

SUPPLEMENTARY INFORMATION

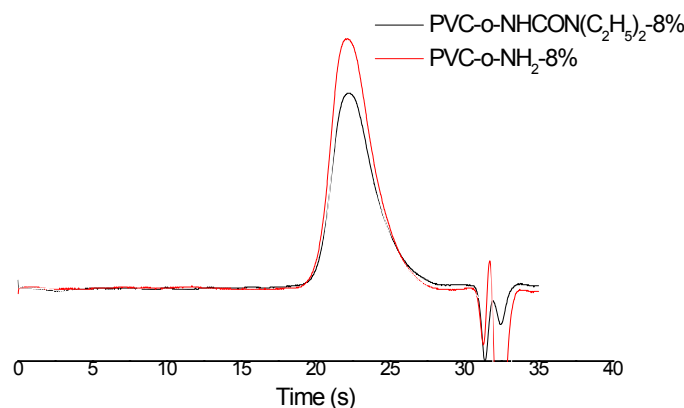
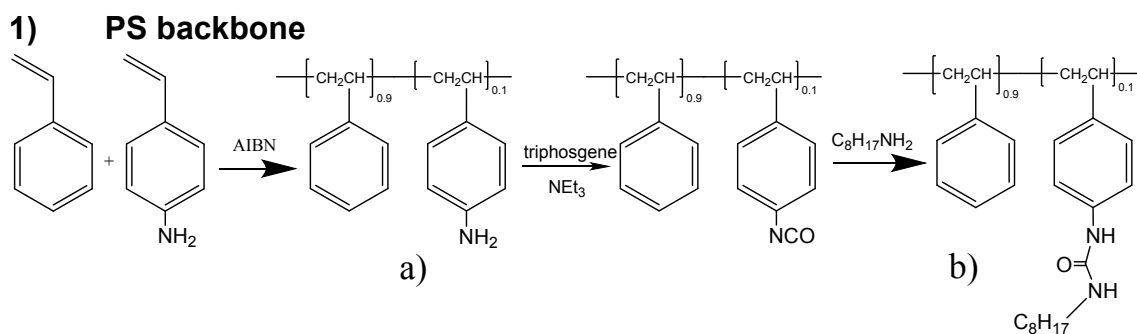


Figure S1: GPC traces of aminated PVC and corresponding polymer after transformation into a multi-isocyanate compound and subsequent reaction with diethylamine.



Preparation of PS carrying NCO groups

1 g (9.5 mmol) of PS-NH₂-10% obtained by classical AIBN initiated radical copolymerization of styrene with 10 mol% of 4-aminostyrene, was dissolved in 100 mL of methylene chloride and 0.27 mL (2.0 mmol) of triethylamine were added. This solution was poured at room temperature to a stirred solution of 95 mg (0.32 mmol) triphosgene in 25 mL methylene chloride. After five minutes reaction the mixture was washed twice with ice/water in order to eliminate the quaternary salts formed, the organic phase was dried over anhydrous MgSO₄

and the solution filtered and precipitated in hexane. After drying 950 mg of PS-NCO-10% were obtained.

Preparation of PVC-NHCON(C₂H₅)₂-8%

950 mg of PS-NCO-10% were dissolved in 50 mL of dry THF, 0.29 mL (1.0 mmol) bis-(2-ethyl-hexyl) amine were added and the mixture stirred for 1 hour at 40 °C. Then, the mixture was precipitated in methanol and the obtained polymer purified by three solution-precipitation cycles in THF-methanol. 1 g soluble polymer whose ¹H-NMR spectrum is shown in figure 2 was obtained.

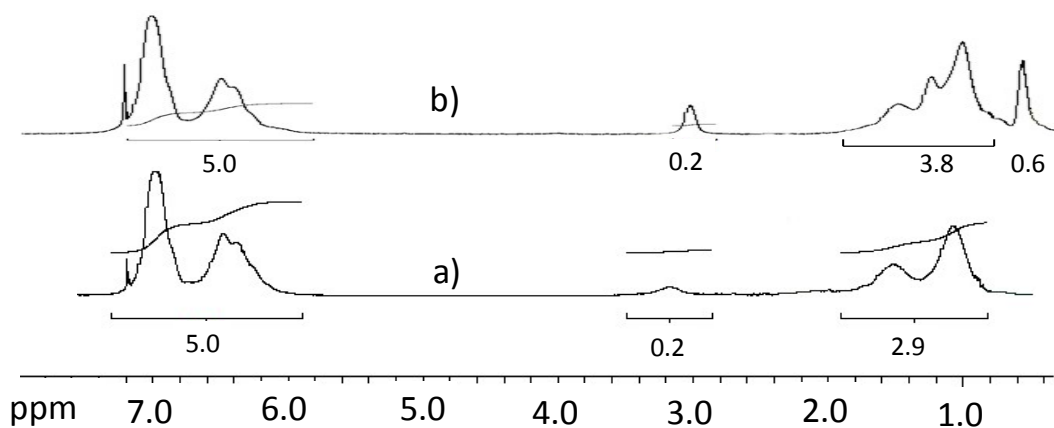
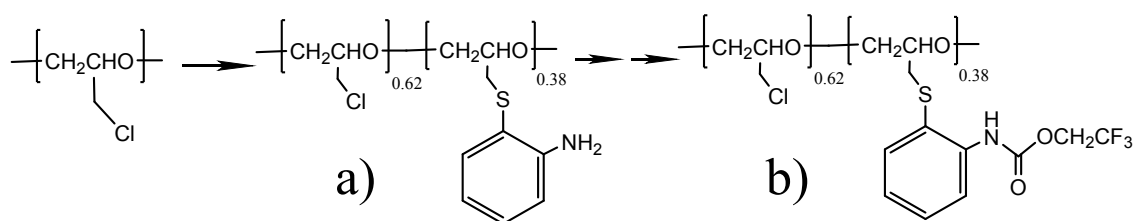


Figure S2: ¹H-NMR spectra of a) copolymer containing 90 mol% styrene and 10 mol% 4-aminostyrene (PS-NH₂-10%) and b) after transformation into the corresponding multi-isocyanate which subsequently reacted with bis-(2-ethyl-hexyl) amine. (¹H-NMR-spectra recorded in CDCl₃)

2) PECH backbone

a) Subsequent reaction with 2,2,2-Trifluoroethanol



Preparation of PECH carrying NCO groups

1 g (7.9 mmol) of PECH-NH₂-38% obtained by nucleophilic substitution of PECH with 2-Aminothiophenol/NaOH in Cyclohexanone at 60°C for 3 hours (purification by three precipitation/solution cycles in methanol/CH₂Cl₂), was dissolved in 100 mL of methylene chloride and 0.84 mL (6.0 mmol) of triethylamine were added. This solution was poured at room temperature to a stirred solution of 298 mg (1.0 mmol) triphosgene in 25 mL methylene chloride. After five minutes reaction the mixture was washed twice with ice/water in order to eliminate the quaternary salts formed, the organic phase was dried over anhydrous MgSO₄ and the solution filtered and precipitated in hexane. After drying 980 mg of PECH-NCO-38% were obtained.

Preparation of PECH-NHCOOCH₂CF₃-38%

980 mg of PECH-NCO-38% were dissolved in 50 mL of dry CH₂Cl₂, 0.240 mg (2.4 mmol) 2,2,2-Trifluoroethanol were added and the mixture stirred for 1 hour at 40 °C. Then, the mixture was precipitated in methanol and the obtained polymer purified by three solution-precipitation cycles in CH₂Cl₂-methanol. 1.2 g polymer whose ¹H-NMR spectrum is shown in figure 2 was obtained.

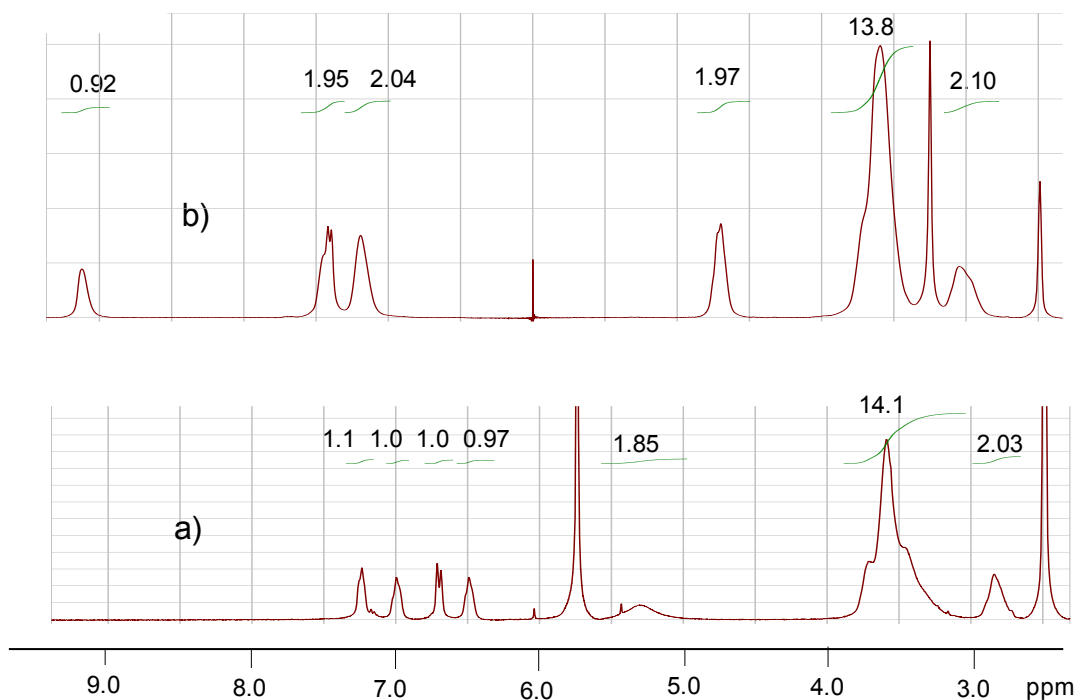


Figure S3: $^1\text{H-NMR}$ spectra of a) pure polyepichlorohydrin (PECH) chemically modified by substitution of 38 mol% of chlorine atoms by *o*-aminothiophenolate (below) and b) after transformation of the aromatic amine groups into the corresponding multi-isocyanate and subsequent reaction with equimolar amounts (with respect to the number of NCO groups) of 2,2,2-Trifluoroethanol (above). ($^1\text{H-NMR}$ -spectra recorded in mixtures of deuterated DMSO and CD_2Cl_2).

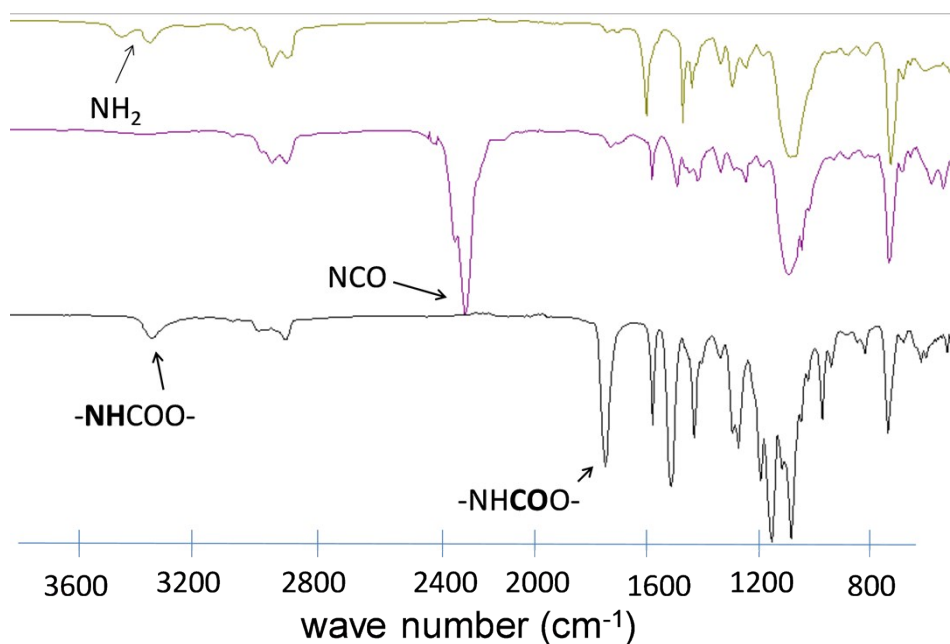
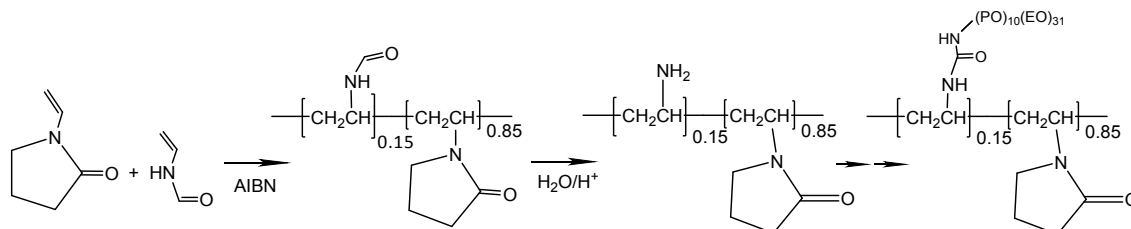


Figure S4: IR spectra of PECH-NH₂-38% (yellow), PECH-NCO-38% (violet) and of the corresponding polymer after reaction with 2,2,2-Trifluoroethanol (black).

3) PVP backbone



Preparation of PVP carrying NCO groups

PVP carrying aliphatic amine groups was obtained by radical AIBN initiated copolymerization of vinylpyrrolidone and 15 mol% vinylformamide in water. After hydrolysis of the formamide groups in water/H₂SO₄ at 80°C the reaction mixture was purified by dialysis and dried. 1 g (9.5 mmol) of PVP-NH₂-15% was dissolved in 100 mL of methylene chloride and 0.41 mL (2.9 mmol) of triethylamine were added. This solution was poured at room temperature to a stirred solution of 141 mg (0.5 mmol) triphosgene in 25 mL methylene chloride. After five minutes reaction the mixture was used without further purification for the subsequent reaction with amine.

Preparation of PVP-Jeffamine-15%

To the reaction solution of crude PVP-NCO-15% from above 2.96 g (1.4 mmol) Jeffamine-M2070 dissolved in 5 ml CH₂Cl₂ were added and the mixture stirred for 30 minutes at room temperature. Then, the mixture was subjected to dialysis in water. 2.8 g polymer whose ¹H-NMR spectrum is shown in figure 2 was obtained.

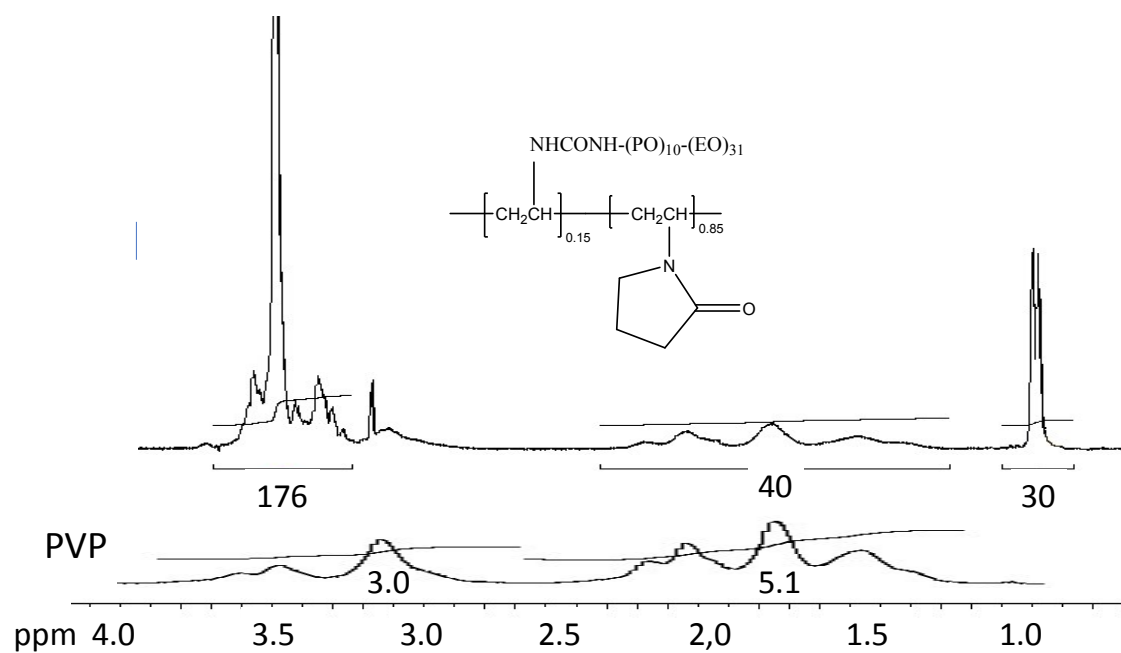


Figure S5:

¹H-NMR spectra of a) Vinylpyrrolidone (VP) copolymerized with 15 mol% vinylformamide and b) polymer obtained after hydrolysis of the copolymer and reaction via multi-isocyanate with a mono-amine terminated (ethylenoxide-propyleneoxide) oligomer (Jeffamine-M2070).

¹H-NMR-spectra recorded in D₂O)