Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Poly(acrylamide-homocysteine thiolactone) as a synthetic platform for the preparation of polymeric ionic liquids by post ring-opening-orthogonal modifications

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1.1. Chemicals

DL-homocysteine thiolactone hydrochloride, 2-chloropropylamine hydrochloride, 1-methyl-imidazole, lithium bis(trifluoromethane)sulfonimide, potassium hydroxide, 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTBSPA), cyanomethyl dodecyl trithiocarbonate (CMDTTC), triethylamine, ethanolamine, propylamine, 1-bromobutene, acrylic acid, methyl acrylate, hydroxyethyl methacrylate, chloromethylstyrene, 1.4-dioxane, DMF, DMSO, diethyl ether were purchased from Sigma Aldrich and used without further purification. Magnesium sulfate, sodium chloride, sodium hydrocarbonate were purchased from Riedel-de Haën (Seelze, Germany) and used without further purification. Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich and recrystallized from methanol before use.

1.2. Characterisation methods

Surface morphology of the electrospun films was observed under a scanning electron microscope (SEM) (JEOL 7001F) after platinum coating. The diameter of the fibers was measured on the basis of SEM images. IR spectroscopy was used to monitor the synthesis of the monomers and polymers. The FT-IR spectra were obtained at 4 cm^{-1} resolution for the 4000 to 600 cm^{-1} spectral range using a spectrometer (JASCO FT/IR-6200) equipped with an ATR (MIRacle single-reflection ATR diamond/ZnSe) or alternatively a Perkin Elmer Spectrum One P03011 Calorimetry was performed using a differential scanning calorimeter (DSC) (DSC8, Perkin Elmer or alternatively DSC Q2000 TA) in a nitrogen atmosphere at 10 ºC/min heating rate. Elemental analyses were obtained with a CHN Euro EA 3000 instrument.

TGA curves were measured on a TGA 850 Mettler Toledo Star. A 70 µl alumina crucible with approximately 5 mg of the polymer and the reference crucible of the same material were placed in the instrument. A temperature scan was performed in the 30-600 ^{o}C range at a constant heating rate of 10 ^{o}C/min, the purge gas was nitrogen at 50 mL/min.

Molecular weight distribution and polydispersity index (PDI) were analyzed by GPC using a Viscotek TDA 302 series system as an integrated instrument, including three HEMA-based columns (105/103/102 Å porosity) from MZ-Analysentechnik GmbH, a dual LS detector (7 and 90º), viscosimeter and RI detectors. The samples were run in DMF, HPLC grade containing 1 g/L of lithium bromide as an additive with a flow rate of 0.8 mL/min at 60 °C The apparatus was

calibrated with well-defined poly(methyl methacrylate) (PMMA)/DMF standards, provided by Polymer Standards Service (PSS)/Mainz Germany.

The polymeric mats were obtained using an electrospinner Fluidnatek LE 100.V1 (BioInicia, Spain).

1.3. Synthetic protocols

Synthesis of acryl homocysteine thiolactone (3).

Sodium hydrocarbonate (19.15 g, 227.9 mmol) were slowly added to an ice-cooled solution of DL-homocysteine thiolactone hydrochloride (**1**, 7.0 g, 45.6 mmol) in a 1:1 mixture of water/dioxane (100 mL). The resulting mixture was stirred for 30 min at 0 ºC. After this, acryloyl chloride (**2**, 8.3 g, 91.2 mmol) was added to the mixture in several portions. The reaction mixture was allowed to reach room temperature overnight. Brine (100 mL) was added and the mixture was extracted with ethyl acetate (3x200 mL). The organic fractions were dried with magnesium sulphate and the solvent vacuum concentrated. The crude residue was purified by column chromatography (silica gel, gradient elution 100 % CH_2Cl_2 followed by CH_2Cl_2:acetone 95:5). Yield – 80 %.

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 8.45 (*d*, 1H), 6.23 ((*dd*, 1H), 6.12 (*dd*, 1H), 5.65 (*dd*, 1H), 4.70 (*ddd*, 1H), 3.42 (*dt*, 1H), 3.30 (*ddd*, 1H), 2.44 (*m*, 1H), 2.09 (*m*, 1H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm) δ 205 (C=O), 131.0 (CH), 126.2 (CH_2), 58.2 (CH), 30.3 (CH_2), 26.8 (CH_2).

Synthesis of *N*-(3-aminopropyl)-*N*'-methyl imidazolium bromide ([APMIM][Br], 5e), 1-Methylimidazole (15 mL, 186 mmol) and 3-bromopropylamine hydrobromide (13.8 g, 61.8 mmol) were dissolved in toluene (23 mL). The mixture was refluxed for 4 hours under constant stirring. On completion, the solution was cooled down to room temperature and the toluene layer was decanted. The crude oil obtained was washed with diethyl ether (3x40 mL) and recrystallised in methanol and methyl *t*-butyl ether obtaining a white solid dried *in vacuo*. Yield 56 %. ^{1}H NMR (300 MHz, DMSO) δ 9.24 (s, 1H), 7.98 (s, 3H), 7.83 (s, 1H), 7.75 (s, 1H), 4.32 (t, *J* = 6.9 Hz, 2H), 3.86 (s, 3H), 2.88 – 2.76 (m, *J* = 7.3 Hz, 2H), 2.19 – 2.05 (m, 2H). ^{13}C NMR (300 MHz, DMSO): (δ, ppm) 136.6, 123.6, 122.0, 45.8, 35.9, 35.5, 27.4. IR (ATR): (ν, cm^{-1}) 661, 737, 785, 844, 870, 1013, 1054, 1174, 1340, 1381, 1397, 1416, 1441, 1458, 1521, 1544, 1560, 1577, 2511, 2530, 2651, 2749, 2813, 2924, 3041, 3075, 3142, 3422.

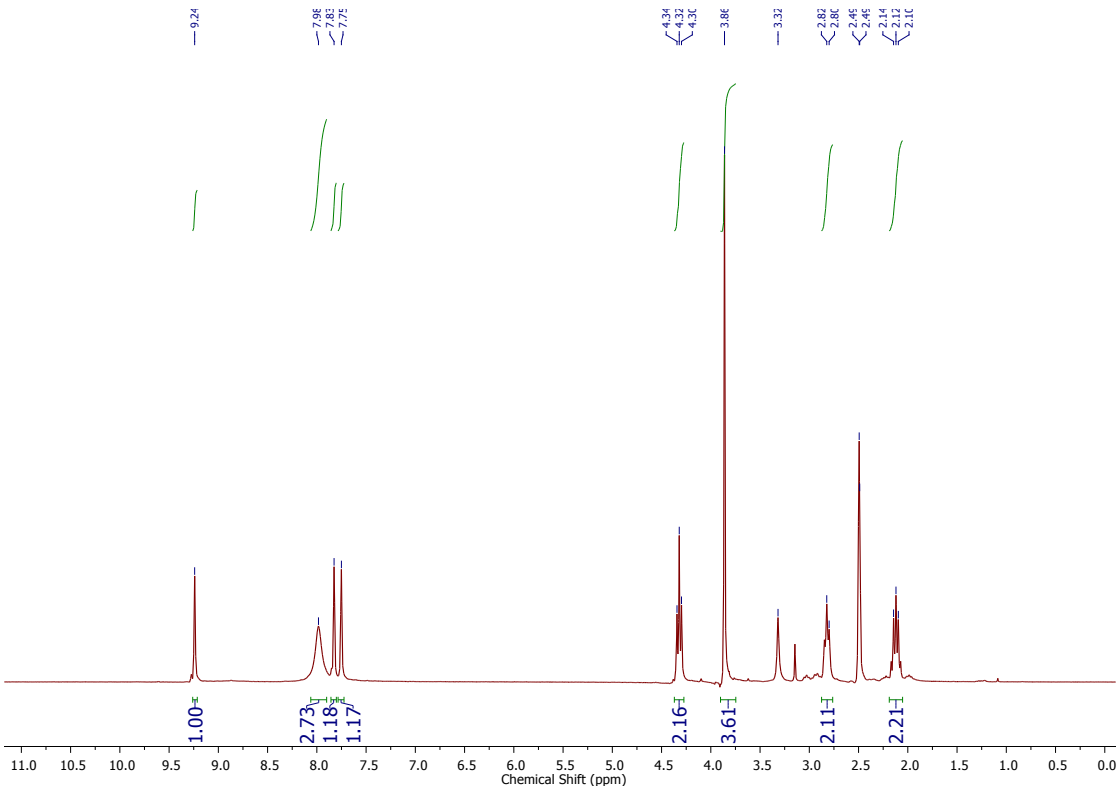


Figure S1. ^{1}H-RMN of **5e**.

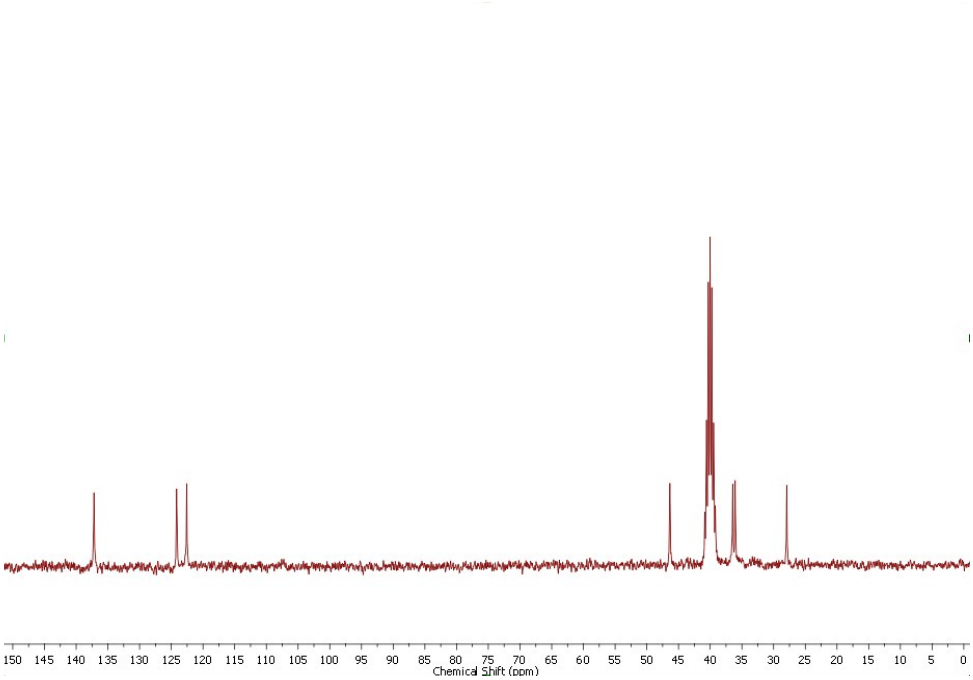


Figure S2. ^{13}C-RMN of **5e**.

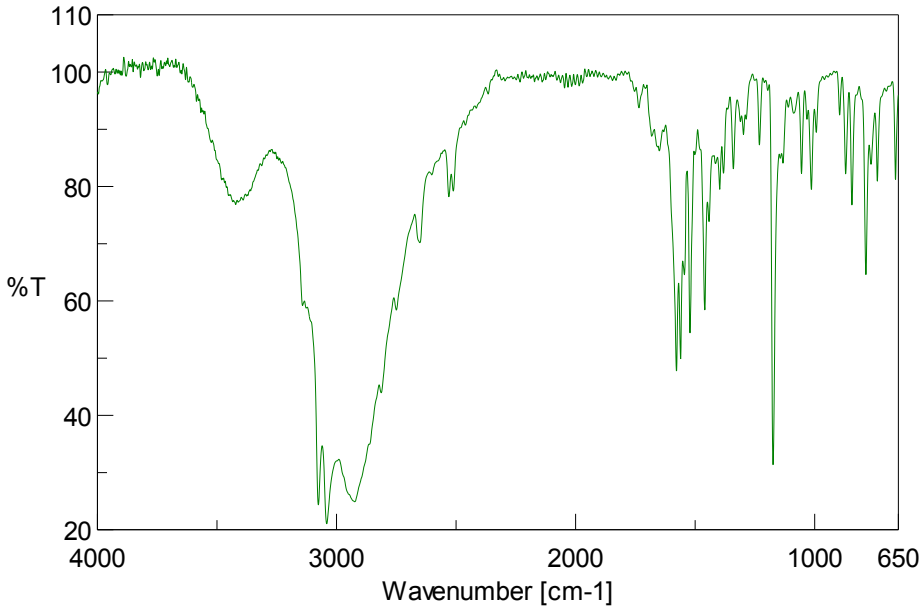


Figure S3. ATR-FT-IR of **5e.**

Synthesis of *N*-(3-aminopropyl)-*N'*-methyl imidazolium bis(trifluoromethylsulfonyl)imide ([APMIM][NTf_2], 5f)

N-(3-aminopropyl)-*N'*-methyl imidazolium bromide (5 g, 16.6 mmol) was dissolved in water (10 mL), the pH of the mixture was adjusted with potassium hydroxide to 8.0 and the mixture was left under stirring for 30 min. Lithium bistriflimide (5.8 g, 20 mmol) was added and the reaction allowed proceeding overnight at room temperature. The obtained crude oil was washed with diethyl ether (3x25 mL) and dried *in vacuo*. The final pure product was a light yellow viscous liquid. Yield – 82 %. ^{1}H NMR (500 MHz, DMSO) δ 9.09 (s, 1H), 7.75 (s, 1H), 7.69 (s, 1H), 4.23 (t, *J* = 7.0 Hz, 2H), 3.84 (s, 3H), 2.55 – 2.51 (m, *J* = 10.7, 4.1 Hz, 2H), 1.87 – 1.80 (m, 2H). ^{13}C NMR (500 MHz, DMSO): (δ, ppm) 136.7, 123.7, 122.2, 46.1, 36.2, 35.8, 28.6. IR (ATR): (v, cm^{-1}) 740, 762, 790, 838, 1051, 1132, 1178, 1328, 1347, 1463, 1574, 1601, 2886, 2962, 3120, 3159, 3305, 3370, 3601.

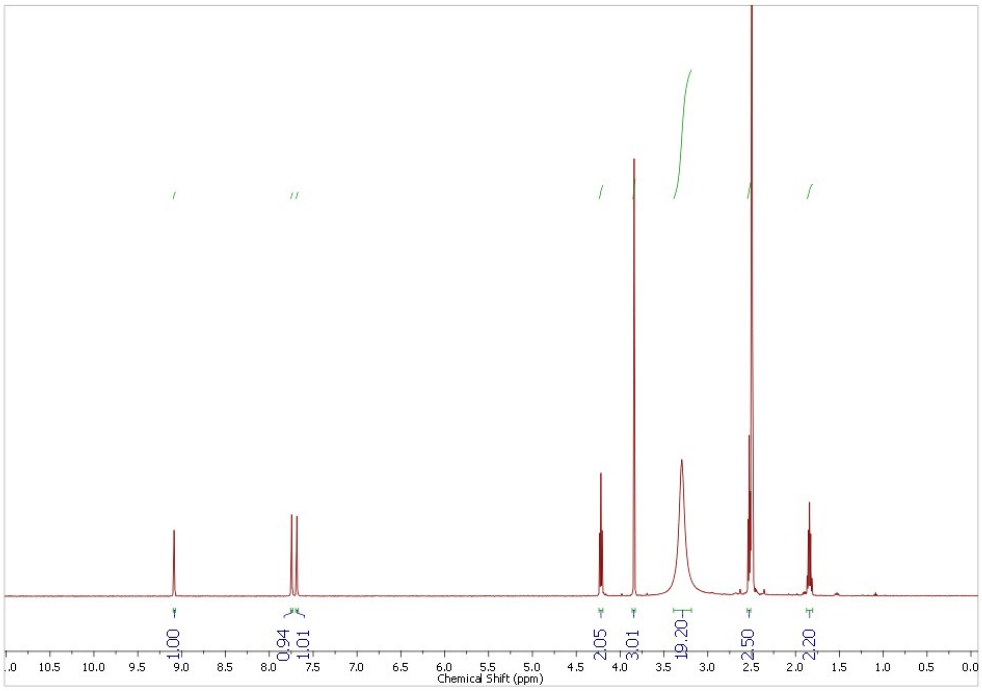


Figure S4. ^{1}H-RMN of **5f**.

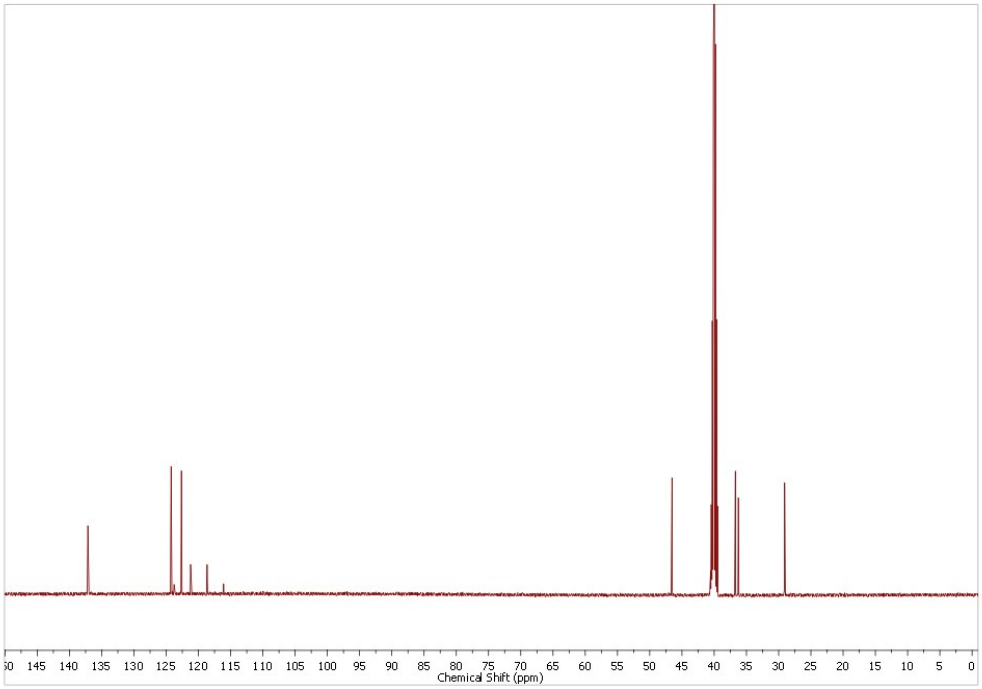


Figure S5. ^{13}C-RMN of **5f**.

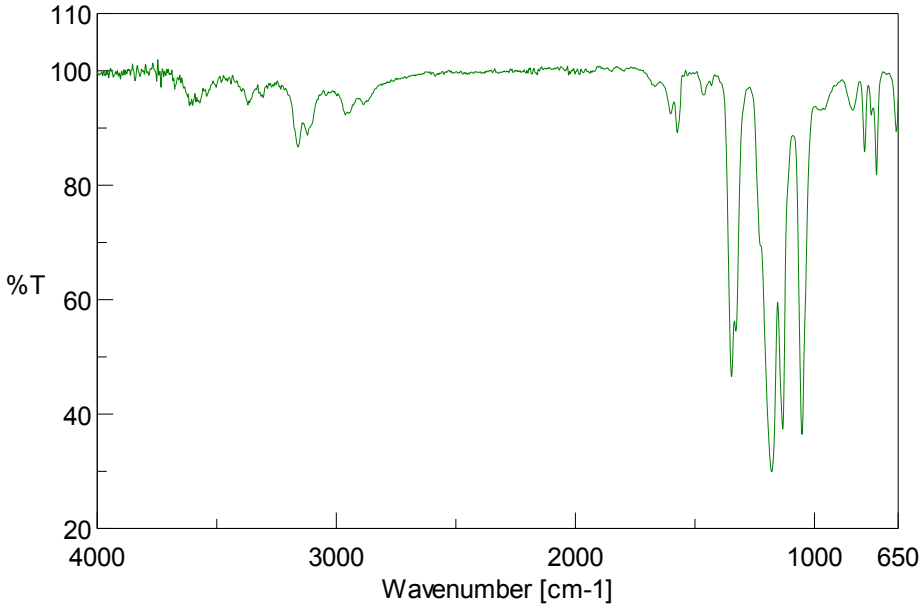


Figure S6. ATR-FT-IR of **5f.**

Synthesis of 3-allyl-1-methylimidazolium bromide (9c). A mixture of 1-methylimidazole (14.0 mmol, 1.127 mL) and allyl bromide (14.0 mmol, 1.249 mL) in 10 mL of ethanol was stirred during 24 h at reflux. Then the reaction was cooled at room temperature and the solvent evaporated under reduced pressure. The resulting oil was washed with Et_2O (3×10 mL) affording 3.32 g of **9c** as a yellow oil (86 %). ^{1}H-NMR ($CDCl_3$, 500.13 MHz): δ 10.32 (s, 1H), 7.47 (s, 1H), 7.36 (s, 1H), 6.03 (ddt, J = 16.6, 10.1, 6.4 Hz, 1H), 5.52-5.41 (m, 2H), 4.12 (c, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 137.1, 129.9, 123.9, 122.5, 122.0, 52.0, 36.8 ppm. IR (ATR): (ν, cm^{-1}) 3414, 3137, 3068, 2851, 1574, 1162, 757. Melting point: - 48.98ºC. MS (ESI^+, m/z): 83.4 [M-(C_3H_5)+H, 5%], 123.4 [(M^+, 100%].

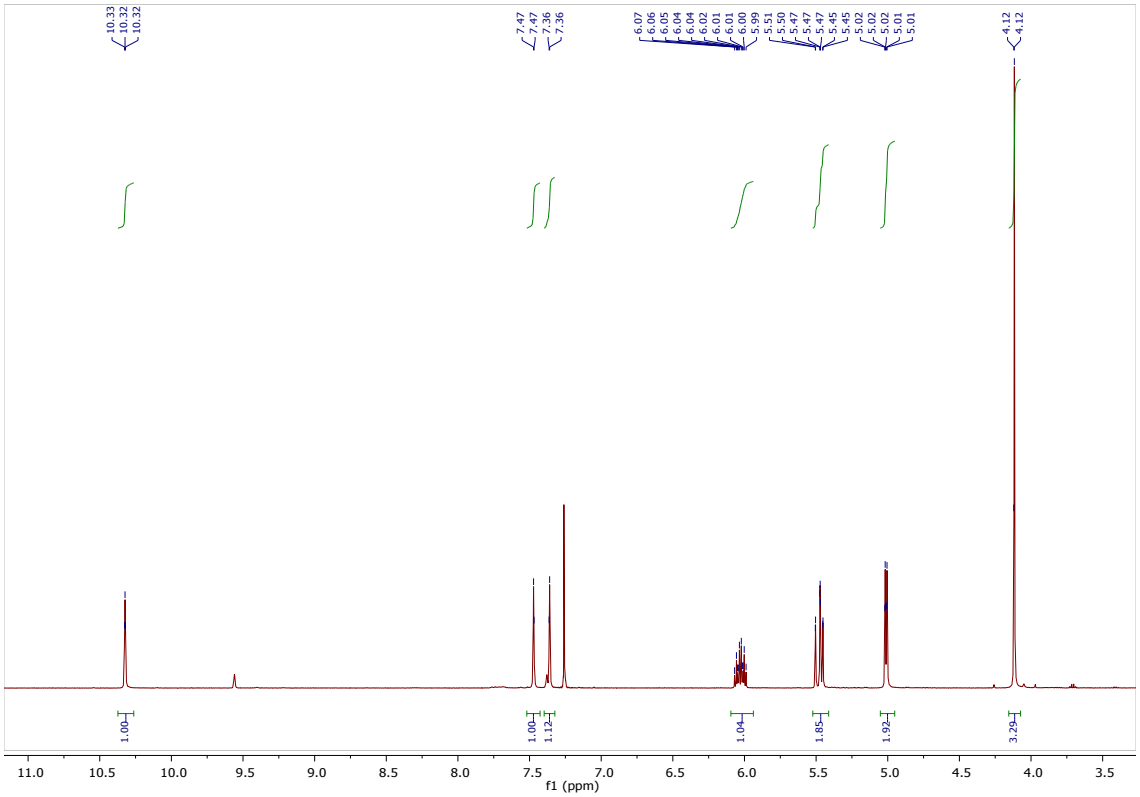


Figure S7. ^{1}H-RMN of **9c**.

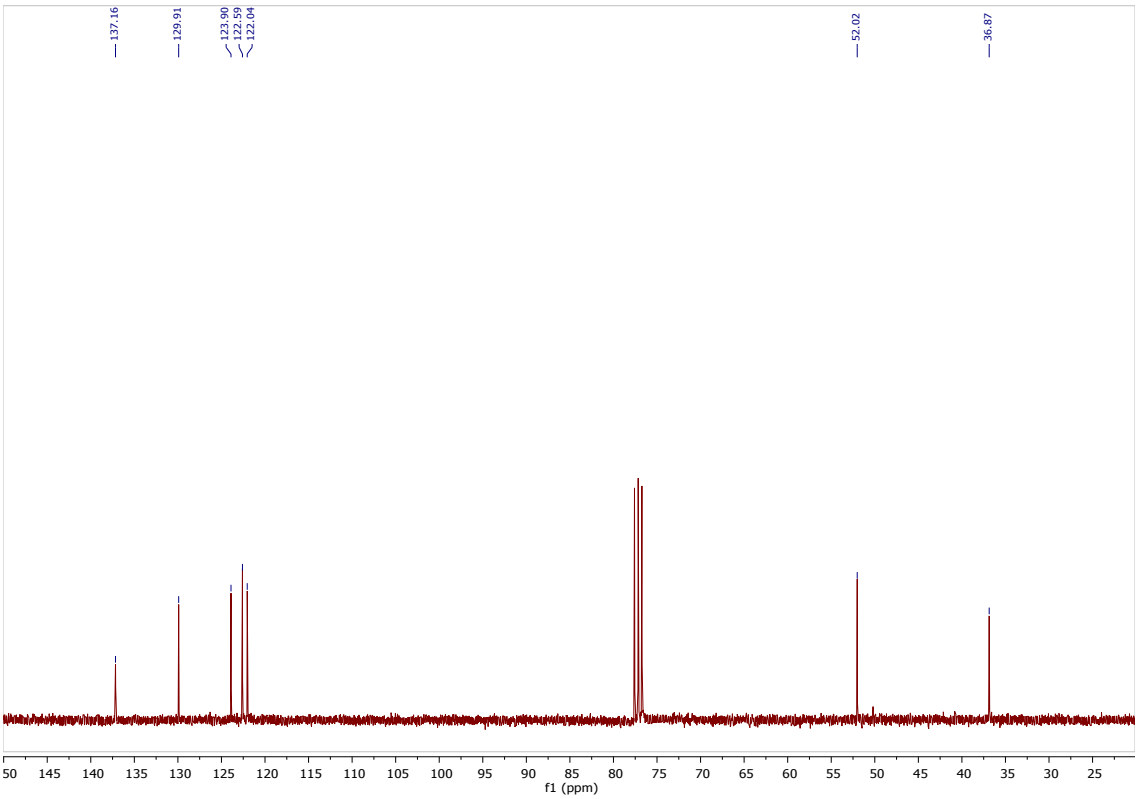


Figure S8. ^{13}C-RMN of **9c**.

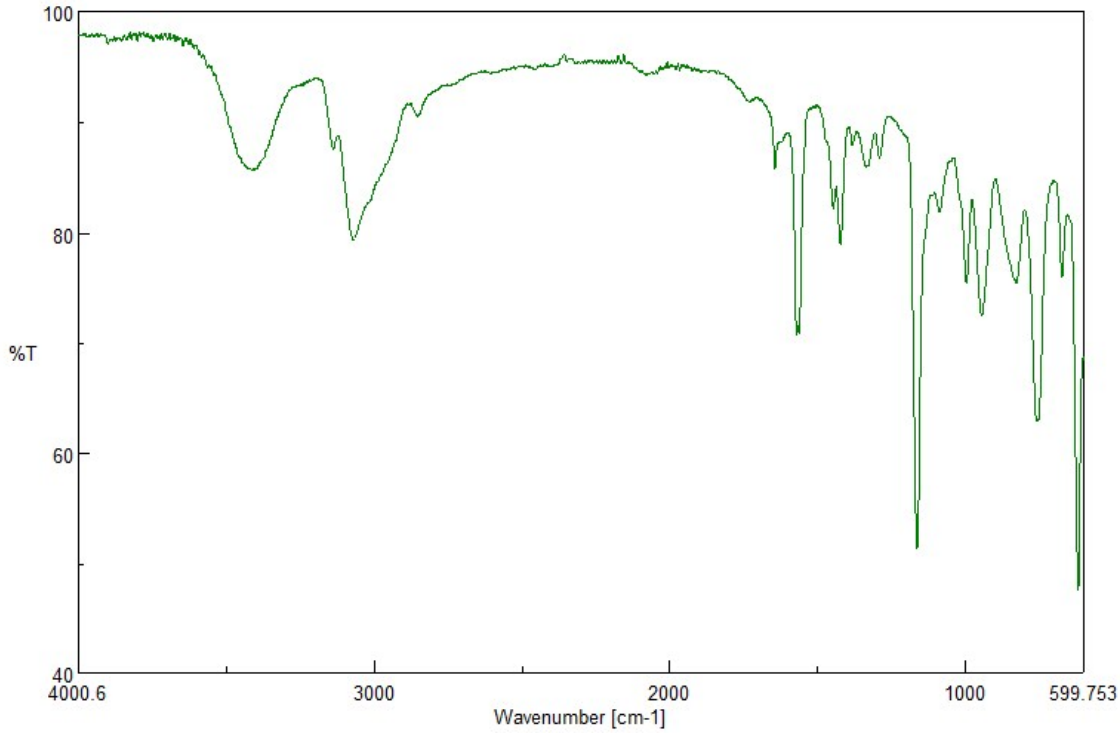


Figure S9. ATR-FT-IR spectra of **9c**.

Synthesis of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide. A mixture of 1-butylimidazole (9.9 mmol, 1.3 mL) and 4-bromo-1-butene (9.9 mmol, 1.0 mL) in 15 mL of ethanol was stirred during 24 h at reflux under nitrogen atmosphere. Then the reaction was cooled at room temperature and the solvent evaporated under reduced pressure. The resulting oil was washed with Et_2O (3×10 mL) affording 2.05 g of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide as a brown viscous liquid (79 %). ^{1}H-NMR ($CDCl_3$, 300.13 MHz): δ 10.51 (s, 1H), 7.42 (s, 1H), 7.35 (s, 1H), 5.88-5.75 (m, 1H), 5.11-5.02 (m, 2H), 4.49 (t, J = 6.8 Hz, 2H), 4.33 (t, J = 7.3 Hz, 2H), 2.68 (q, J = 6.8 Hz, 2H), 1.95-1.82 (m, 2H), 1.43-1.26 (m, 2H), 0.94 (td, J = 7.3, 4.9 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 136.5, 132.3, 122.4, 122.0, 119.2, 49.5, 48.8, 34.3, 31.9, 19.1, 13.2 ppm. IR (ATR): (ν, cm-1) 643, 754, 865, 920, 997, 1027, 1114, 1162, 1336, 1361, 1457, 1560, 1640, 2872, 2934, 2959, 3072, 3132, 3408.

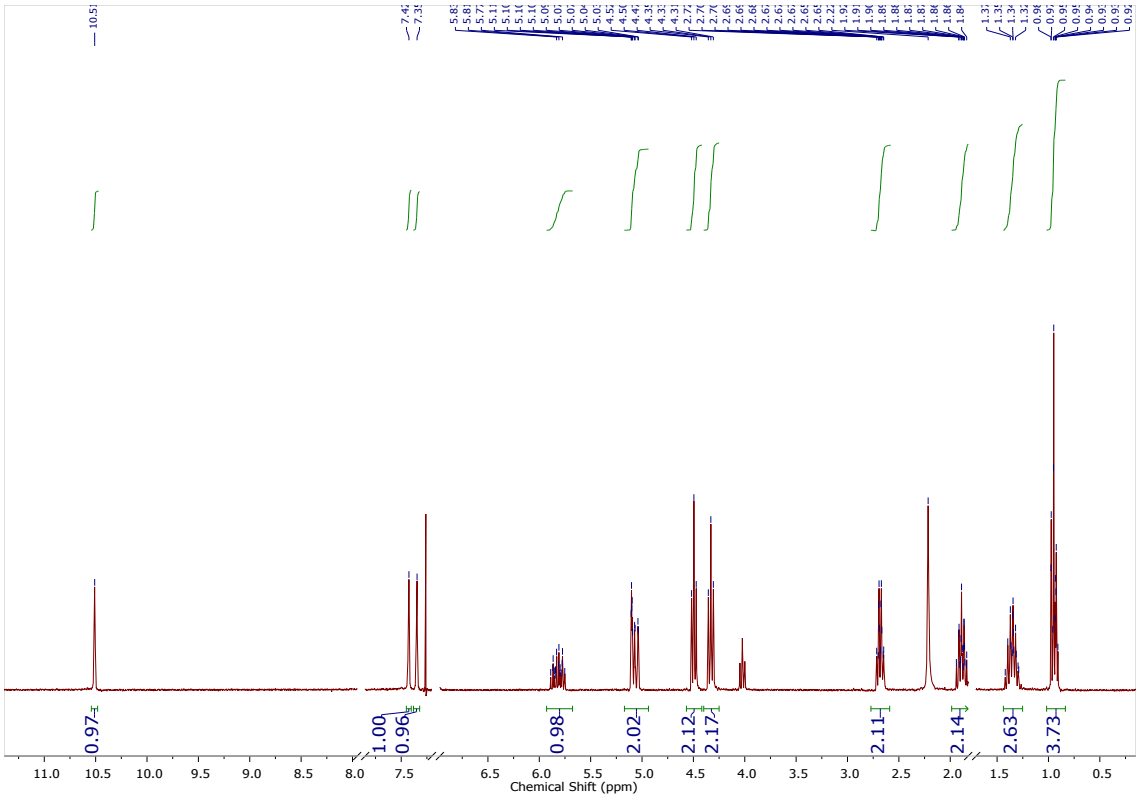


Figure S10. ^{1}H-RMN of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide.

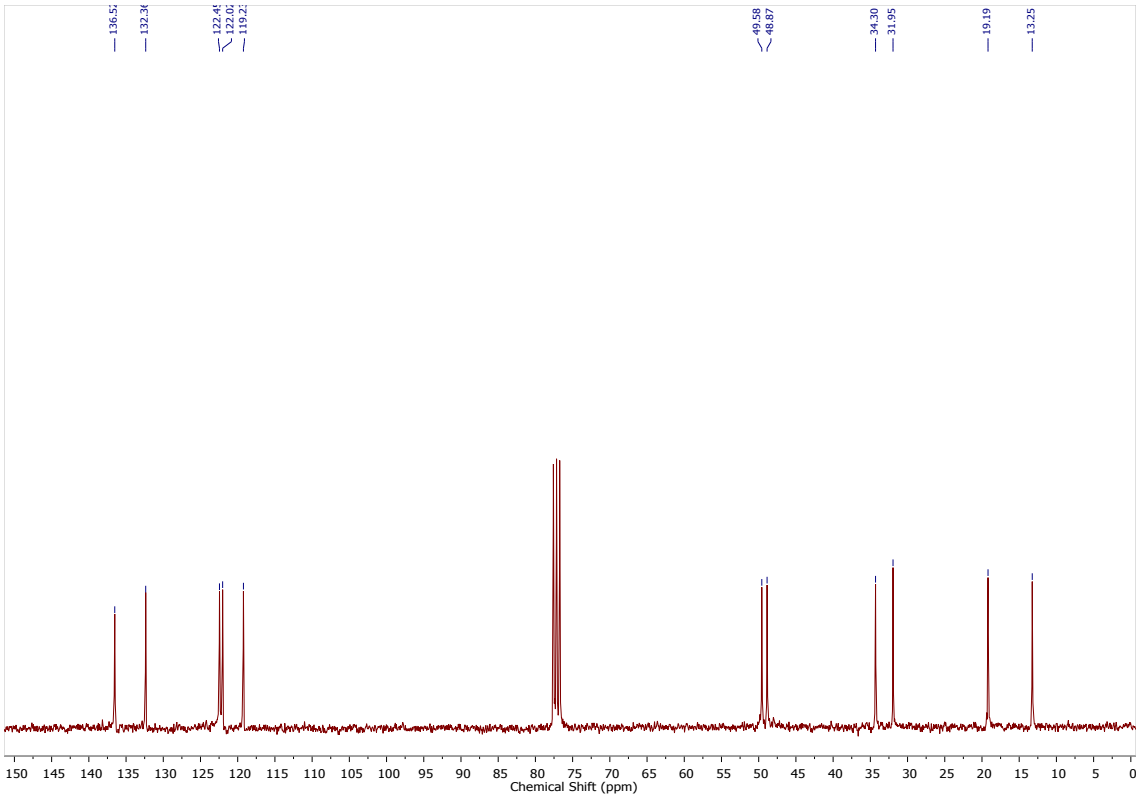


Figure S11. ^{13}C-RMN of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide.

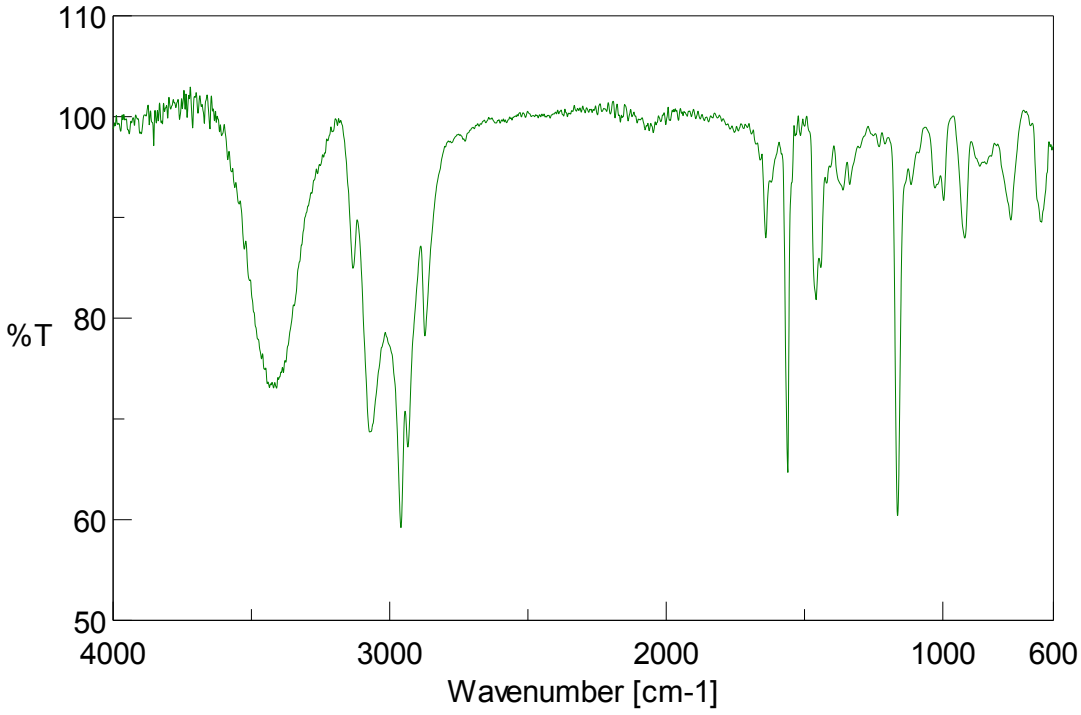


Figure S12. ATR-FT-IR spectra of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide.

Synthesis of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bis((trifluoro methyl) sulfonyl)amide (9b). To a solution of 3-(but-3-en-1-yl)-1-butyl-1H-imidazol-3-ium bromide (1.06 g, 3.8 mmol) in MeOH (3 mL) was added a mixture of lithium bis(trifluoromethane) sulfonimide (1.22 g, 4.2 mmol) in Milli-Q H_2O (1 mL), and the resulting solution was stirred for 24 h at room temperature. Then the MeOH was evaporated at reduced pressure and $CHCl_3$ (5 mL) was added to the mixture and the solution washed with Milli-Q H_2O (3×10 mL). The organic phase was dried over Na_2SO_4 and the solvent evaporated under reduced pressure affording 1.27 g of **9b** as a pale brown liquid (73 %).

^{1}H-NMR ($CDCl_3$, 300.13 MHz): δ 8.66 (s, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 5.30-5.20 (m, 1H), 4.58-4.49 (m, 2H), 3.76 (t, J = 6.8 Hz, 2H), 3.66 (t, J = 7.1 Hz, 2H), 2.10-2.04 (m, 2H), 1.31-1.22 (m, 2H), 0.78-0.69 (m, 2H), 0.40 (t, J = 7.3 Hz, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 135.4, 132.1, 122.6, 122.4, 119.7, 49.9, 49.3, 34.3, 32.0, 19.3, 13.2 ppm. IR (ATR): (ν, cm^{-1}) 604, 616, 651, 739, 788, 850, 929, 997, 1052, 1134, 1181, 1226, 1330, 1348, 1463, 1563, 2878, 2938, 2965, 3091, 3115, 3149.

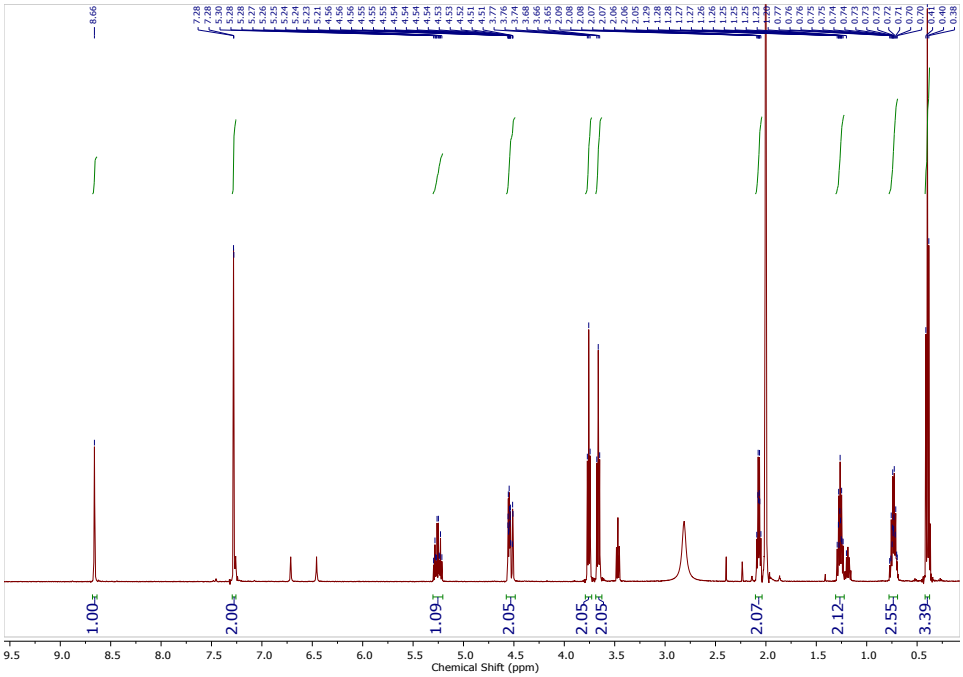


Figure S13. ^{1}H-RMN of **9b.**

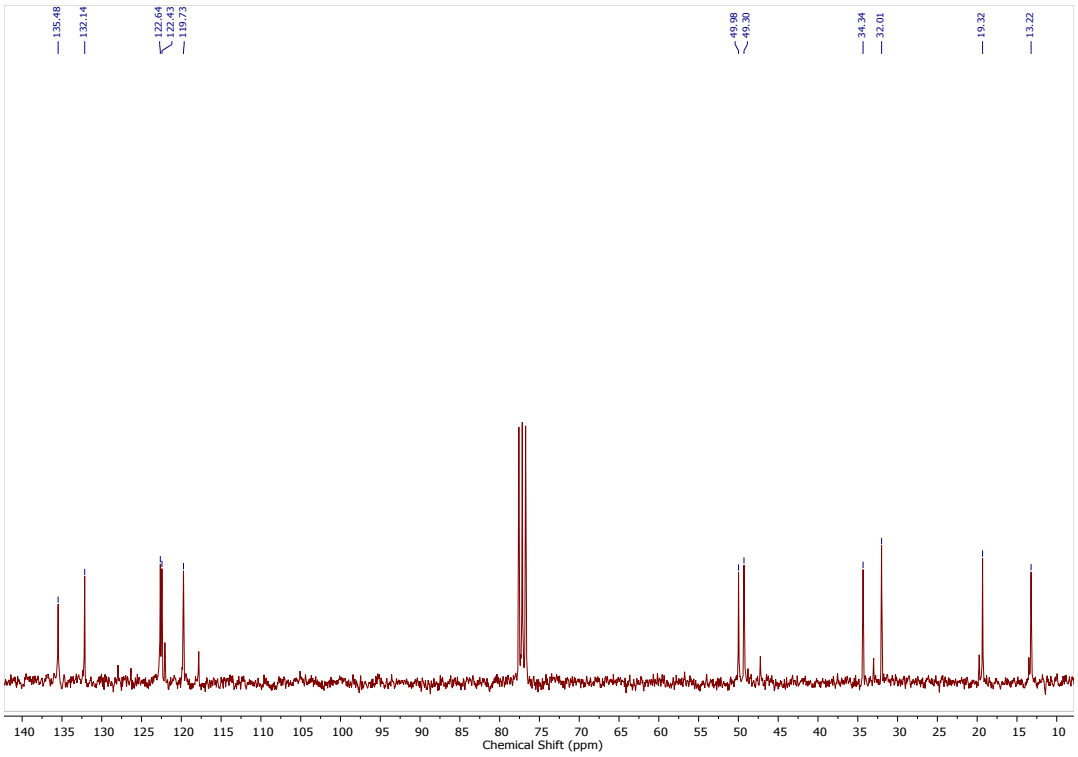


Figure S14. ^{13}C-RMN of **9b.**

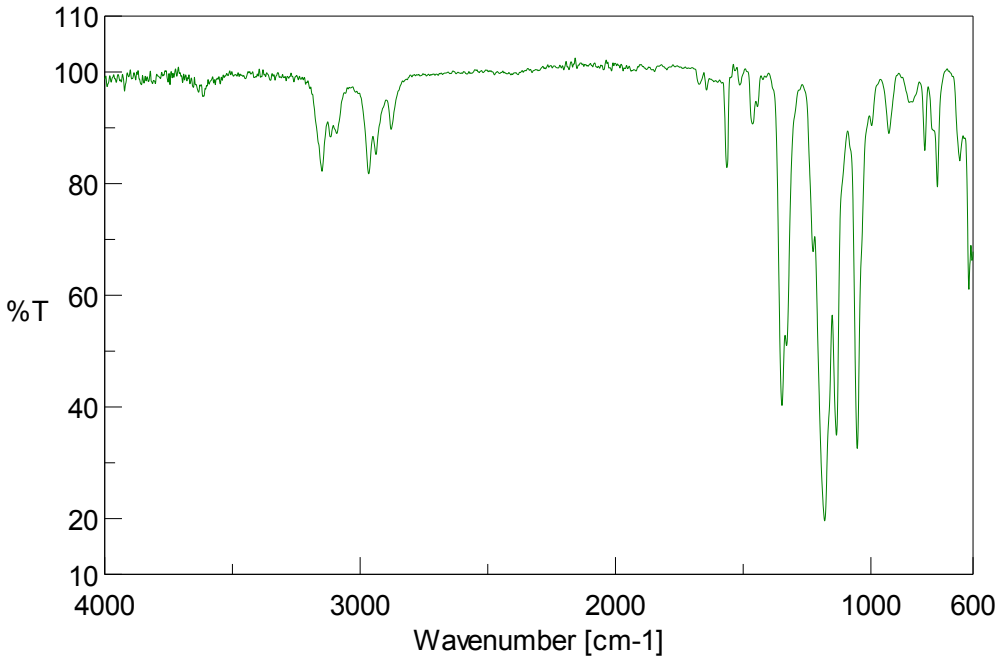


Figure S15. ATR-FT-IR spectra of **9b**.

Synthesis of Poly (acryloyl homocysteine thiolactone) (4)

Our initial attempts to homopolymerise **3** were based on the conditions reported by Du Prez (ref 22 main text). Accordingly, 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) was used as the chain transfer agent (CTA) and AIBN as the initiator in 1,4-dioxane ($[M]_0/[CTA]/[AIBN]$ = 150/1/0.095). Besides, the polymerisation was also assayed using 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CTBSPA) and cyanomethyl dodedyl trithiocarbonate (CMDTTC) as alterative CTAs. The reaction mixture was degassed through 3 freeze-thaw cycles and the polymerisation was carried out at 70 °C for 24 hours. At the end of this period, the presence of a precipitate was observed.

Table SI.1. Results for the homopolymerisation in dioxane.

Entry	CTA	Precipitation	Precipitate description	Yield[a]
1	DDMAT	✓	Transparent sticky solid	28%
2	CTBSPA	✓	White solid	0%
3	CMDTTC	✓	Transparent sticky solid	40%

a. After isolation by filtration and washing with 1,4-dioxane and MeOH

The solid obtained was isolated, washed with 1,4-dioxane and MeOH and analysed. When DDMAT and CMDTTC were used as CTAs, the precipitate corresponded to the desired homopolymer and was isolated in modest yields (28% and 40%, respectively). The ATR-FT-IR spectra showed the disappearance of the band at 1620 cm-1 that is characteristic for vinyl group and a broadening, overlapping and shifting of the bands at 1650-1720 cm^{-1} associated with the thiolactone group (Fig. S16, ESI). However, when CTBSPA was used, the white precipitate isolated in 1,4-dioxane was fully dissolved in MeOH during the purification process. The analysis of the soluble fraction revealed that in this case the solid obtained was essentially the initial monomer. This indicates the lower reactivity under these conditions using CTBSPA.

To understand these results it is important to analyse the solubility of both the monomer and the homopolymer in 1,4-dioxane. In this solvent, the monomer is only soluble when heating but precipitates under cooling, when the polymer formed shows a low solubility. Accordingly, the solubility of the monomer and the polymer was evaluated in different solvents (see Table S1). This study suggest that DMF, where both polymer and monomer are highly soluble, is the most appropriate solvent. CH_2Cl_2 is also a good solvent in terms of solubility but the lower boilding point limits the temperature range affordable to carry out the polymerisation. Therefore, DMF was selected as solvent to evaluate the RAFT

polymerisation of 3. CMDTTC was selected as CAT because it showed the higher level of conversion for the initial assays in 1,4-dioxane.

Table SI.2. Solubility study for 3 and 4.[a]

Entry	Solvent	Monomer 3	Polymer 4
1	Dioxane	± (+)	-
1	MeOH	++	-
2	CH_2Cl_2	++	++
3	DMSO	++	++
4	DMF	++	++

a: Measured at a polymer concentration of 100 mg mL^{-1} at 30 ^oC. The qualitative solubility was tested with 5 mg of a sample in 1 mL of stirred solvent. Notation: ++, soluble at room temperature; +, soluble at 80 ^oC; ±, partially soluble at rt, - insoluble at rt. DMSO, dimethyl sulfoxide; DMF, N,N-dimethylformamide; CH_2Cl_2, dichloromethane.

Synthesis of Poly (acryloyl homocysteine thiolactone) (4) 1,4-dioxane. Acrylhomocystheine thiolactone **3** (171 mg, 1 mmol), CTA (6.6 µmol) and AIBN (0.1 mg, 0.6 µmol) were dissolved in 1,4-dioxane. The mixture was degassed through 3 freeze-thaw cycles. The reaction was allowed to proceed for 24 hours at 70 °C. The precipitate (if formed) was filtered, washed with 1,4-dioxane and dried *in vacuo*. If any precipitate is not formed, the product was purified by reprecipitation from 1,4-dioxane to methanol and washed with diethyl ether.

Poly(acryloyl homocysteine thiolactone) 4 synthesis in DMF. Acrylhomocystheine thiolactone **3** (171 mg, 1 mmol), CMDTTC (2.12 mg, 6.6 µmol), AIBN (0.1 mg, 0.6 µmol) were dissolved in DMF. The mixture was degassed through 3 freeze-thaw cycles. The reaction was allowed to proceed for 24 hours at 110 ºC. The polymerisation was stopped by feezing the mixture in liquid nitrogen. The product was precipitated in methanol, purified by reprecipitation from DMF to methanol and washed with diethyl ether. Yield of crude product: 85-90 %.

^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 7.21-8.25 (*br. m*, 1H), 7.58 (*br. d?*, 1H), 3.40 (*br. d*, 2H), 2.47 (*br. s*, 1H), 2.11 (*br. s*, 2H), 1.52 (*br. d*, 2H).

^{13}C NMR (500 MHz, DMSO-d_6, ppm) δ 206.4 (C), 174.3 (C), 58.9 (CH), 41.5 (CH), 36.0 (CH_2), 30.3 (CH_2), 27.2 (CH_2).

Synthetic protocol for polymer 8 by modification of 4. Polymer **4** (100 mg) the amine **5** according with Table 1 (1.2 equiv.) and Et_3N (3 equiv.) were dissolved in DMF (250 µL) in inert atmosphere of N_2. The reaction mixture was allowed to react during 1 hour at room temperature. After this time, 5 equivalents of the acrylate **7** according with Table 1 were added to the reaction medium. The reaction was allowed to proceed during 24 additional hours. The polymer was precipitated in methyl-tert-butyl-ether (MTBE) and purified by dialysis against MeOH.

Synthesis of the polymer 10a by modification of 4. Polymer 4 (100 mg) the dimethyl-propilamine **5d** (110 µL, 1.5 equiv.), Et_3N (240 µL, 3 equiv.), were dissolved in DMF (250 µL) in inert atmosphere of N_2. The reaction mixture was allowed to react during 1 hour at room temperature. After this time, 3 equivalents of the IL **9a** and 3equiv. of AIBN were added to the reaction medium. The reaction was allowed to proceed during 24 additional hours. The polymer was precipitated in methyl-tert-butyl-ether (MTBE) and purified by dialysis against MeOH.

Synthesis of 10b by modification of 4. Polymer **4** (100 mg), the dimethyl-propilamine **5d** (110 µL, 1.5 equiv.), Et_3N (240 µL, 3 equiv.), the IL **9b** (3 equiv., 976.8 mg) and 2-2-dimethoxy-2-phenylacetophenone (DMAP, 1 eq, 154.2 mg) were dissolved in DMF (250 µL) in inert atmosphere of N_2. The reaction was stirred at 150 rpm at room temperature during 2 hours. After this time, the reaction was irradiated with a Hg lamp during 16 hours. The polymer was precipitated in methyl-tert-butyl-ether (MTBE) and purified by dialysis against MeOH.

Synthesis of 10c by modification of 4. Polymer **4** (100 mg), the dimethyl-propilamine **5d** (110 µL, 1.5 equiv.), Et_3N (240 µL, 3 equiv.) the IL **9c** (3 eqiv, 350.9 mg) and 2-2-dimethoxy-2-phenylacetophenone (DMAP, 1 eq, 154.2 mg) were dissolved in DMF (250 µL) in inert atmosphere of N_2. The reaction was stirred at 150 rpm at room temperature during 2 hours. After this time, the reaction was irradiated with a Hg lamp during 16 hours. The polymer was precipitated in methyl-tert-butyl-ether (MTBE) and purified by dialysis against MeOH.

Synthesis of self-crosslinked gel 11b. Polymer **4** (103 mg), IL **5e** (210.7 mg, 1.2 equiv.) and Et_3N (340 µL, 4.2 equiv.) were dissolved in DMSO (650 µL).The reaction mixture was bubbled up with O_2 and allowed to proceed at 70 ºC for 4 hours. During the reaction an increase on the viscosity was observed and finally a transparent gel was formed.

Procedure of cleavage of disulfide bonds in 11b. 11b (25 mg) was stirred in distilled water (3 mL) together with DTT (14 mg, 0.09 mmol) for 24 h at room temperature until the insoluble network was completely dissolved.

1.4. Structural characterisation of polymeric materials: ^{1}H-NMR and IR spectra and SEM pictures

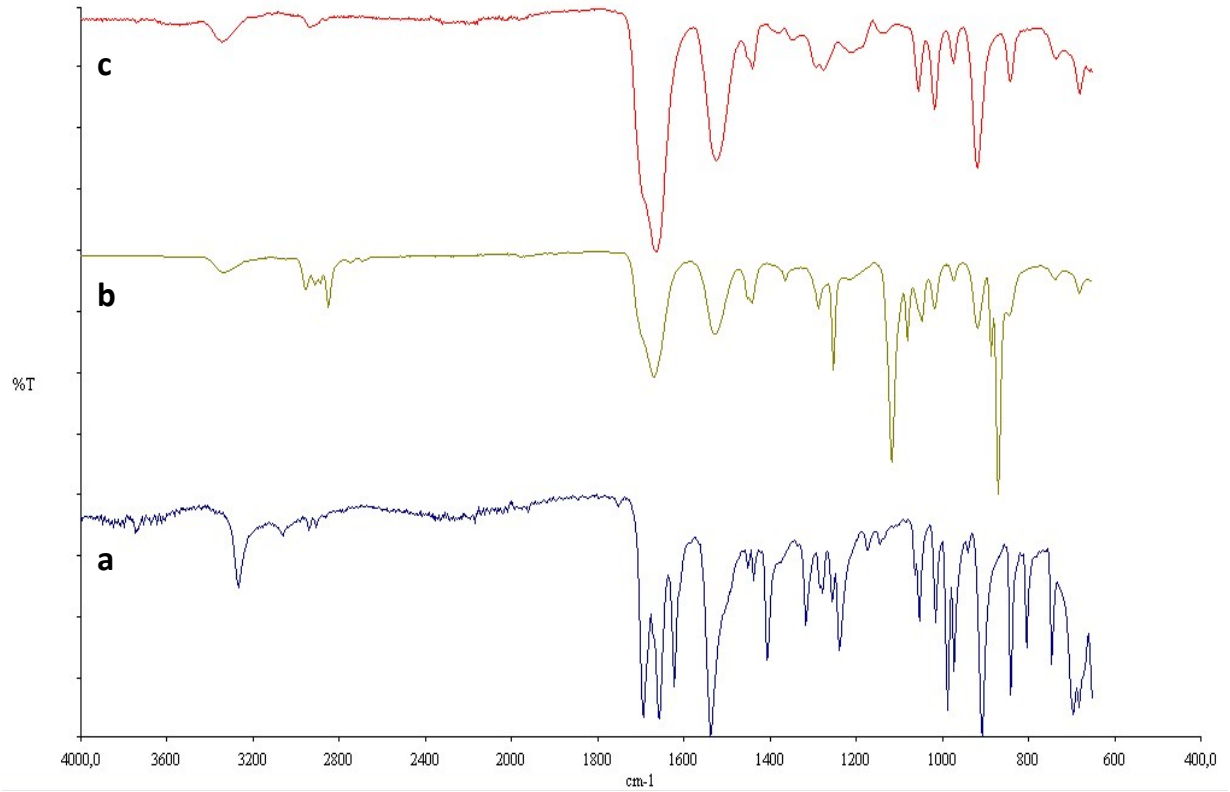


Figure S16. ATR-FT-IR spectra of monomer (a) and products of polymerisation with DDMAT (b) and CMDTTC (c) as a RAFT agent.

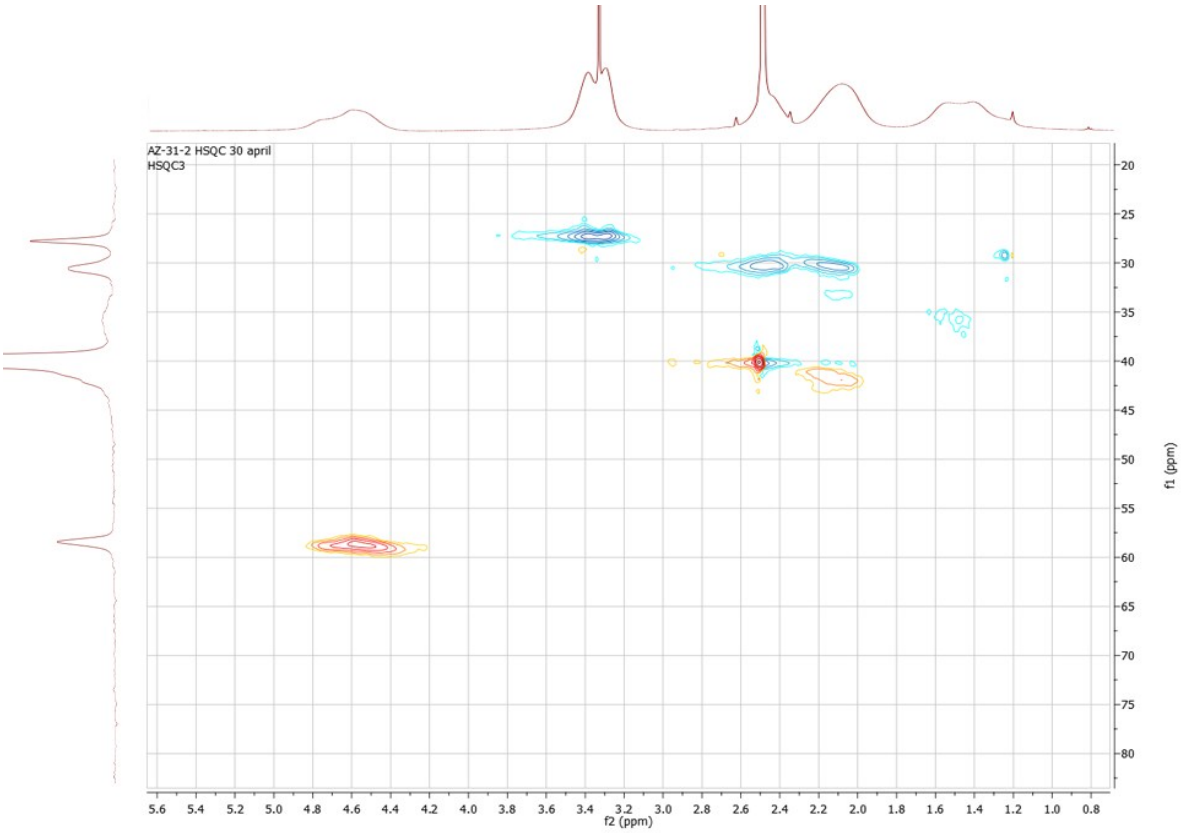


Figure S17. ^{1}H-^{13}C HSQC spectra of PAHT.

In order to prove the assignment for H***e*** and to check if the doublet at 4.75 ppm belongs to a single proton, a phase-sensitive HSQC experiment was carried out. The broad peak of H***a***+H***b*** at 1.2-1.6 ppm shows a week correlation with C***a*** at 36.05 ppm because of the significant broadening on the ^{13}C NMR spectrum. Correlation for C***b*** and H***b*** was detected at 2.1 ppm and 41.57 ppm overlapped with one of the H***e*** signals. It is clear from PS-HSQC that peak at 4.75 ppm corresponds to the same methylene group.

Muestra	Mn (Da)	Mw (Da)	Polydispersity (MW/Mn)	Volumen de retención (min)
SM_4P97	20669 Da	32709 Da	1,582	17,616

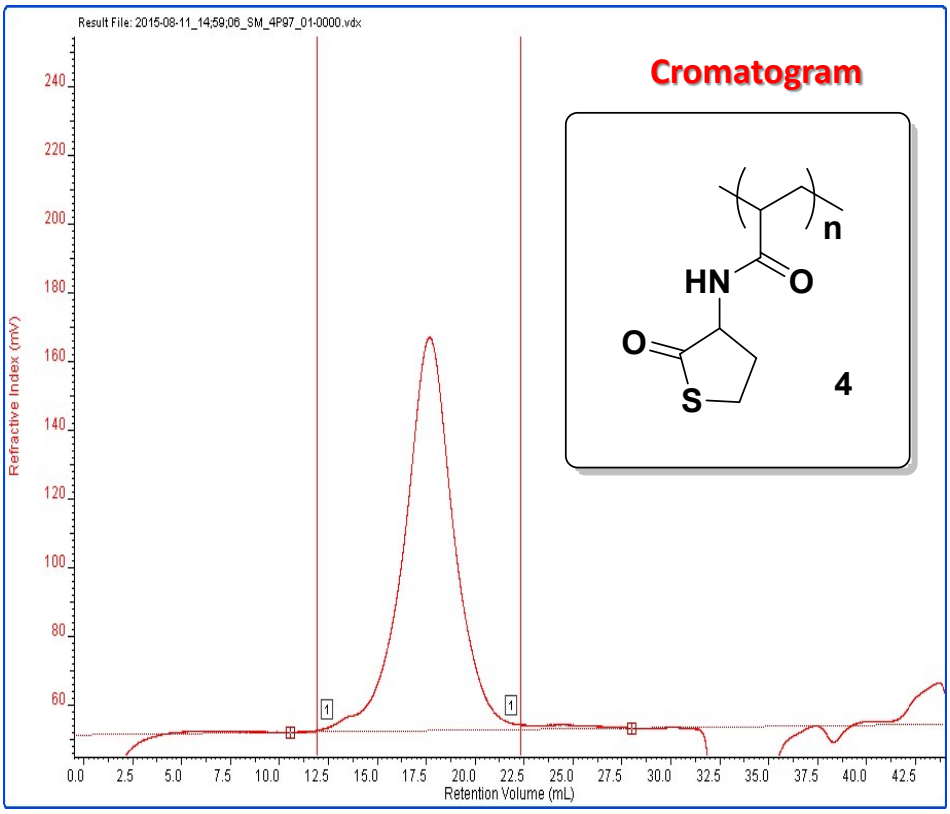


Figure S18. Size exclusion chromatography obtained for **4** in DMF (8 mg/mL) and 0.1% (w/w) of LiBr.

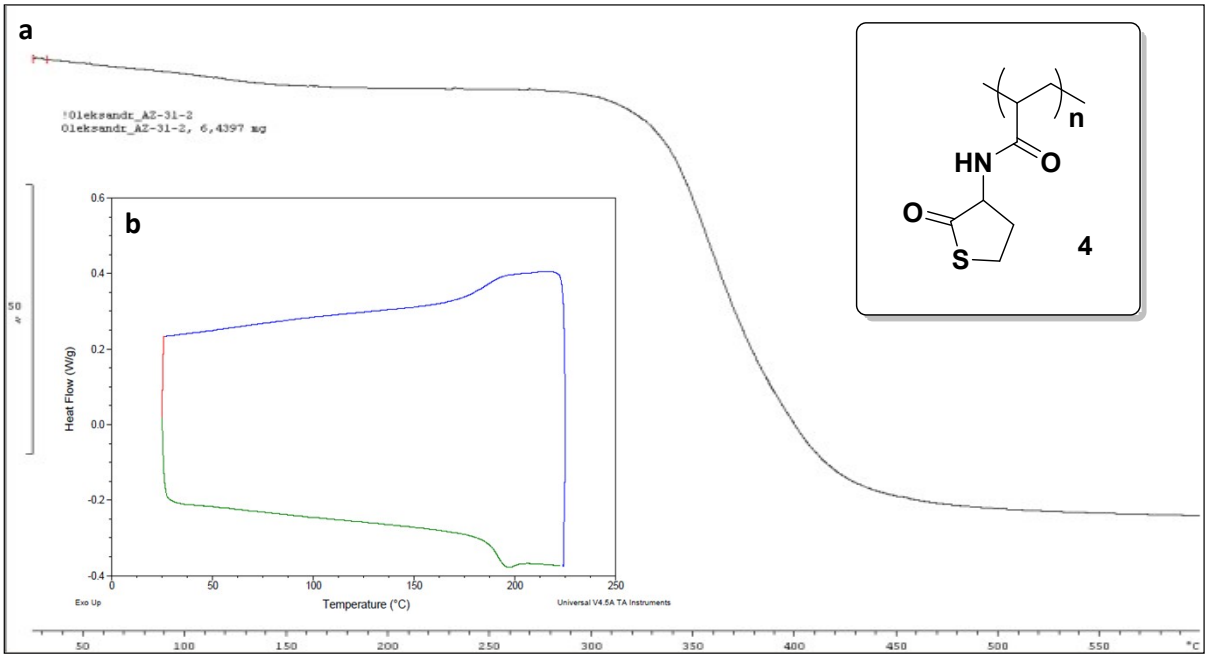


Figure S19. a: TGA obtained from 25 to 600 °C. for **4**. **b**: DSC obtained for **4** between 25 and 200 °C (1st cycle heating cooling)

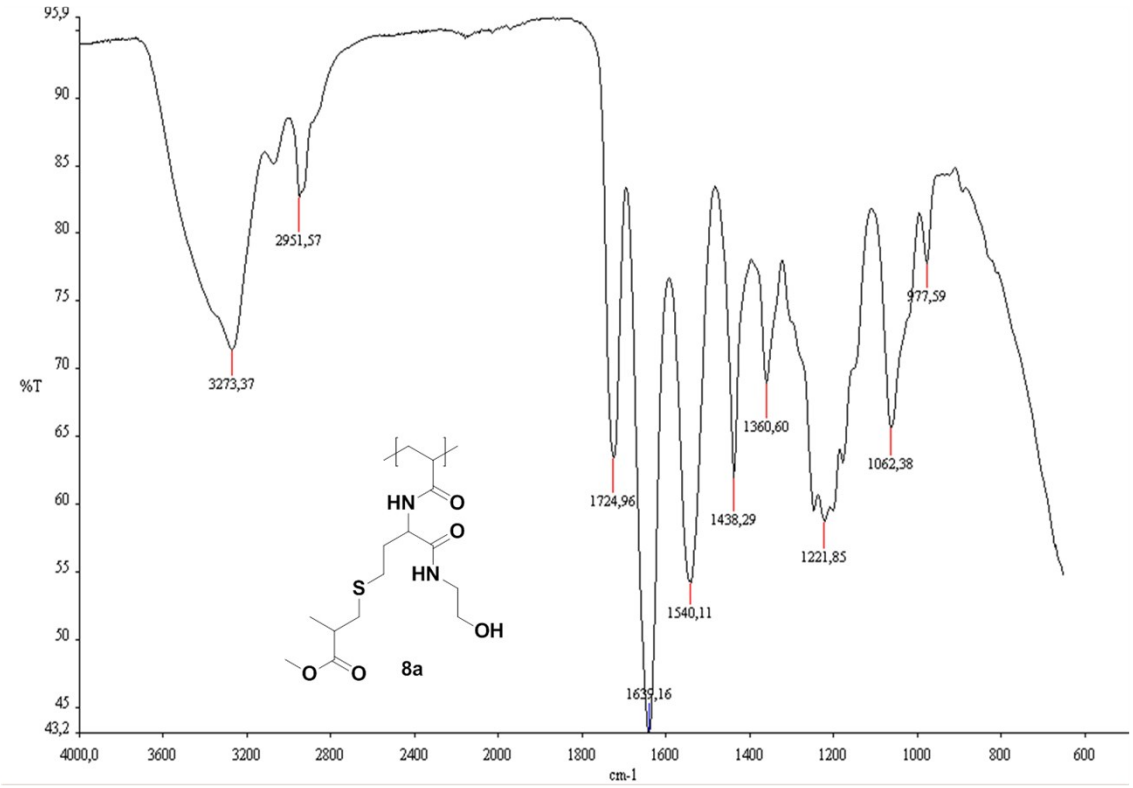


Figure S20. ATR-FT-IR spectrum for polymer **8a** obtained by post-modification of **4** with **5a** and **7a.**

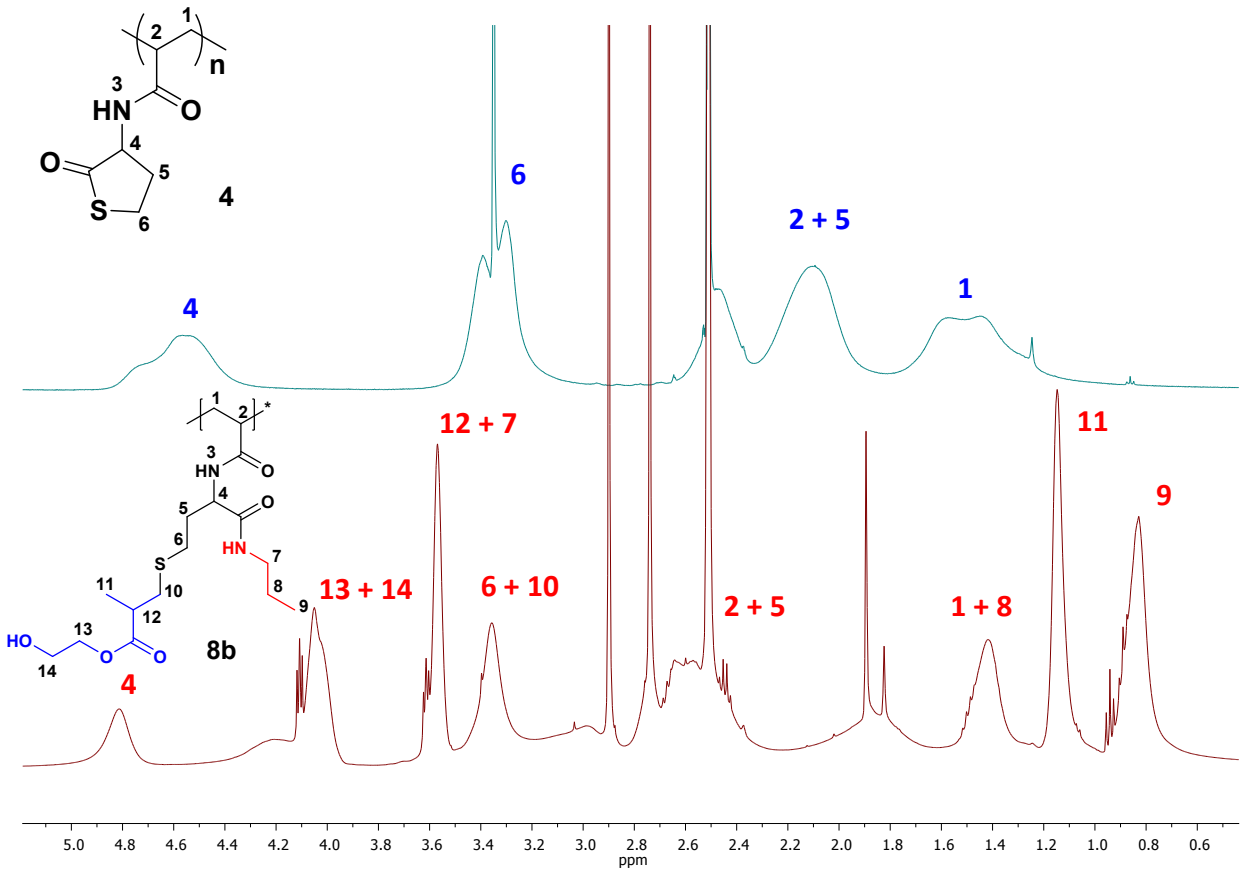


Figure S21. Comparison of the ^{1}H-NMR for polymer **4** and modified polymer **8b** obtained by post-modification with **5b** and **7b.**

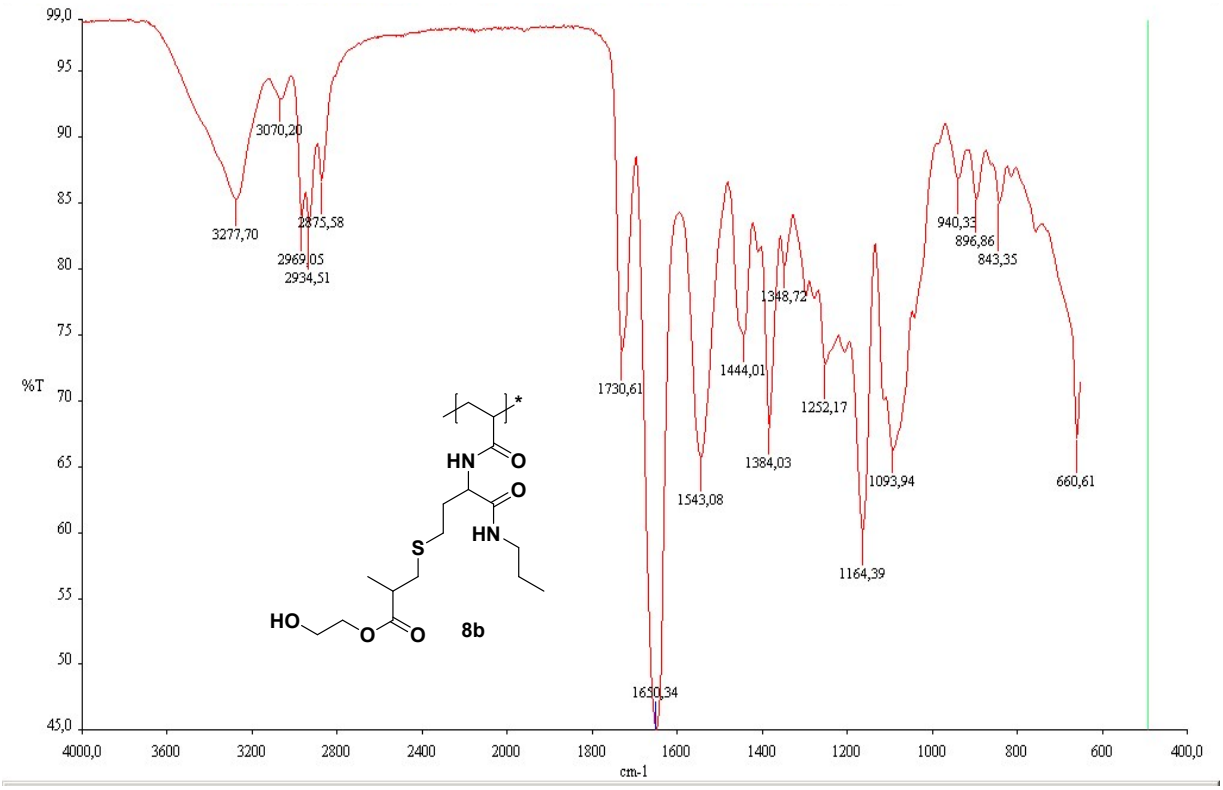


Figure S22. ATR-FT-IR spectrum for polymer **8b** obtained by post-modification of **4** with **5b** and **7b.**

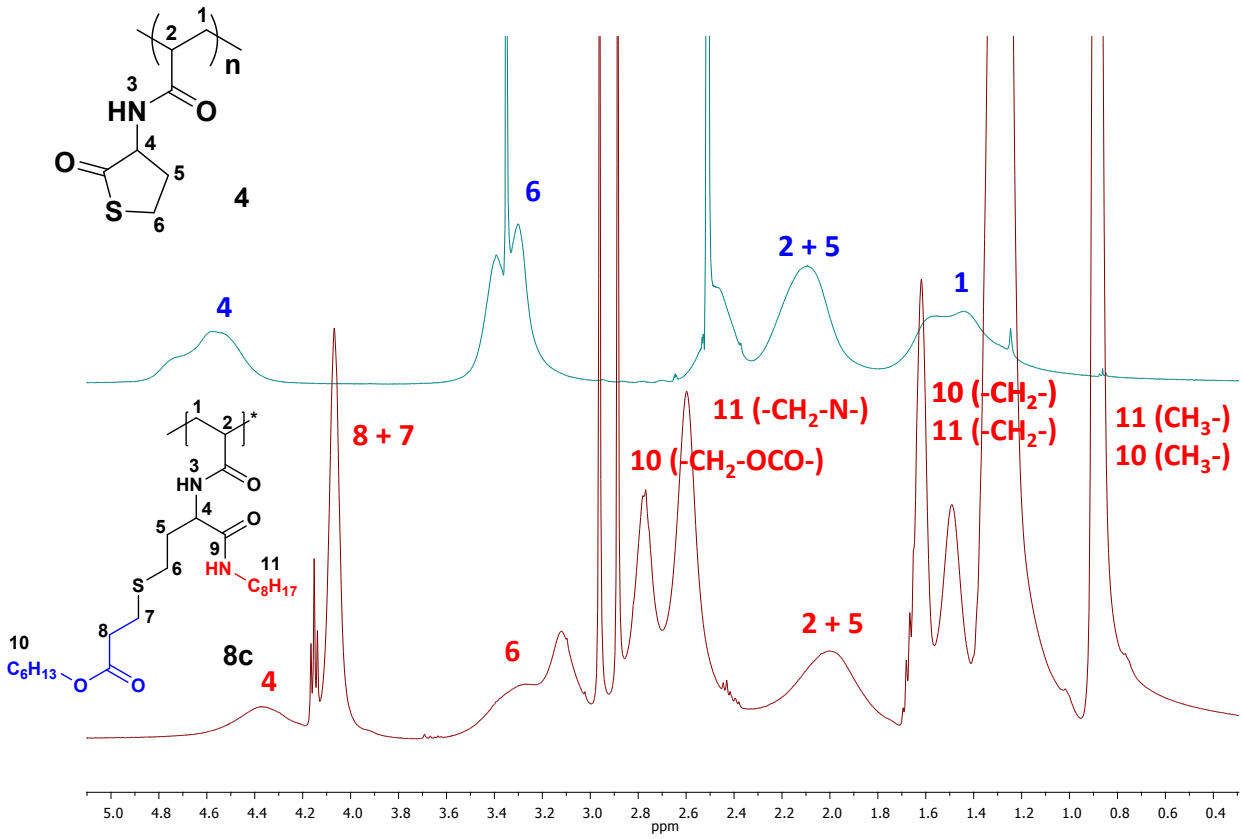


Figure S23. Comparison of the ^{1}H-NMR for polymer **4** and modified polymer **8c** obtained by post-modification with **5c** and **7c.**

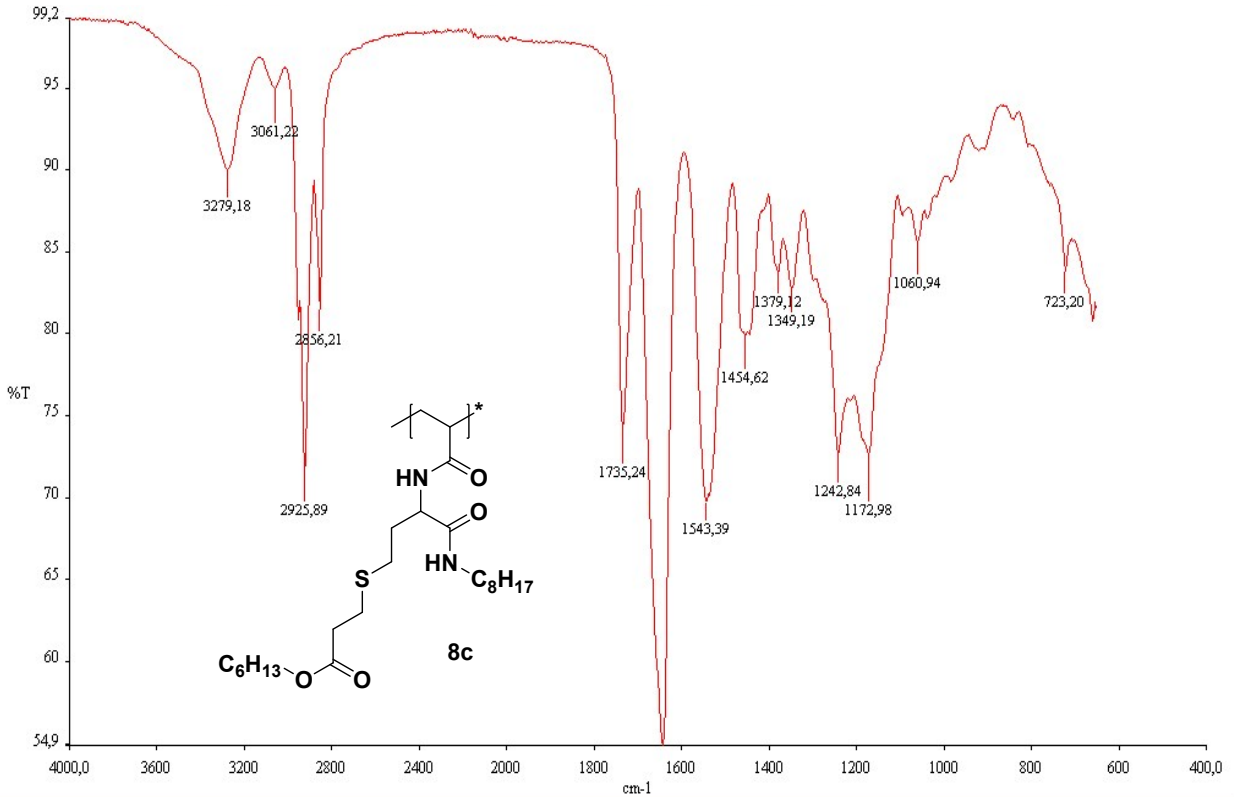


Figure S24. ATR-FT-IR spectrum for polymer **8c** obtained by post-modification of **4** with **5c** and **7c.**

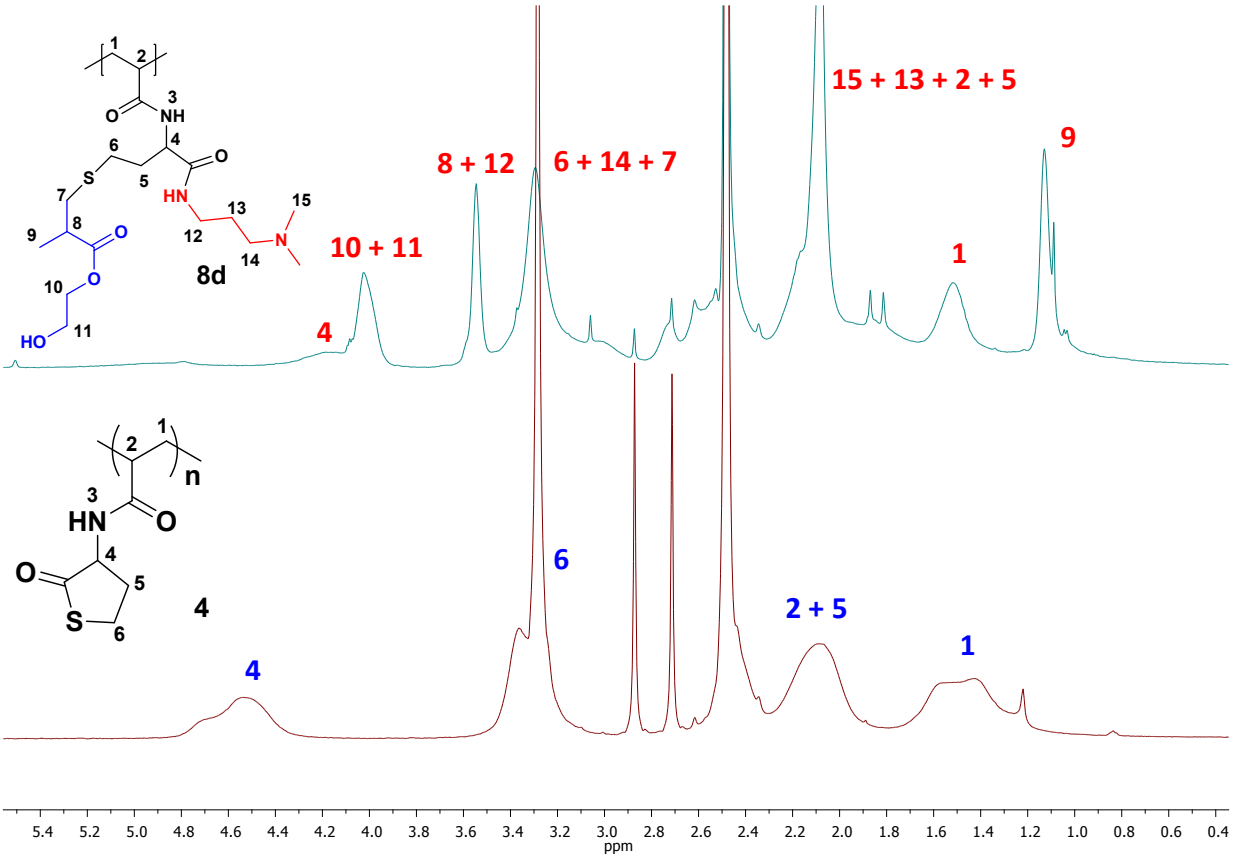


Figure S25. Comparison of the ^{1}H-NMR for polymer **4** and modified polymer **8d** obtained by post-modification with **5d** and **7b.**

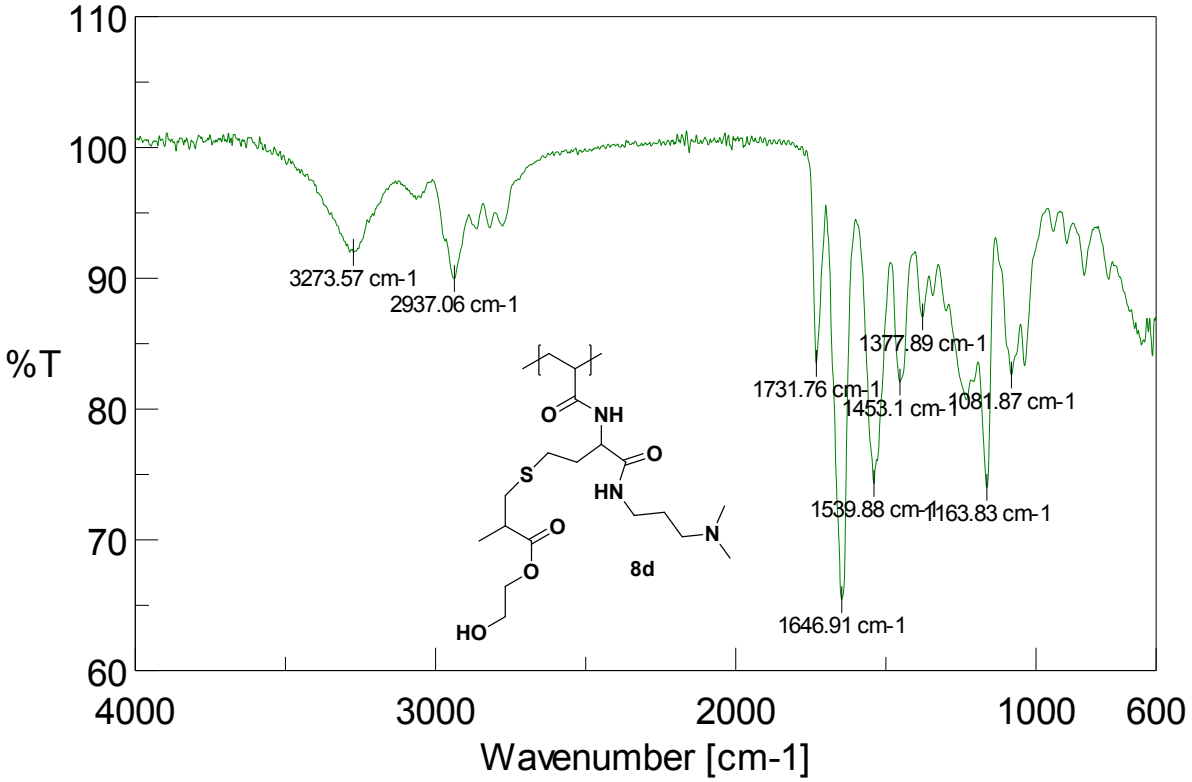


Figure S26. ATR-FT-IR spectrum for polymer **8d** obtained by post-modification of **4** with **5d** and **7b.**

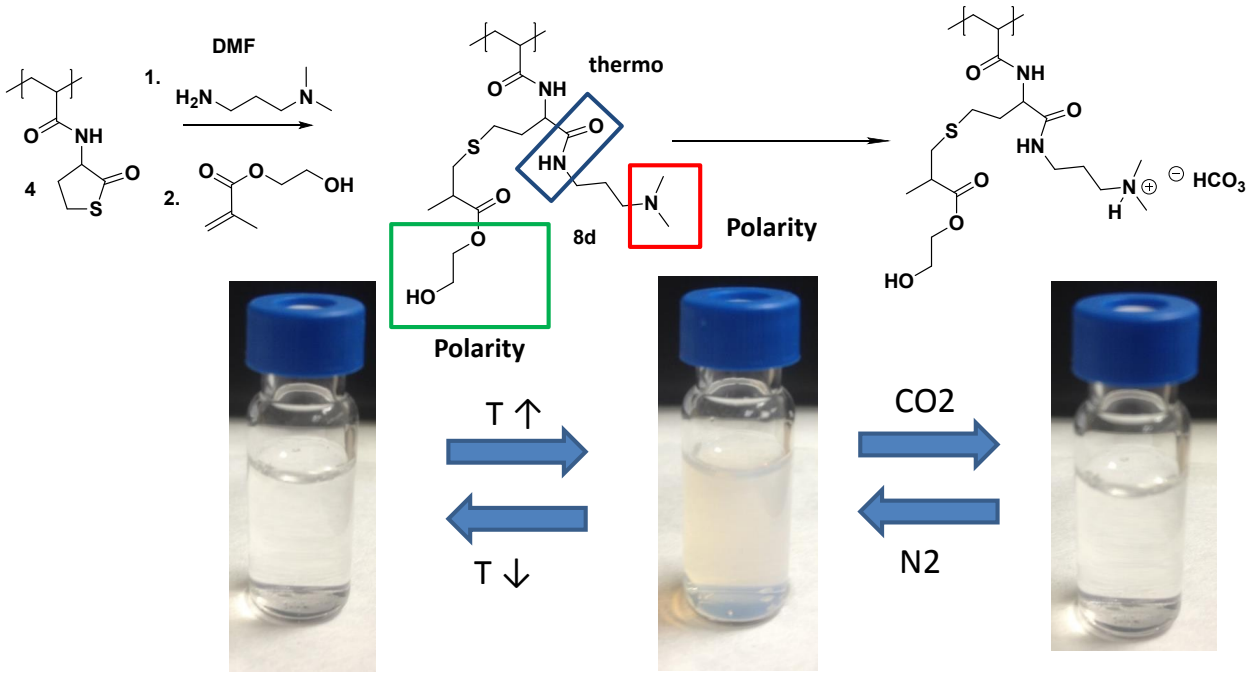


Figure S27. Thermal and CO_2 sensitive behaviour in water of the polymer **8d** obtained by obtained by post-modification of **4** with **5d** and **7b.**

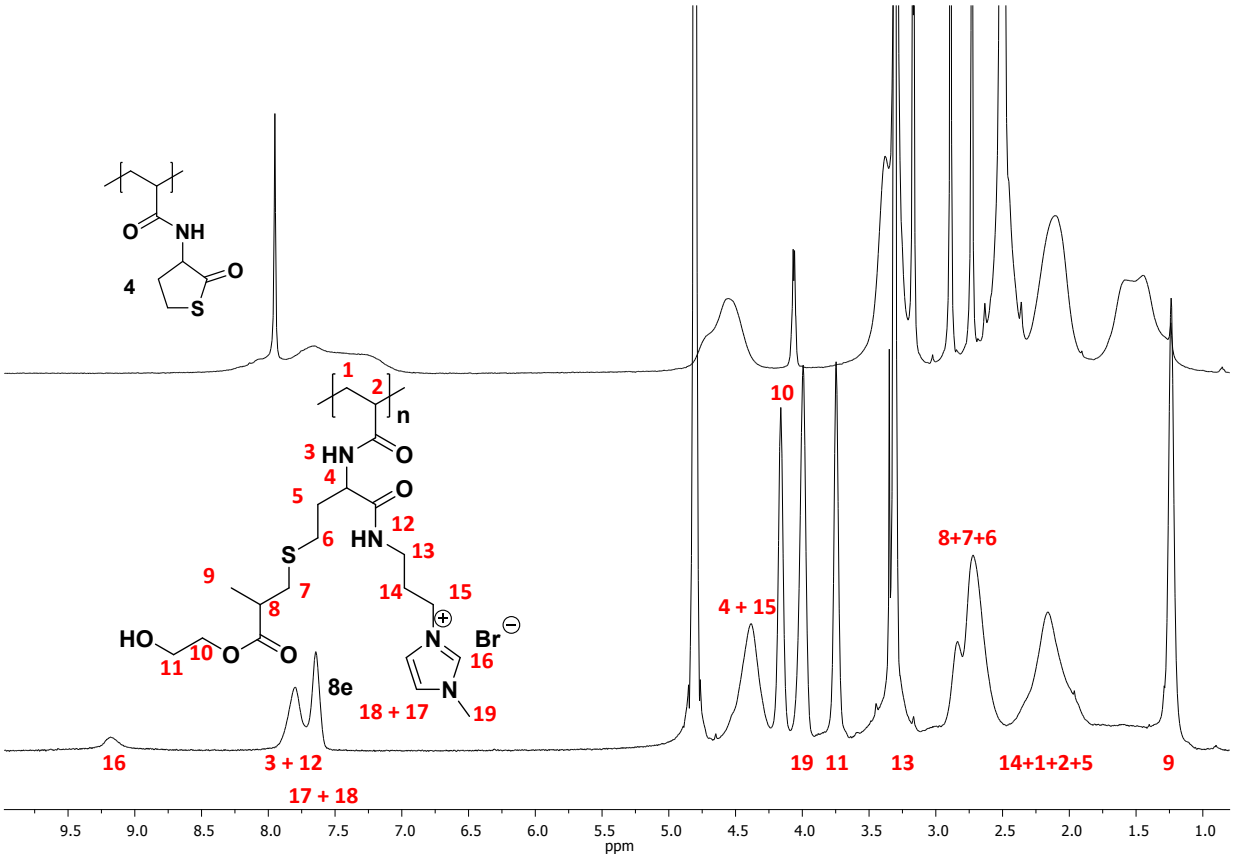


Figure S28. Comparison of the ^{1}H-NMR for polymer **4** and modified polymer **8e** obtained by post-modification with **5e** and **7b.**

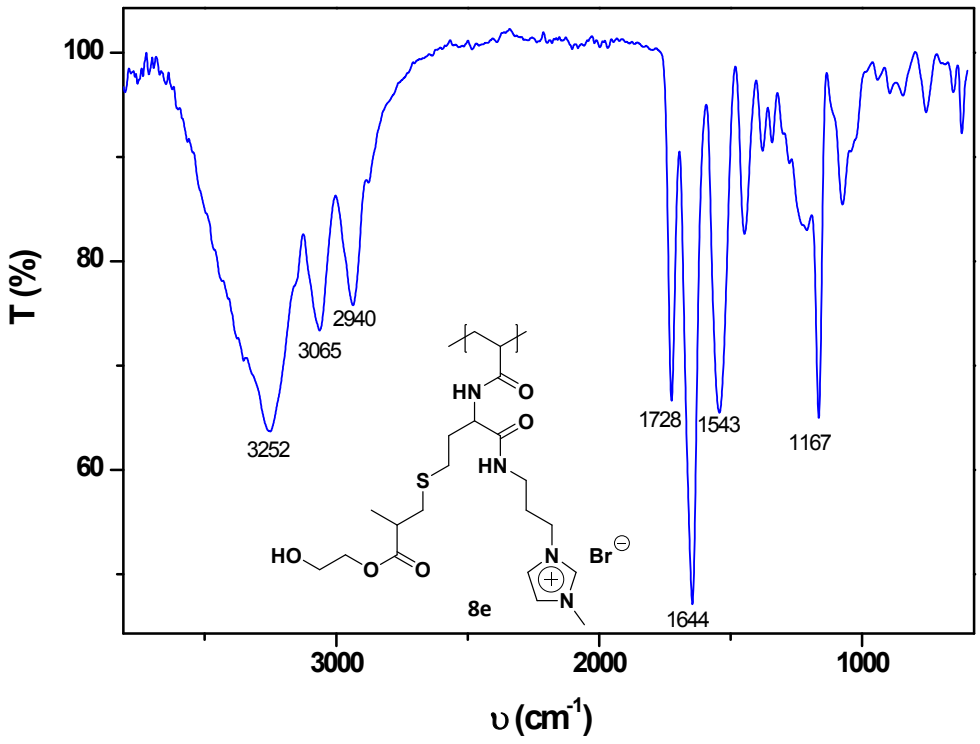


Figure S29. ATR-FT-IR spectrum for polymer **8e** obtained by post-modification of **4** with **5e** and **7b.**

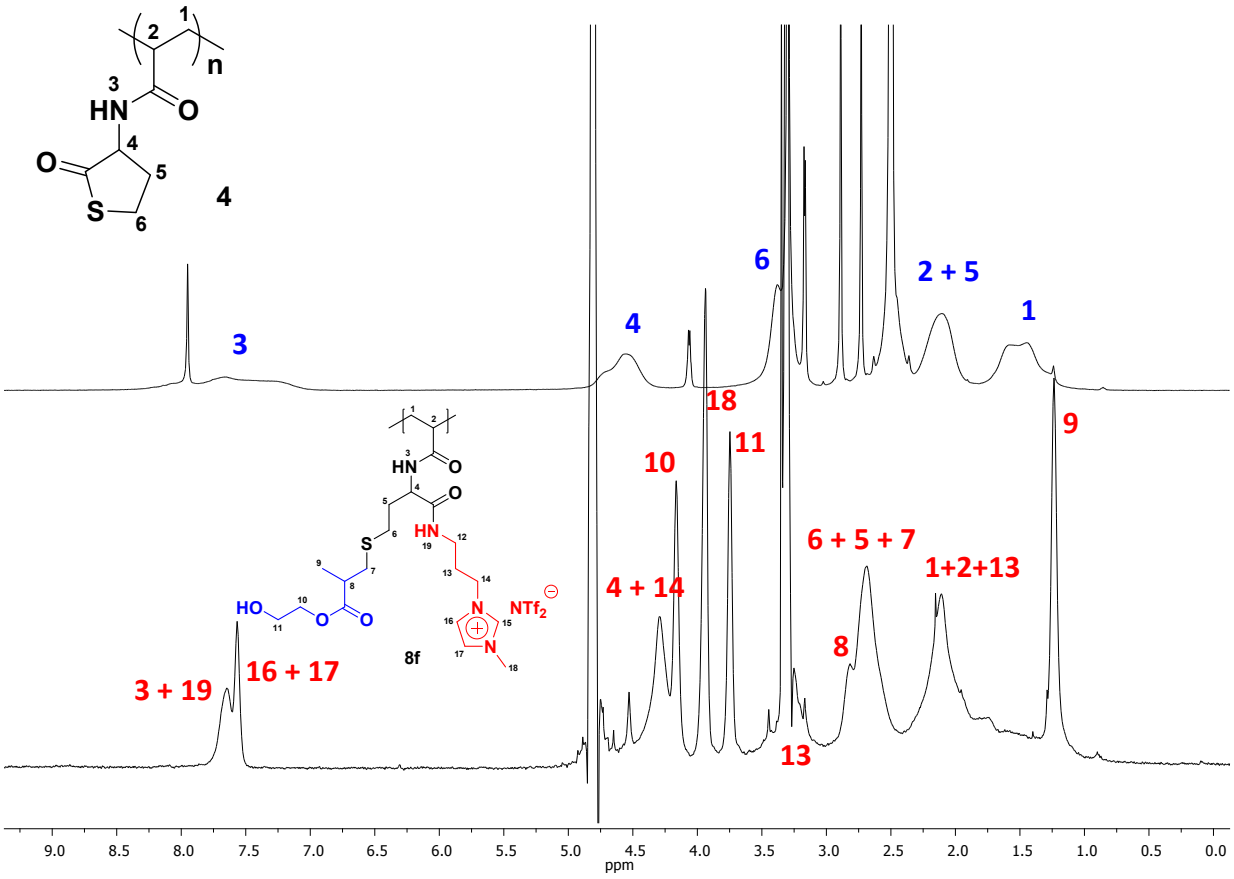


Figure S30. Comparison of the ^{1}H-NMR for polymer **4** and modified polymer **8f** obtained by post-modification with **5f** and **7b.**

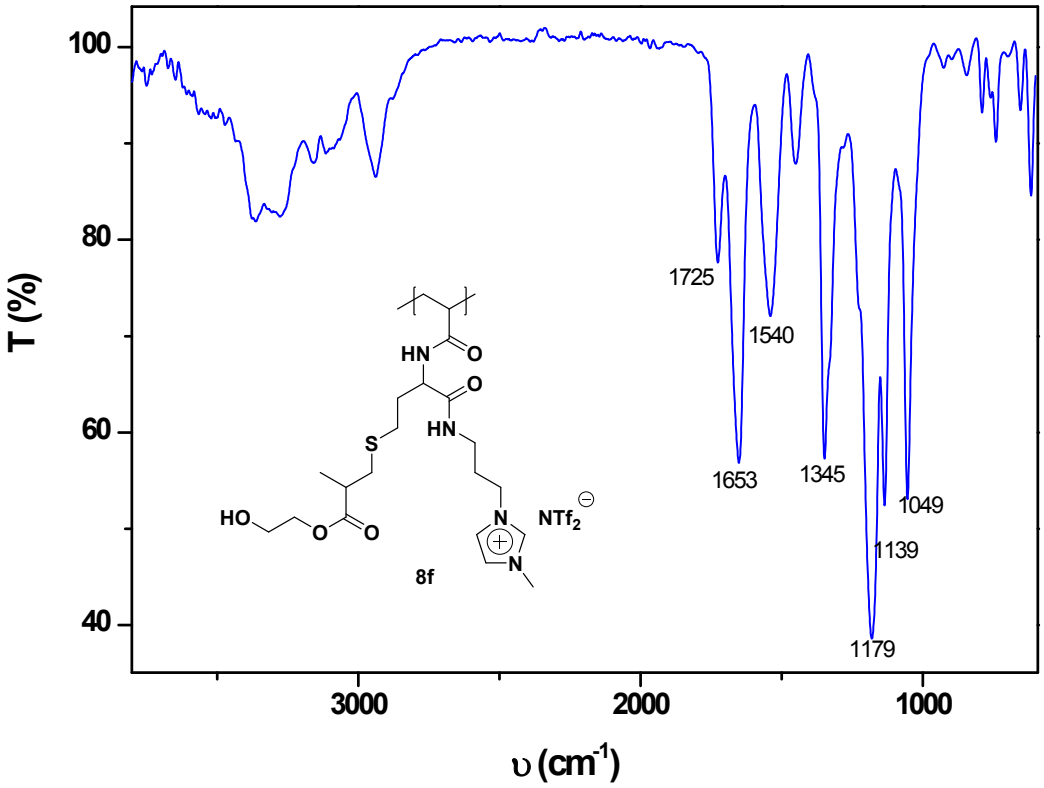


Figure S31. ATR-FT-IR spectrum for polymer **8f** obtained by post-modification of **4** with **5f** and **7b.**

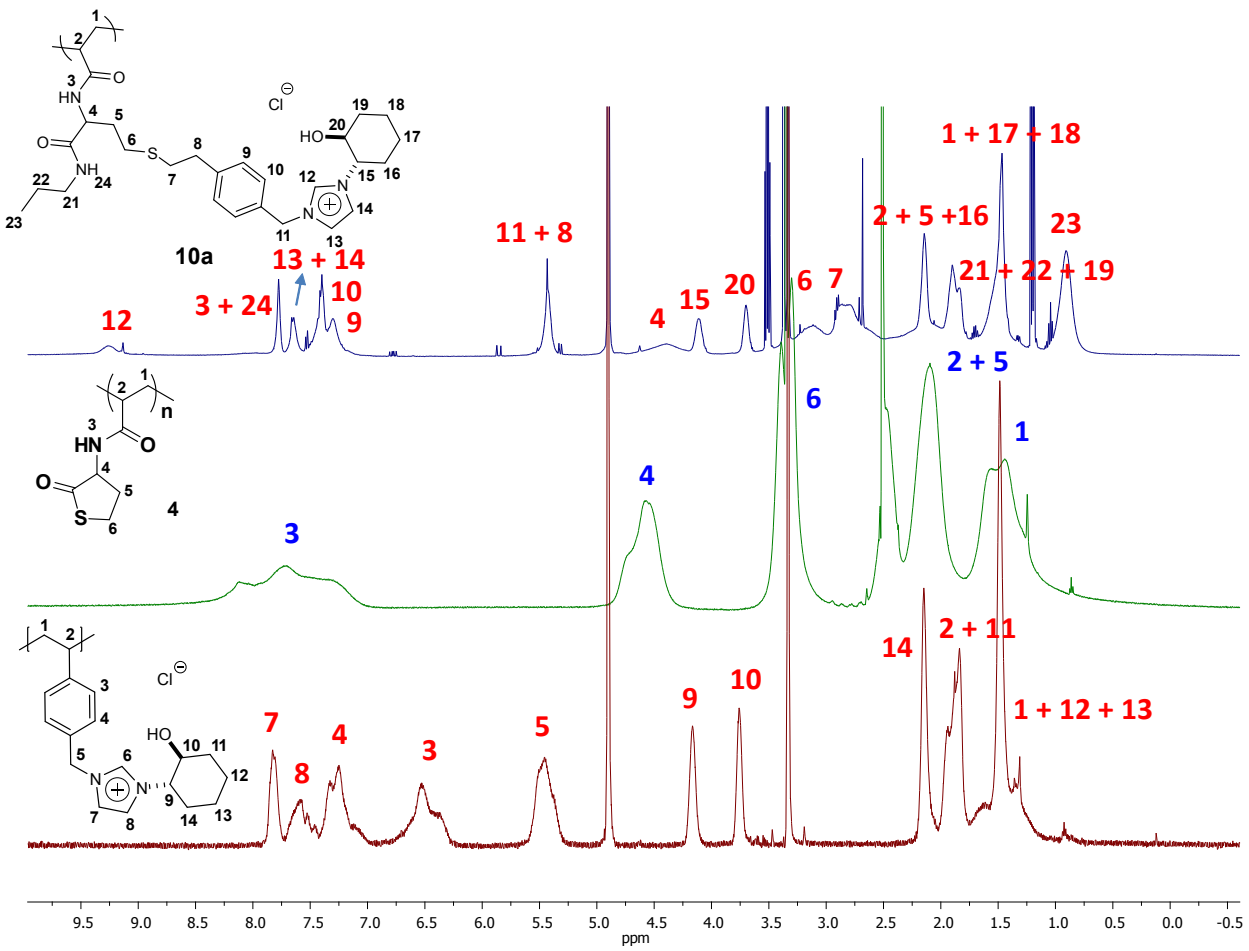


Figure S32. Comparison of the ^{1}H-NMR for polymer **10a** obtained by post-modification with **5b** and **9a** with polymer **4** and the homopolymer obtained by polymerisation of **9a.**

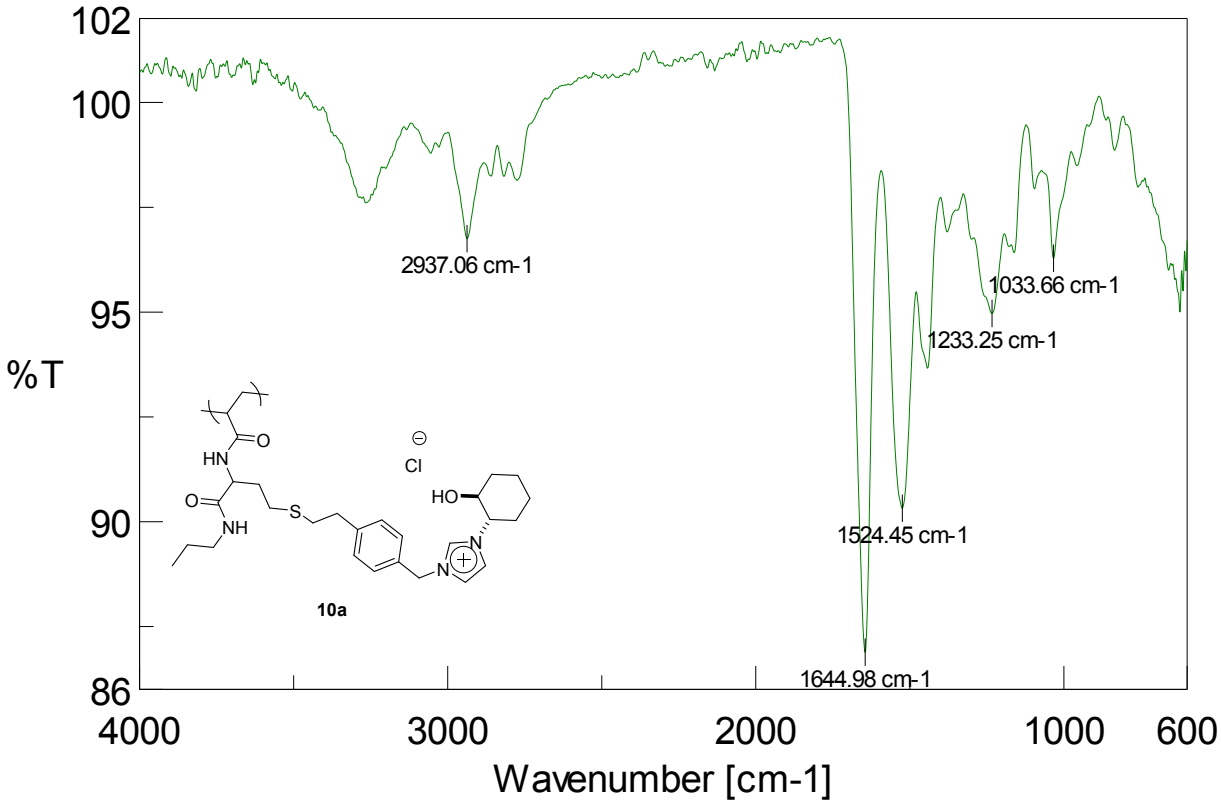


Figure S33. ATR-FT-IR spectrum for polymer **10a** obtained by post-modification of **4** with **5b** and **9a**.

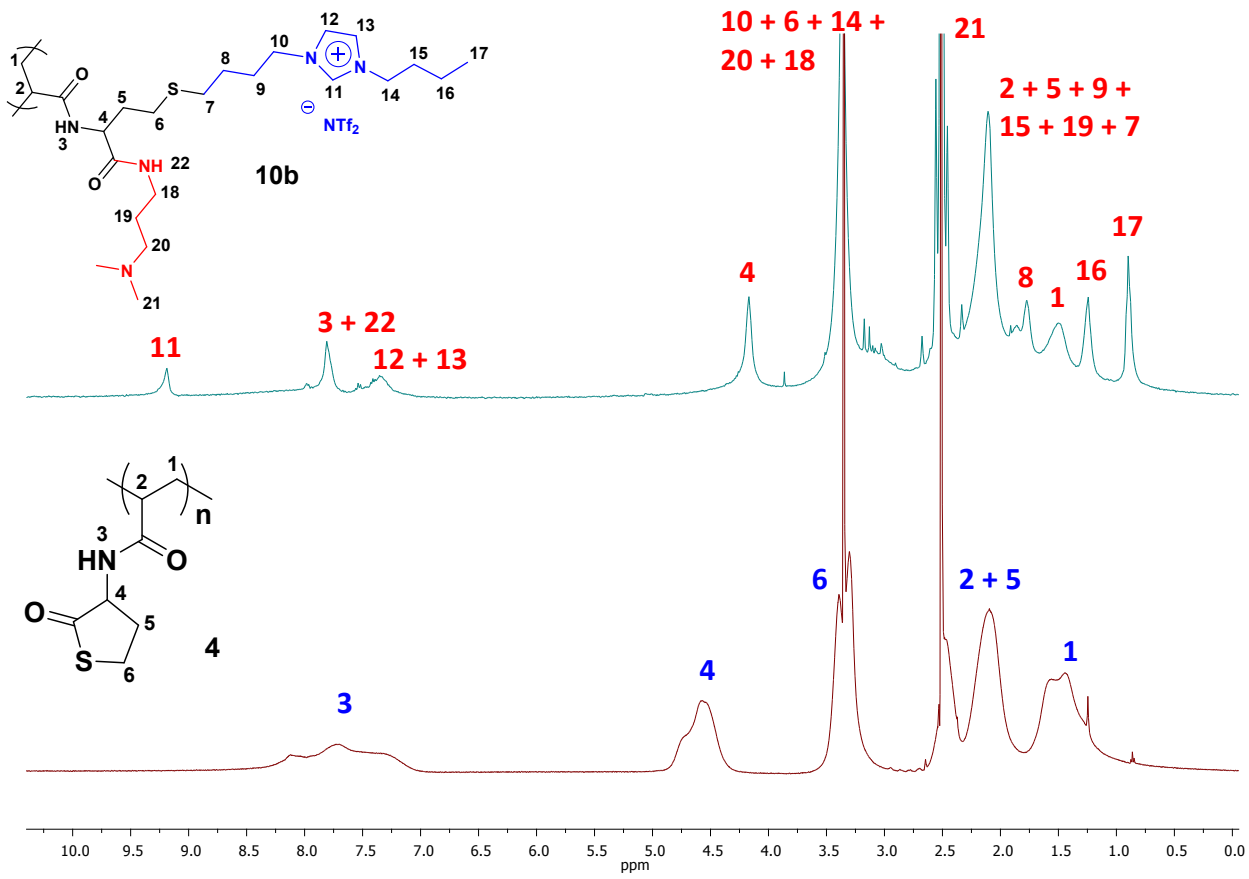


Figure S34. Comparison of the ^{1}H-NMR for polymer **10b** obtained by post-modification of 4 with **5d** and **9b**.

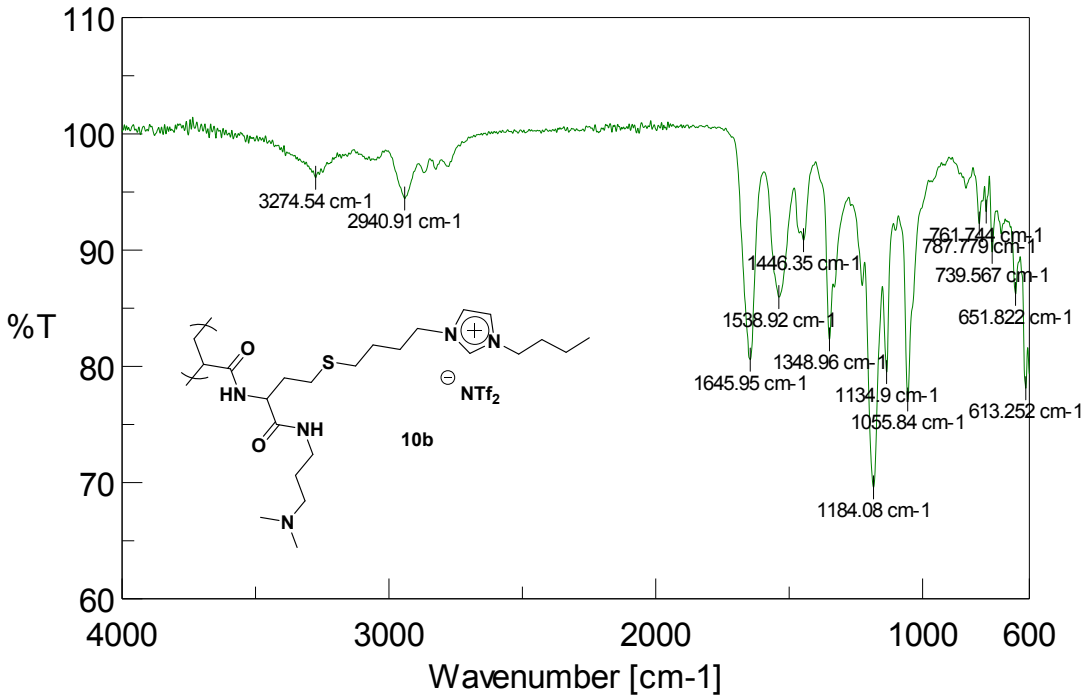


Figure S35. ATR-FT-IR spectrum for polymer **10b** obtained by post-modification of **4** with **5d** and **9b**.

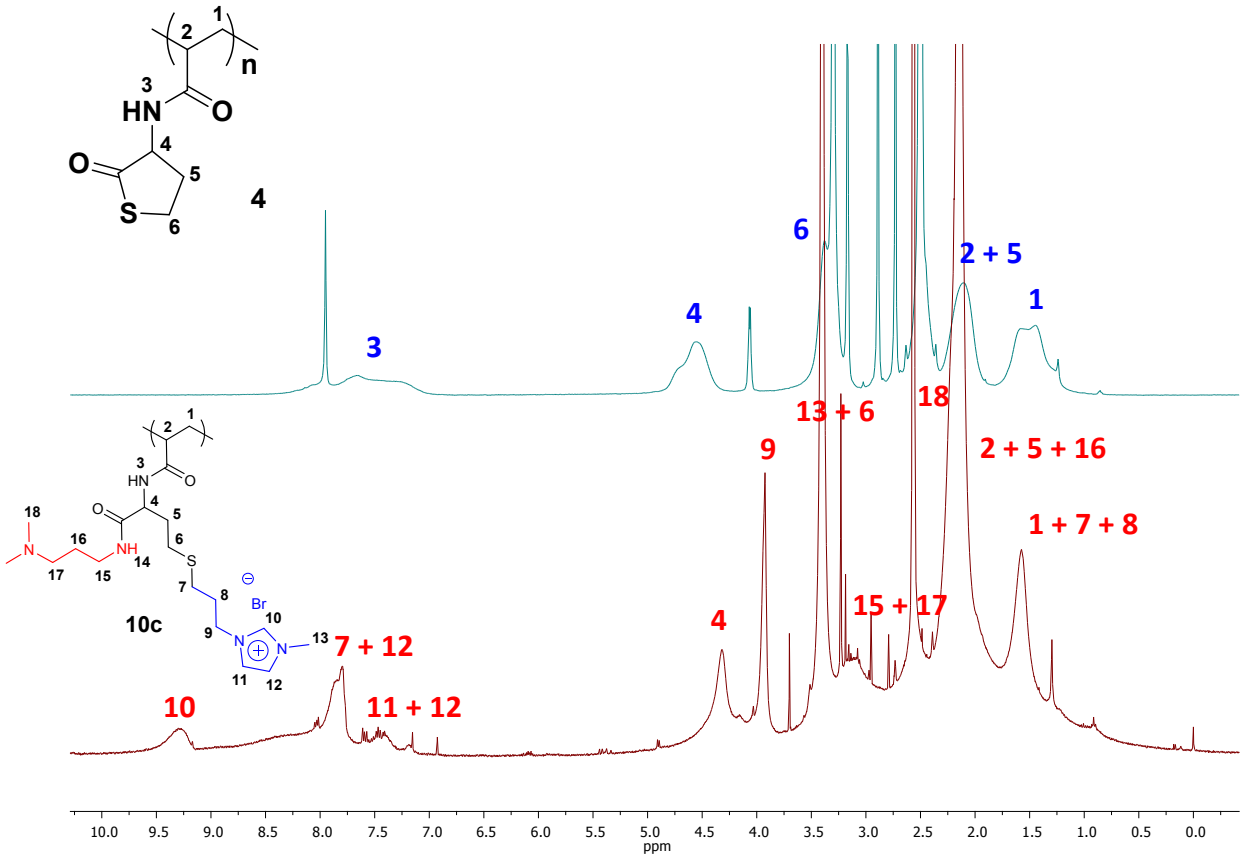


Figure S36. Comparison of the ^{1}H-NMR for polymer **10c** obtained by post-modification of 4 with **5d** and **9c**.

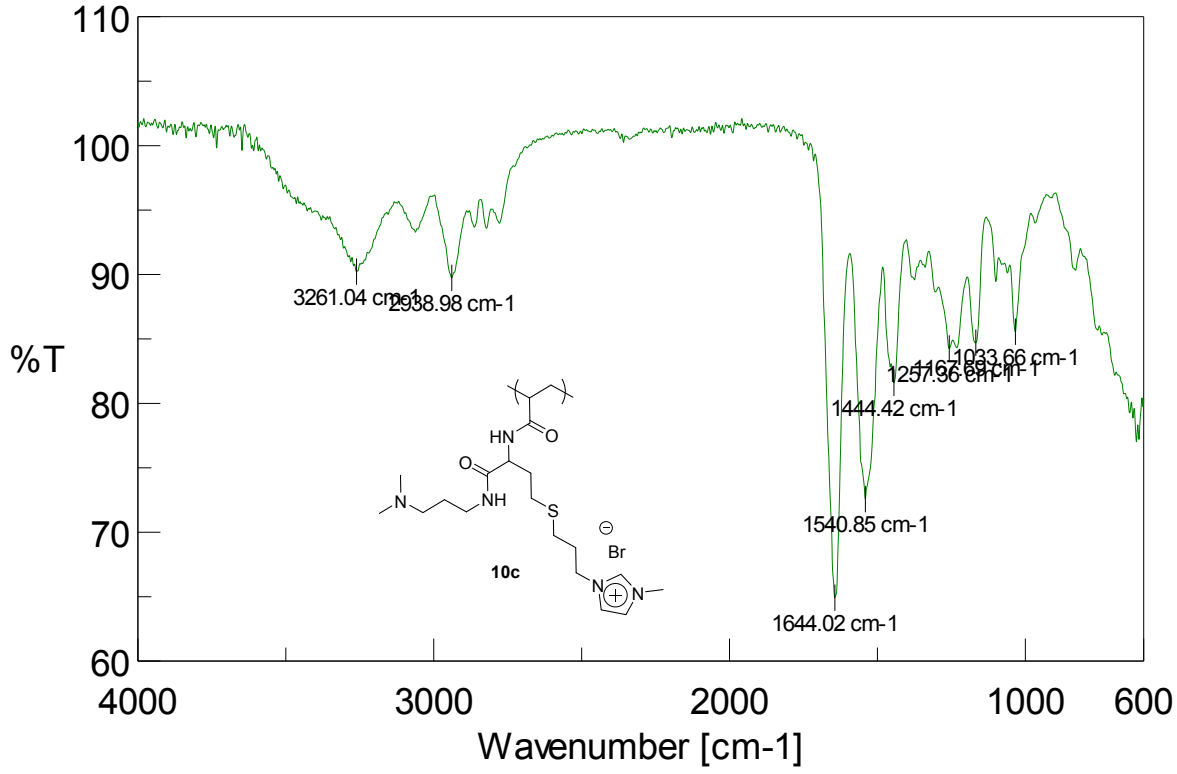


Figure S37. ATR-FT-IR spectrum for polymer **10c** obtained by post-modification of **4** with **5d** and **9c**.

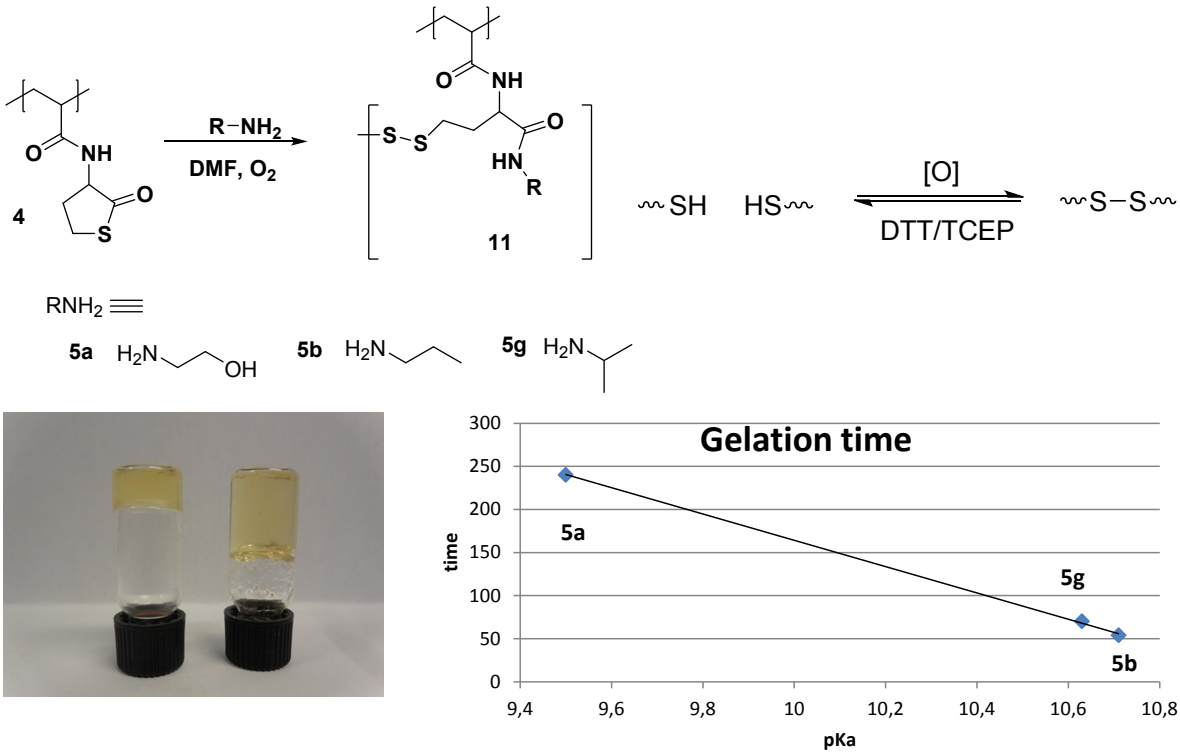


Figure S38. Gel formation with different *n*-alkyl-amines and dependence of gelation time on pKa.

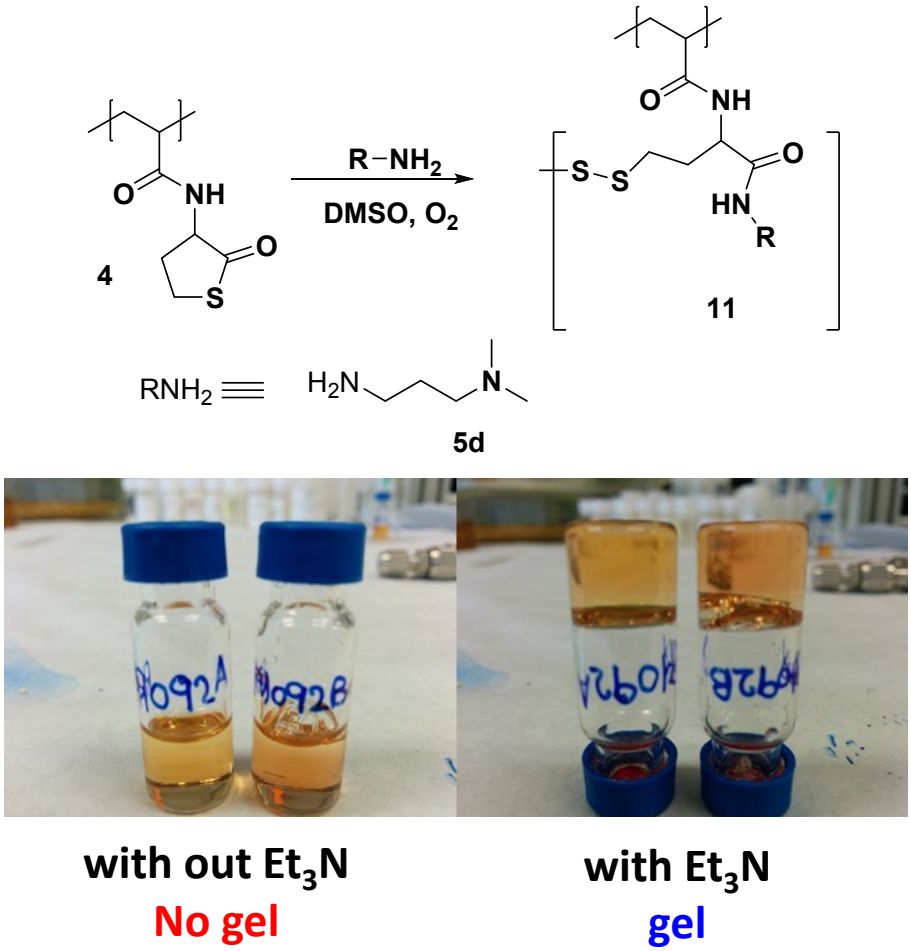


Figure S39. Gel formation procedure to prepare ionogels using amines functionalised with ILs.

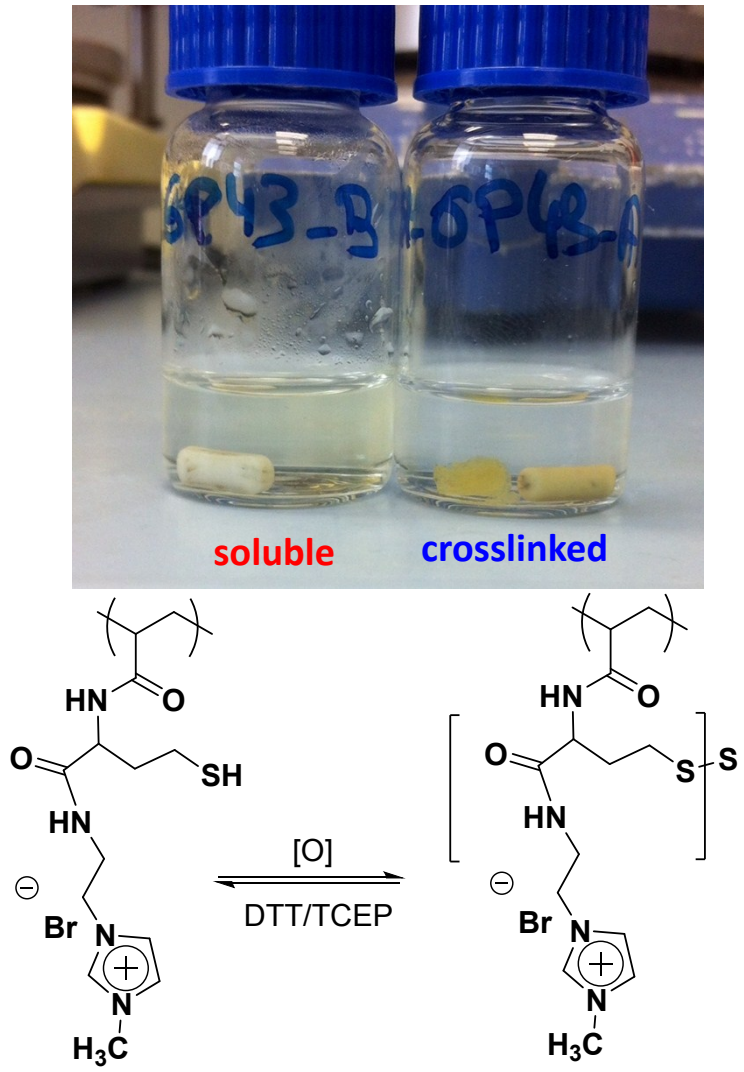
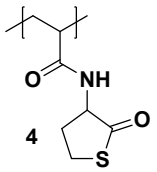


Figure S40. Destruction of the gel through the reduction of the S-S bonds using DTT or TCEP.

Electrospinning process

The electrospinner used in this study was a Fluidnatek LE 100.V1 (BioInicia, Spain). The polymer solutions were loaded into a plastic syringe equipped with a stainless steel needle tip (0.9 mm inner diameter). The tip-collector working distance was fixed at 16 cm. The applied voltage was kept between +12, -5 kV and the flow rate at 1.5 mL/h. The electrospun fibers were collected on aluminum foil that covered a rotating collector. All electrospinning experiments were carried out at room temperature and relative humidity of 36 %. The obtained membranes were vacuum dried overnight in the oven at 50 ºC.



4

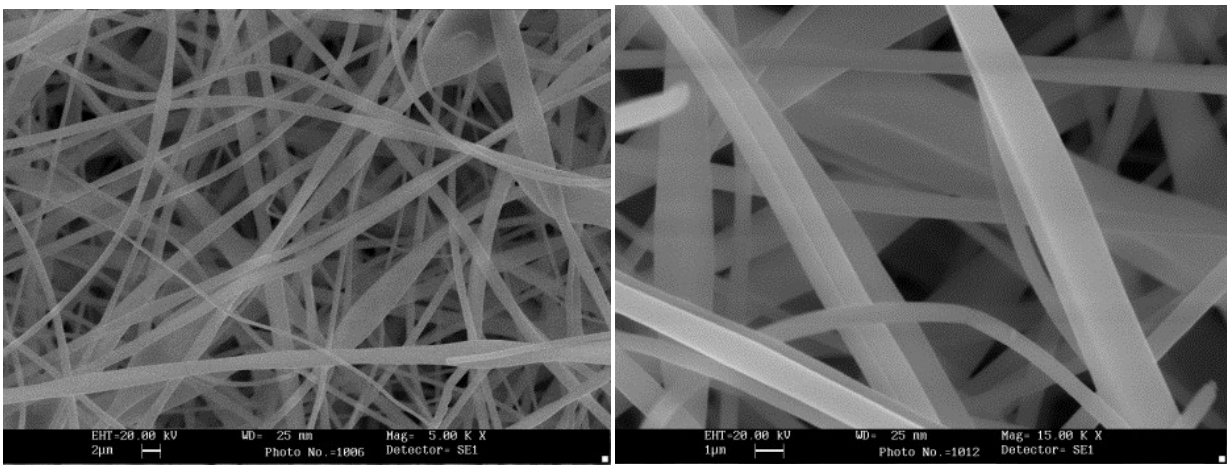


Figure S41. SEM pictures of the mat polymer fibers obtained by electrospinning of 50 % weight solution of **4** in DMF. **Electrospinning conditions:** J = 5 mL, d = 12 mm, A = 16 cm, c = 1.5 mL/h, V = +12, -5 kV Vol = 5 mL and Sweep = 200-230 mm. **Mean size diameter of the fibers:** 900nm.

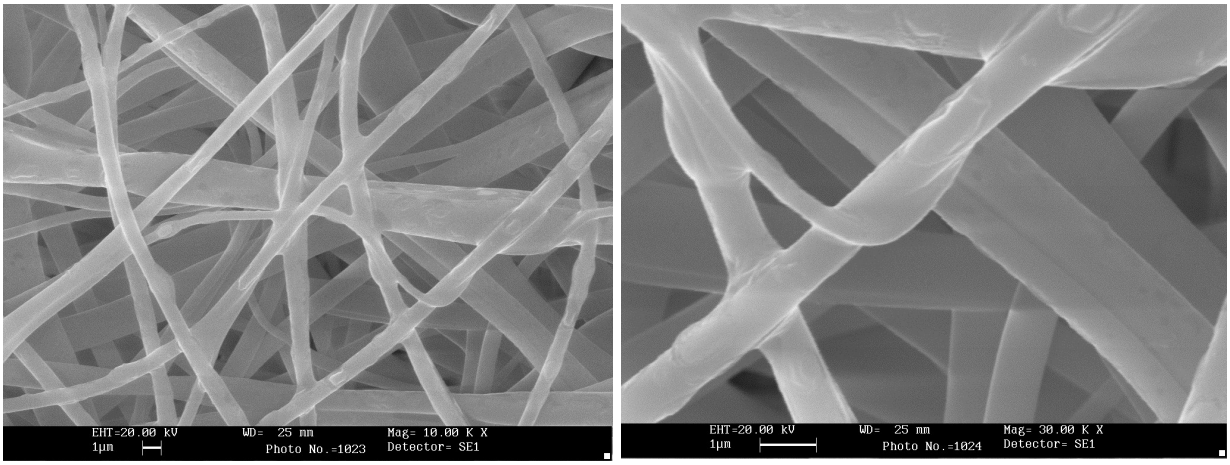


Figure S42. SEM pictures of the mat polymer fibers **13a** obtained by post-modification of **4** with hexamethylenediamine (**12a**). **Mean size diameter of the fibers:** 1.239 µm.

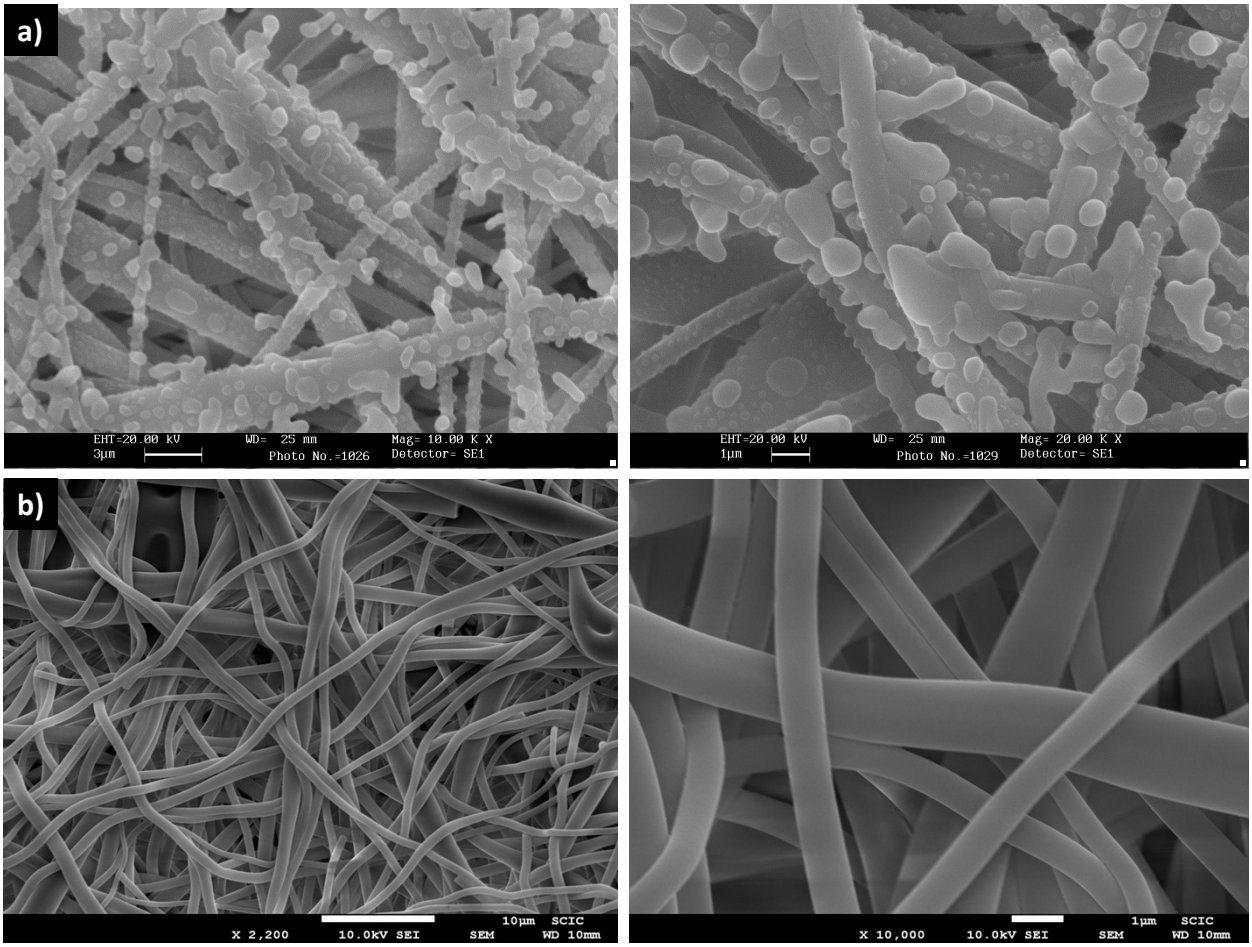


Figure S43. SEM pictures of the mat polymer fibers **13b** obtained by post-modification of **4** with butylenediamine (**12b**). a) using 0.5 equiv. of **12b Mean size diameter of the fibers:** 2.12 µm b) using for 1.5 equiv. of **12b. Mean size diameter of the fibers:** 938 nm.

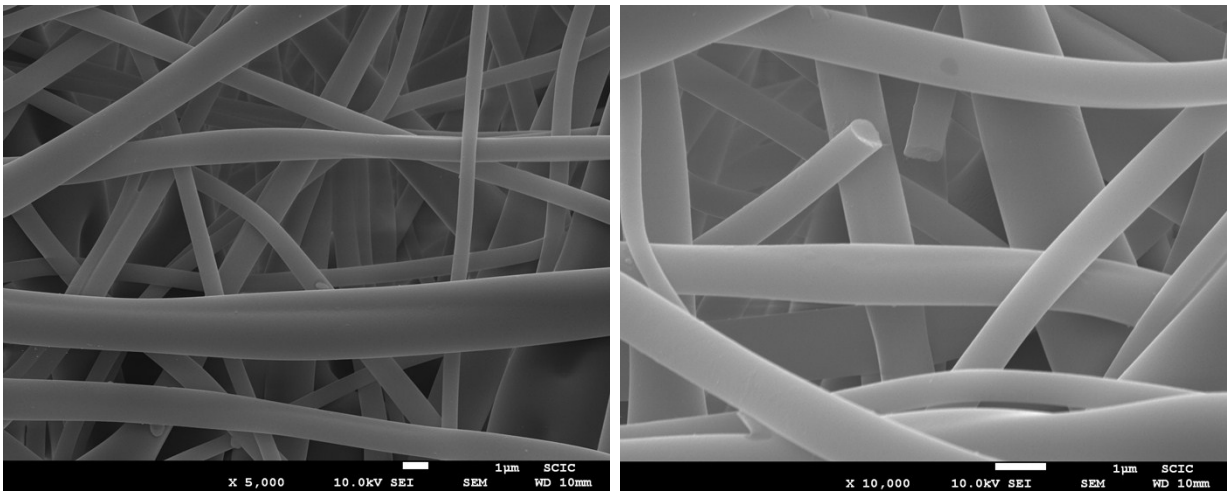


Figure S44. SEM pictures of the mat polymer fibers **13c** obtained by post-modification of **4** with ethylenediamine (**12c**). **Mean size diameter of the fibers:** 1.488 µm.

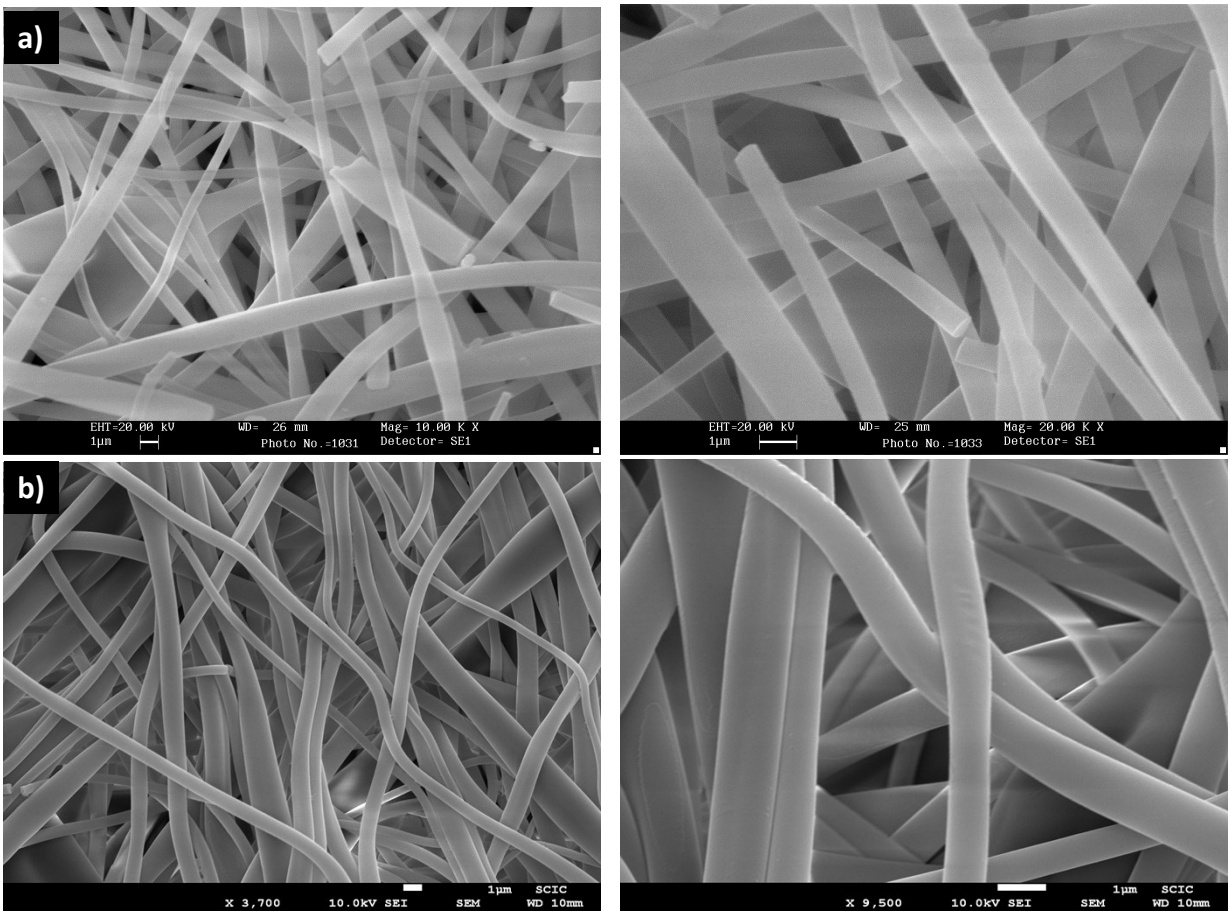


Figure S45. SEM pictures of the mat polymer fibers **13d** obtained by post-modification of **4** with n-butylamine, **12d**. a) using 0.5 equiv. of **12d Mean size diameter of the fibers:** 1.458 µm b) using for 1.5 eq of **12d. Mean size diameter of the fibers:** 990 nm.

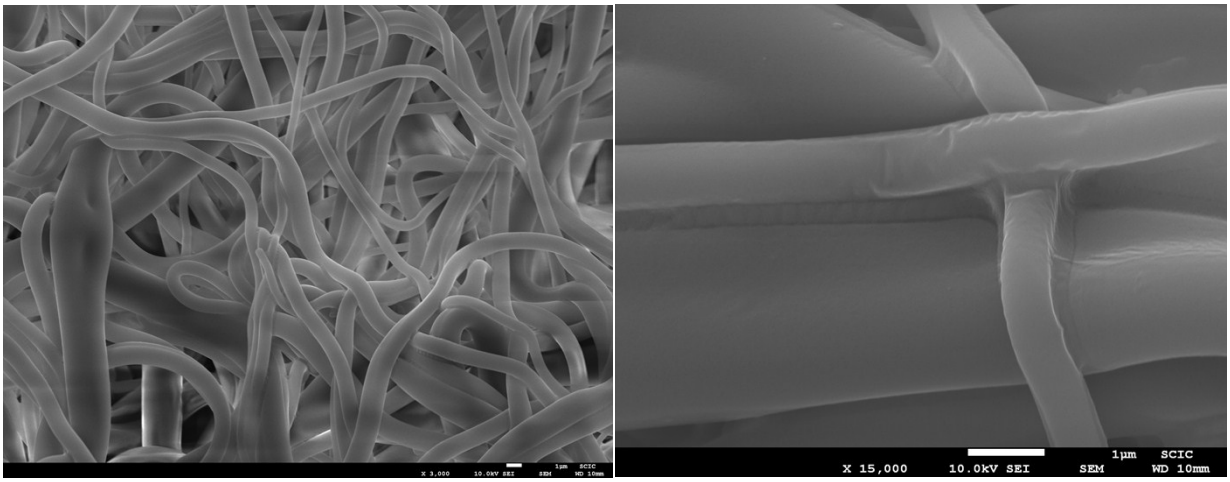


Figure S46. SEM pictures of the mat **14** obtained after modification of the polymer mat **4** with **12b** and **7a**. **Mean size diameter of the fibers:** 1.35 µm.

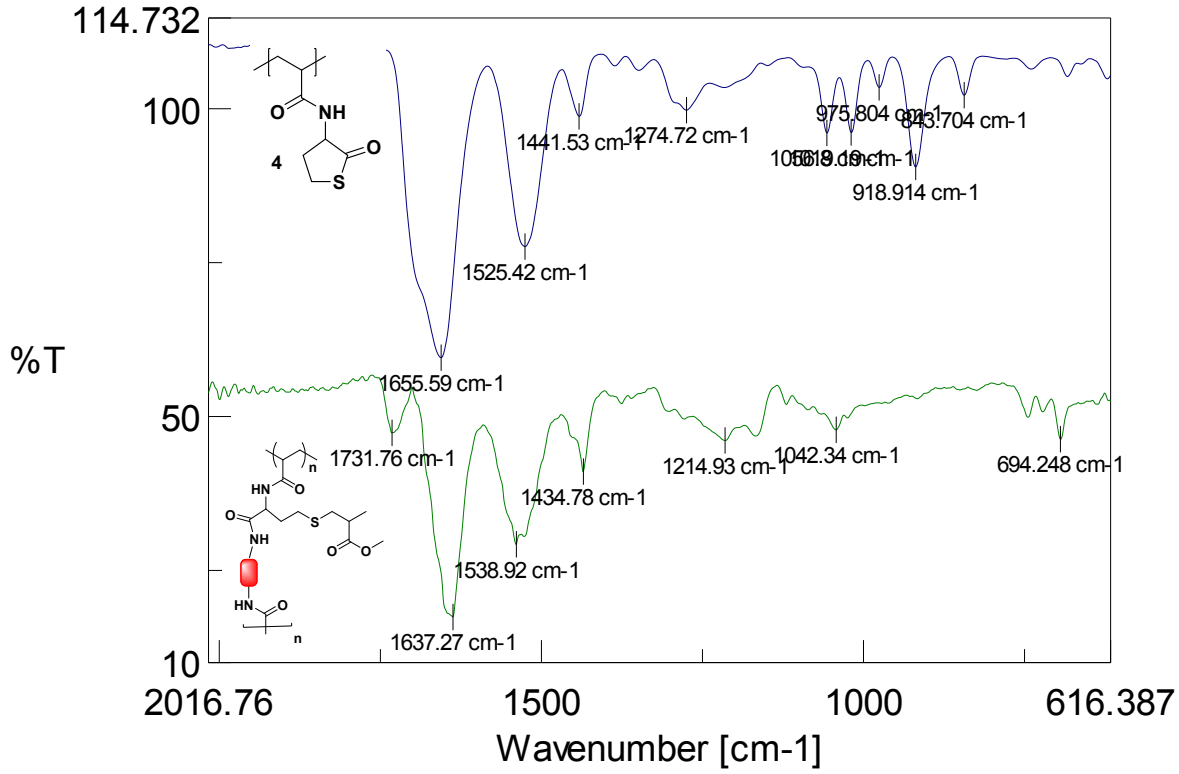


Figure S47. ATR-FT-IR spectra for fiber mat **14** obtained by post-modification **7a** and **12b.**

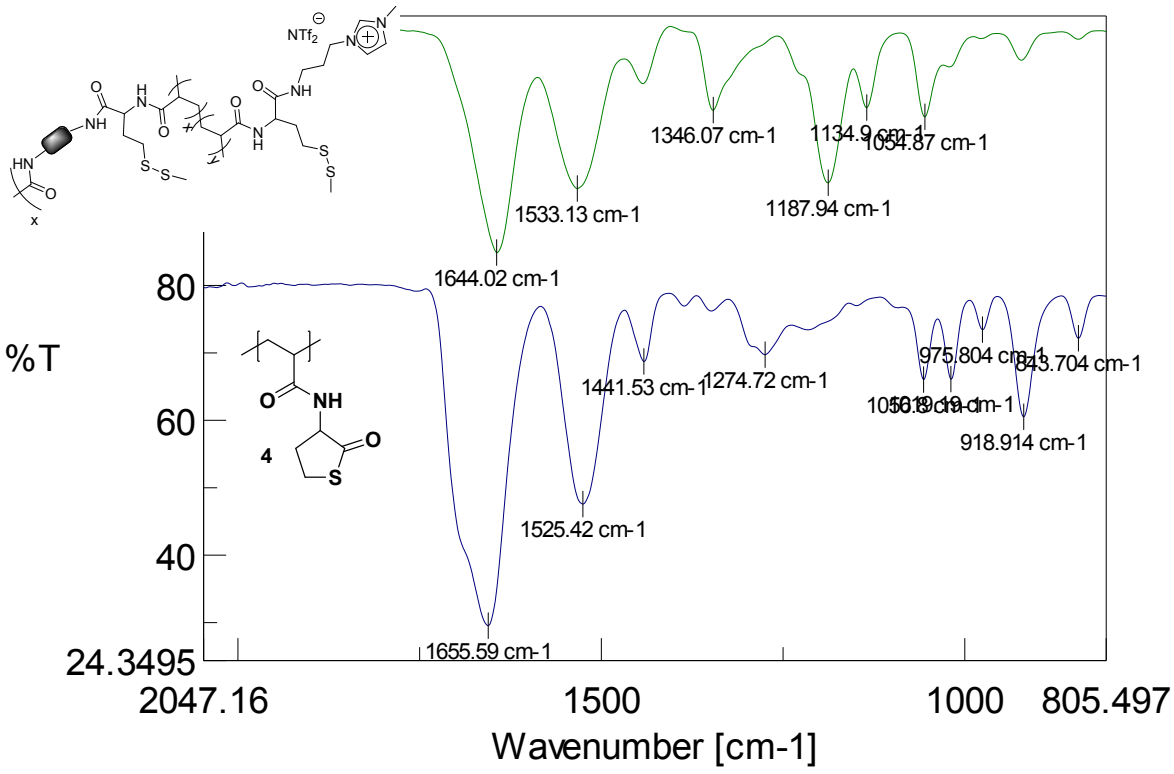


Figure S48. ATR-FT-IR spectra for fiber mat **15** obtained by post-modification **5f** and **12b.**