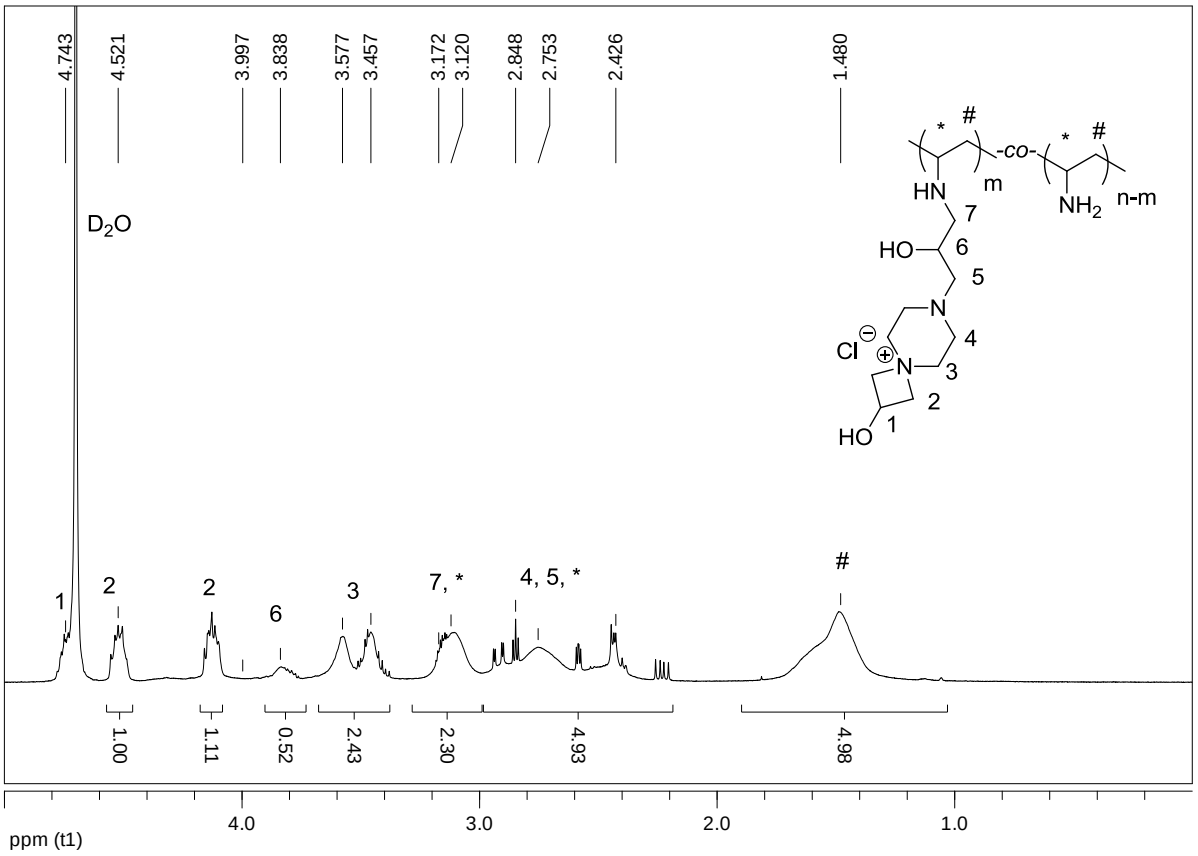
To a solution of poly(vinyl amine) (0.09 g, 0.00209 mol repeating unit) in distilled water (10 mL), the bifunctional coupler **3** (0.114 g, 0.00042 mol) was added. The solution was stirred for 2.5 hours at 90°C and then cooled down to room temperature.



^{1}H NMR (D_2O, 400MHz): δ = 4.74 (m, H^1), 4.52 & 4.13 (m, H^2, $H^{2'}$), 3.84 (m, H^6), 3.6-3.4 (m, H^3), 3.2-3.0 (H^7, H^*), 2.8-2.6 (m, H^4, H5, H^7), 1.7-1.3 ($H^\#$) ppm.

Calculation for the degree of functionalization by ^{1}H NMR spectroscopy:

The degree of functionalization was calculated from the integration related to the protons H^2 (δ = 4.52 ppm) and the protons attached to the polymer backbone $H^\#$ (δ = 1.48 ppm)



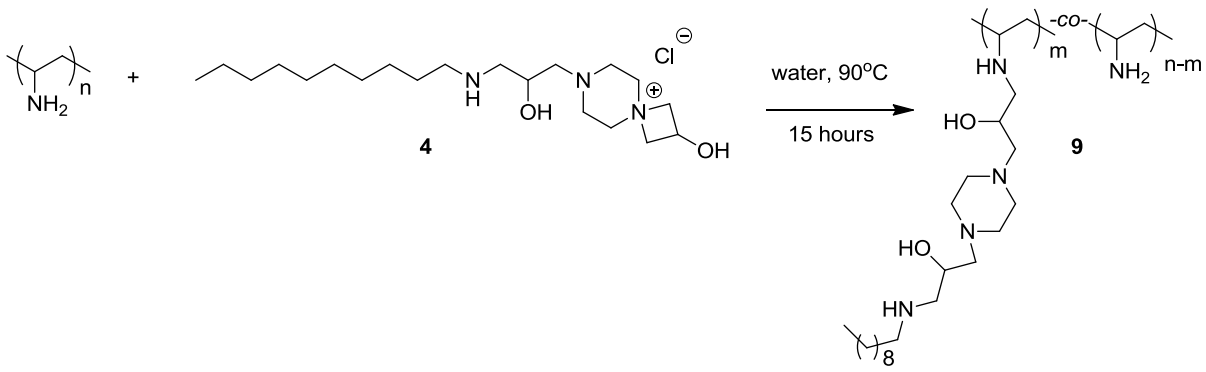
From the current NMR spectrum, I (H^2)/I ($H^{\#}$) = 4m/2n

2m/n = I (H^2)/I ($H^{\#}$) = 2.11/ 4.98

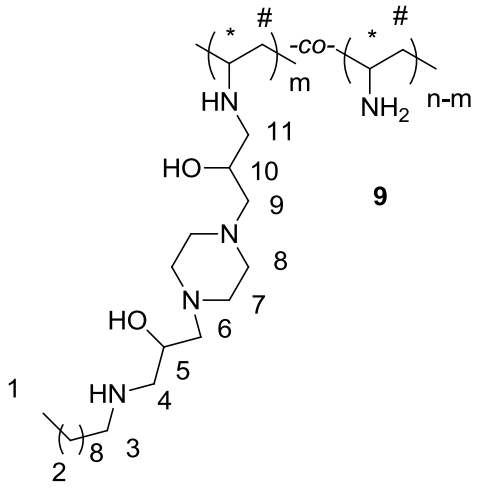
m/n = 1.055/4.98

m = 21.18% of n, (The expected functionalization was 20%)

Preparation of alkyl functionalized poly(vinyl amine) 9, (procedure for 20% functionalization of the amine groups using the functionalized coupler 4):



To a solution of poly(vinyl amine) (0.1 g, 0.002 mol repeating unit) in distilled water (8 mL), the functionalized coupler **4** (0.157 g, 0.0004 mol) was added. The solution was stirred for 15 hours at 90°C and then cooled down to room temperature.

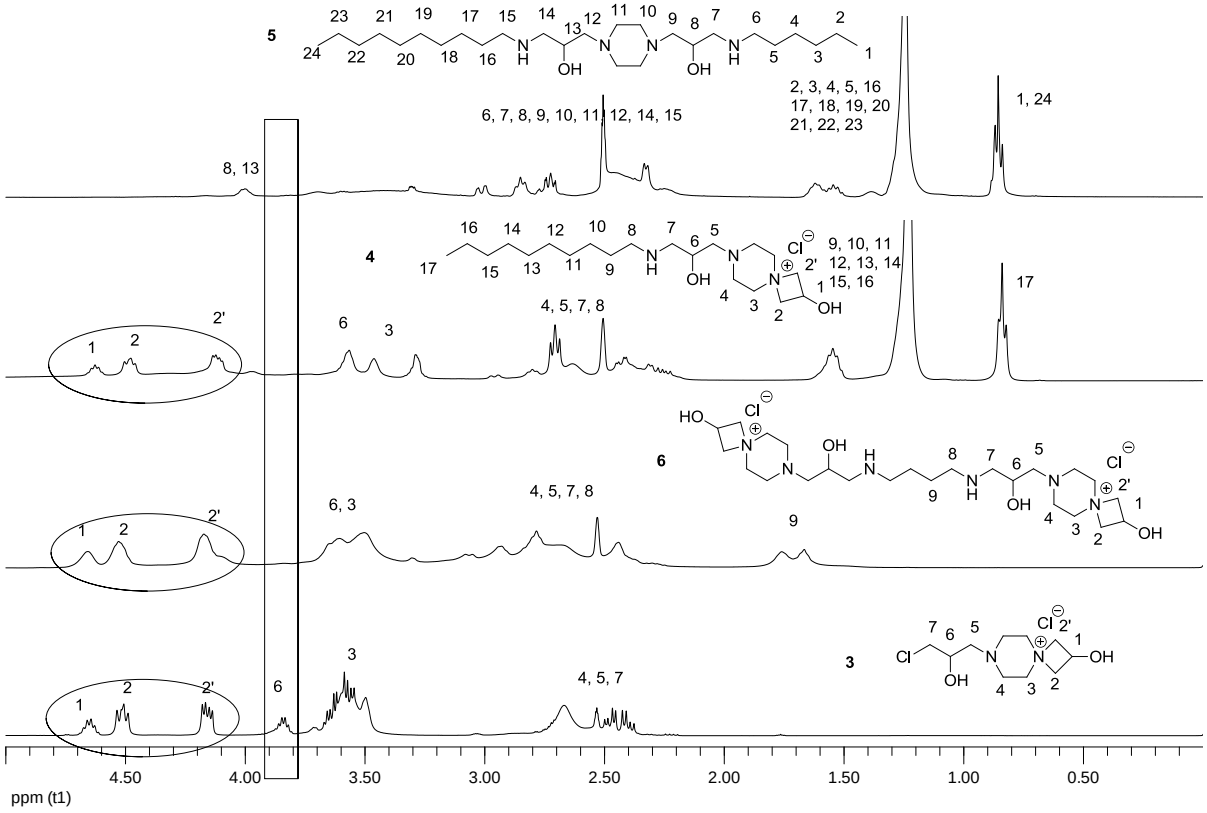


^{1}H NMR (CD_3OD, 400MHz): δ = 3.81 (m, H^5), 3.33 (m, H^{10}), 3.1 (m, H^6, H^7), 3-2.1 (m, H^3, H^4, H^6, H^9, H^{11}, H^*), 1.6-1.0 (m, H^2, $H^\#$), 0.92 (m, H^1) ppm.

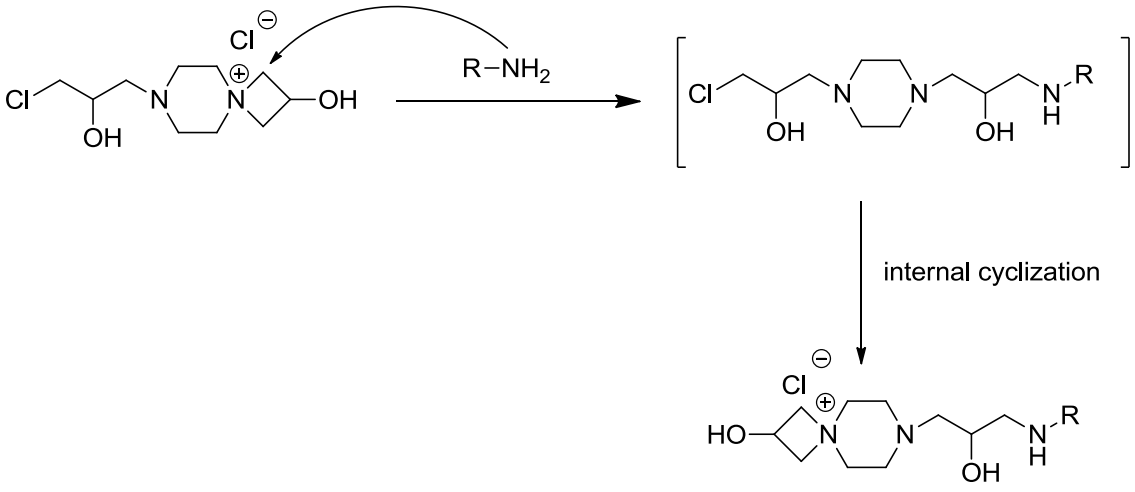
GPC analysis of the prepared PVAm polymers: For GPC analysis the above described polymers were prepared using HPLC grade water using the above mentioned procedure. The results are given below:

Polymer	M_n	M_w	PDI
Poly(vinyl amine) (PVAm)	$3.60 * 10^5$	$7.45 * 10^5$	2.07
Azetidinium functionalized PVAm **8**	$3.63 * 10^5$	$1.03 * 10^6$	2.83

Figure SI 1: ^{1}H NMR analysis for model reactions (DMSO-d^6):



Proposed mechanism for the reaction of the bifunctional coupler with primary amines:



Network formed by crosslinking during prolonged heating of azetidinium functionalized PVAm **8 :**