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Polymer-analogous transformations of poly(*N*-vinylpyrrolidone) to produce new complexing macromolecular systems

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Experimental technique

IR spectra of the samples were recorded on Shimadzu IRAffinity-1 (in KBr pellets). The NMR spectra of the compounds and total product mixtures were recorded in $CDCl_3$ or DMSO-d_6 using an Avance III spectrometer (Bruker) operating at a frequency of 400 MHz and 100 MHz for ^1H and ^{13}C experiments, respectively, with sample temperatures of 22 °C. Mass spectra were obtained on a Shimadzu Nexera X2 LCMS-9030 with electrospray ionization (under nitrogen flow), in methanol or a MeOH/MeCN mixture. Melting points of the samples were determined on a Kofler hot-stage microscope NAGEMA PHMK 05 at a heating rate of 1 K min^{-1}. The reaction progress was monitored by TLC on Silufol-254 plates ($CHCl_3$-MeOH, 9:1 v/v). Samples were obtained from solutions of polymers using Labconco-6 vacuum sublimation dryer. The number of carboxylate groups in hydrolyzed PVP was determined by conductometric titration of samples with NaOH (0.1M) solution, according to the described method [A. Conix and G. Smets, *J. Polym. Sci.*, 1955, **15**, 221]. pH control during conductometric titration was carried out on a Sartorius PP-20 pH meter.

All chemicals except those described below were obtained from commercial sources (reagent grade, analytical grade or related Russian qualifications) and used as purchased. PVP (K30) was dried by distillation of azeotrope mixture of water and benzene, followed by distillation of benzene under reduced pressure and final drying of PVP in a vacuum desiccator until mass was a constant. *N*-Methyl-2-pyrrolidone (NMP), dimethyl sulfate were purified by vacuum distillation immediately before use.

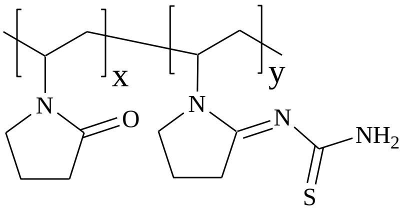
(1-Methylpyrrolidin-2-ylidene)thiourea 1. A mixture of NMP (1.00 g, 0.01 mol) and dimethyl sulfate (1.26 g, 0.01 mol) was heated and stirred at 80°C for 2 h. The mixture was cooled to below 15°C, and concentrated solution of NaOMe (prepared from Na metal, 0.230 g, 0.01 mol) was added under vigorous stirring. After 5 min, at stirring at room temperature thiourea (0.76 g, 0.01 mol) was added. The mixture was kept at room temperature for 12 h. The white precipitate formed after the addition of a few drops of water was filtered off, washed three times with hexane and dried in a vacuum desiccator. The yield was 1.05 g (67%), light yellow crystals. Mp 140.0-142.5°C.

IR (KBr pellets, 4000-400 cm^{-1}): 3446 (N-H(as)), 3337 (N-H(s)), 2957 (C-H), 1633 broad. (C=N), 1231 broad. (C-N), 1005 (C=S).
NMR ^1H, δ, ppm (*J*, Hz): 1.85 (2H, m, C^3H_2), 2.13-2.26 (2H, m, C^5H_2), 2.70 (3H, s, C^6H_3), 3.25-3.37 (2H, m, C^1H_2), 8.09 (2H, s, NH_2).
NMR ^{13}C, δ, ppm.: 17.7 (C^3), 29.5 (C^5), 30.6 (C^6), 49.2 (C^1), 174.5 (C^4), 184.2 (C^8).
HiRes MS-EI, *m*/*z*: 158.0750 $[M + H]^+$ (calc. for $C_6H_{11}N_3S$: $[M]^+$ 157.0674, $[M + H]^+$ 158.0746).

2-(1-Pyridin-4-ylethylidene)hydrazine-1-carbothioamide 2. A solution of thiosemicarbazide (377 mg, 4.13 mmol) and 4-acetylpyridine (0.5 g, 4.13 mmol) in *n*-butanol (10 mL) with a catalytic amount of acetic acid was boiled under reflux for 3 h. The precipitated solid was filtered off and washed with cold *n*-butanol (10 mL). The yield was 0.64 g (80%), orange-yellow crystals. Mp 194.0-196.0°C.
IR (KBr pellets, 4000-400 cm^{-1}): 3290 (N-H, NH_2), 3169 (N-H, NH), 3001-3100 (C-H(Ar)), 2989 (C-H), 1629 (C=N), 1513 (C-C(Ar)), 1485 (C-N), 1109 (N-N), 1087 (C=S).
NMR ^1H, δ, ppm. (*J*, Hz): 2.30 (3H, c, C^9H_3), 7.89 (2H, broad. d, $J = 5.4$ Hz, $C^3{}_{Ar}H$, $C^5{}_{Ar}H$), 8.12 (1H, s, NH_2(I)), 8.44 (1H, s, NH_2(II)), 8.57 (2H, d, $J = 5.4$ Hz, $C^2{}_{Ar}H$, $C^6{}_{Ar}H$), 10.42 (1H, s, NH).
NMR ^{13}C, δ, ppm: 13.8 (C^9), 121.1 (C^1, C^5), 145.2 (C^3), 145.4 (C^7), 150.2 (C^2, C^6), 179.8 (C^{11}).
HiRes MS-EI, *m*/*z*: 195.0699 $[M + H]^+$ (calc. $C_8H_{10}N_4S$: $[M]^+$ 194.0626, $[M + H]^+$ 195.0699).

Hydrolyzed PVP 3. Hydrolysis of PVP was performed according to a modified method [A. Conix and G. Smets, *J. Polym. Sci.*, 1955, **15**, 221]. PVP (1.00 g) was dissolved in 0.1M NaOH (100 mL) and heated in a PTFE autoclave (140℃, 48 h). The resulting solution after cooling was acidified to pH = 2-3 with 1M HCl, partially evaporated and dialyzed (3 kDa membrane) against distilled water for 48 h with permanent change of the solvent. The resulting solution was frozen and freeze dried. The weight of obtained polymer was 890 mg, as a white fibrous substance. The amount of hydrolyzed γ-lactam cycles was 4.7-5.0% mol per unit mass of the polymer.
IR (KBr pellets, 4000-400 cm^{-1}): 576 w, 650 w, 741 w, 849 w, 1018 w, 1169 m, 1222 m, 1291 s, 1321 m, 1374 m, 1422 s, 1439 s, 1465 s, 1490 s, 1498 s, 1507 s, 1601 s, broad, 2920 s, 2960 s, 3441 s, broad.

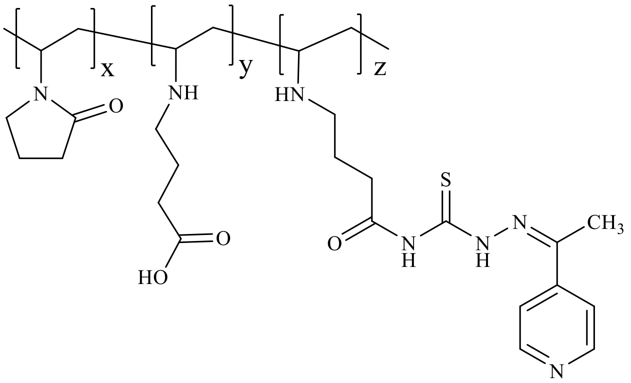
PVP containing (1-methylpyrrolidin-2-ylidene)thiourea fragments 4.



A solution of PVP (2.0 g, 0.0180 mol) and Me_2SO_4 (1.14 g, 0.0180 mol) in methanol (40 mL) was boiled for 2 h, cooled to 10-15°C, NaOMe (prepared from Na metal, 0.414 g, 0.0180 mol) was added and stirred until it dissolved completely. A solution of thiourea (1.37 g, 0.0180 mol) in methanol (20 mL) was added dropwise to the resulting mixture with stirring. The resulting solution was kept at room temperature for 2 h and evaporated under reduced pressure. The resulting white viscous solid was dissolved in methanol and dialyzed against methanol (3 kDa membrane) for 3 days with a permanent change of solvent. The substance obtained after evaporation of the solvent was dissolved in water, frozen and freeze dried. The yield was 1.80 g (90%), a white fibrous substance.

^{1}H NMR, δ, ppm (*J*, Hz): 1.16-1.73 (2H, m, C^1H_2), 1.75-1.96 (2H, m, C^4H_2), 2.03-2.42 (2H, m, C^5H_2), 2.85-3.25 (2H, m, C^3H_2), 3.45-3.89 (1H, m, C^2H), 4.04-4.15 (0.08 H, br. d, *J* = 5.1 Hz, NH_2).

PVP containing 2-(1-pyridin-4-ylethylidene)hydrazine-1-carbothioamide fragments 5.



Substance **3** (0.500 g, n(COOH) = 0.05 - n(2) = 0.222 mmol) was dissolved in absolute methanol (15 mL). A solution of DCC (0.0690 g, 0.334 mmol) and NHS (0.0385 g, 0.334 mmol) in absolute methanol (10 mL) was added to the resulting solution. The mixture was stirred at room temperature for 1 h. Then a solution of compound **2** (0.0650 g, 0.335 mmol) dissolved in absolute methanol (35 mL) was added. The solution was continued to stir for 1 h. After completion of the reaction, the solution was evaporated under reduced pressure and water (5 mL) was added. The precipitate was filtered off, methanol (5 mL) was added to the supernatant. Dialysis was performed against methanol for 96 hours. At the end, the solvent was evaporated under reduced pressure. The resulting viscous mass was frozen and freeze dried. The yield was 0.43 g (86%), a white fibrous substance.

^{1}H NMR, δ, ppm: 1.16-1.73 (2H, m, C^1H_2), 1.75-1.96 (2H, m, C^4H_2), 2.03-2.42 (2H, m, C^5H_2), 2.85-3.25 (2H, m, C^3H_2), 3.45-3.89 (1H, m, C^2H), 7.84-8.09 (0.06 H, two br. d, CH(Ar)).

Figure S1 ^{1}H NMR spectrum of **1**

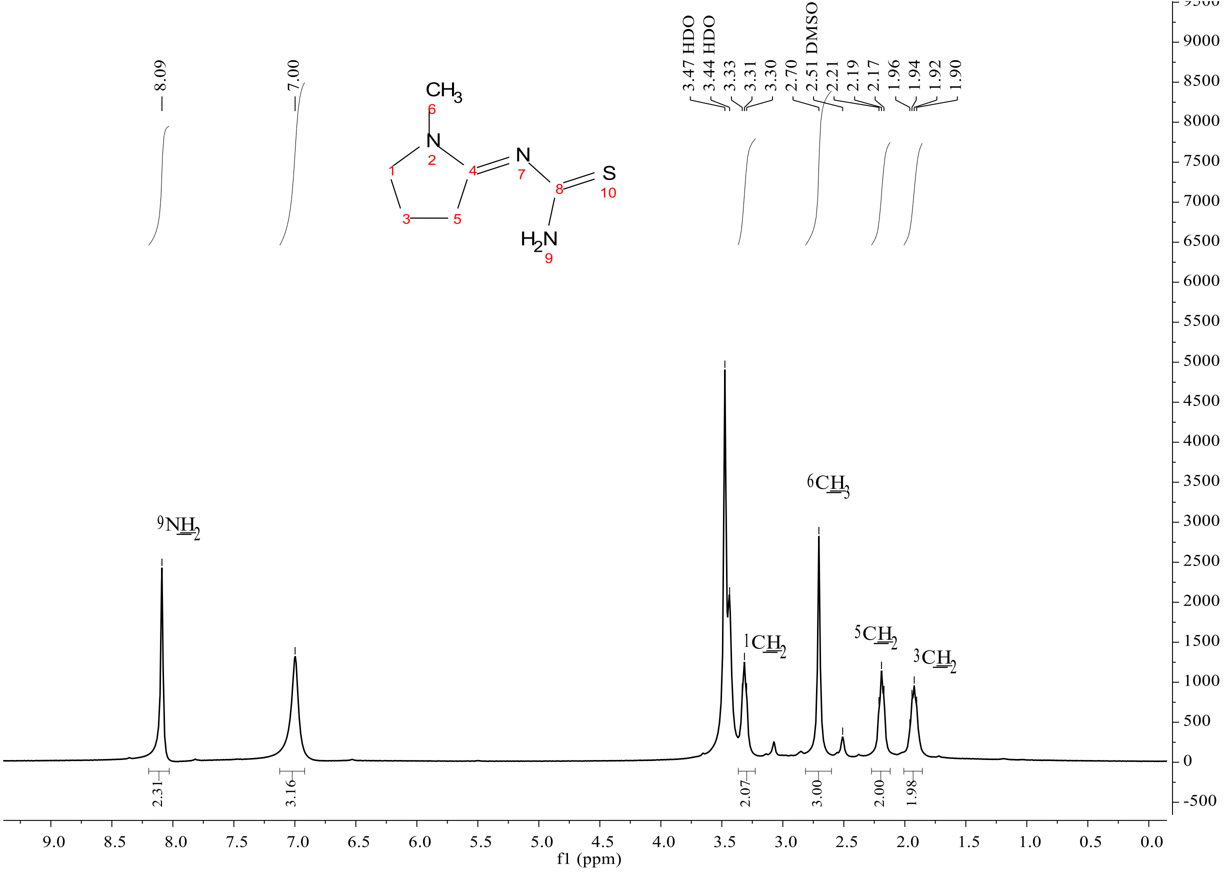


Figure S2 ^{13}C NMR spectrum of **1**

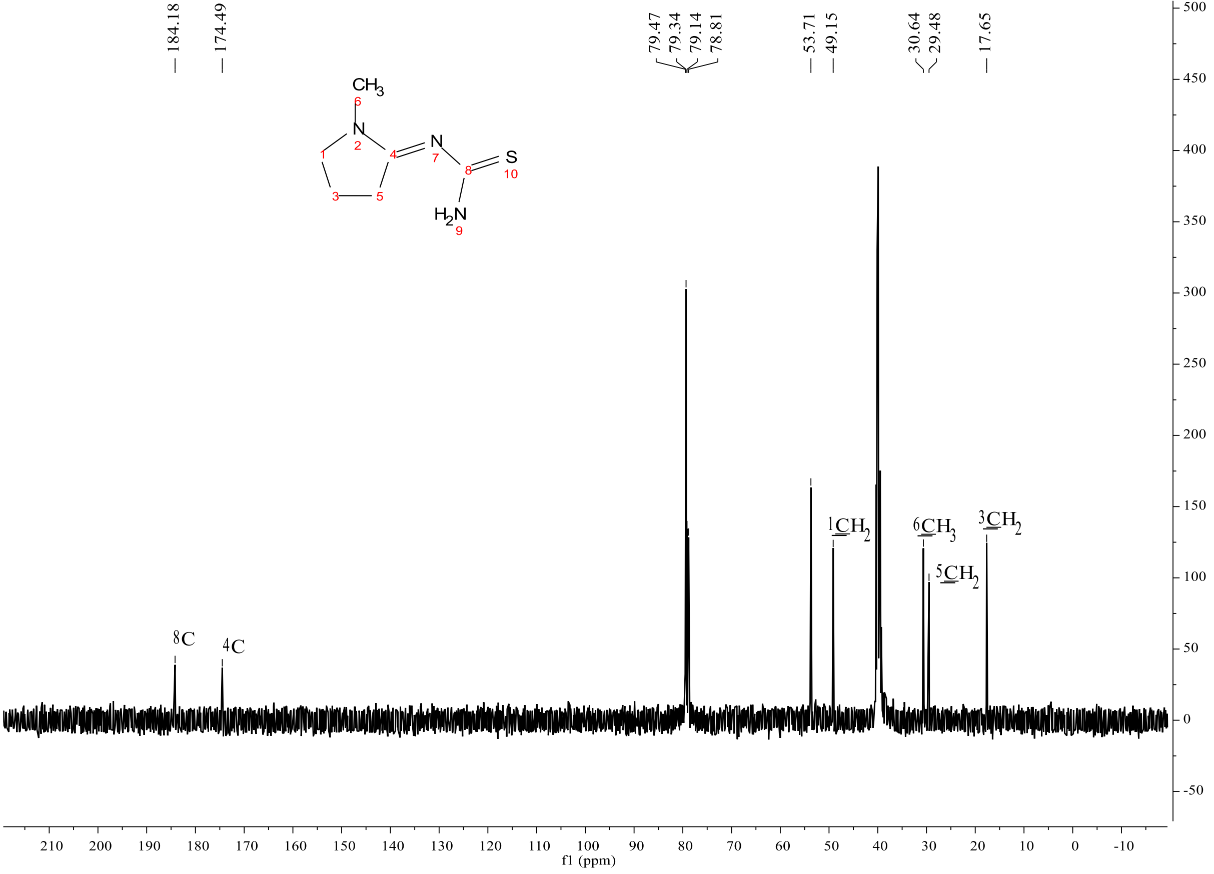


Figure S3 IR spectrum **1**

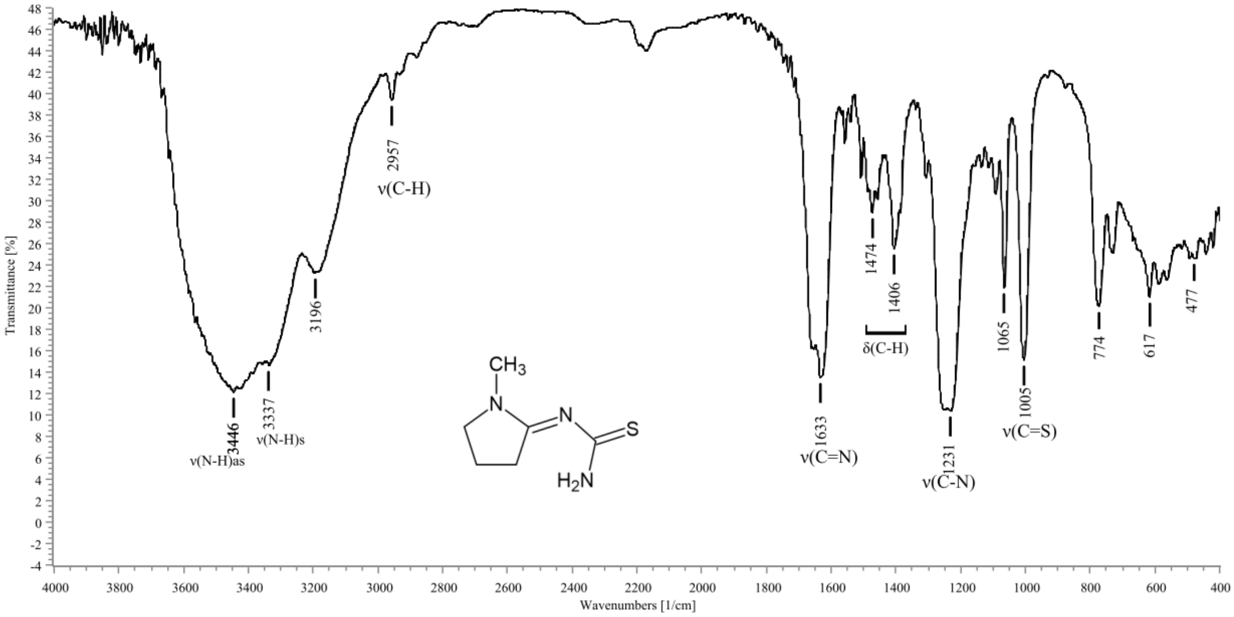


Figure S4 ^{1}H NMR spectrum of **2**

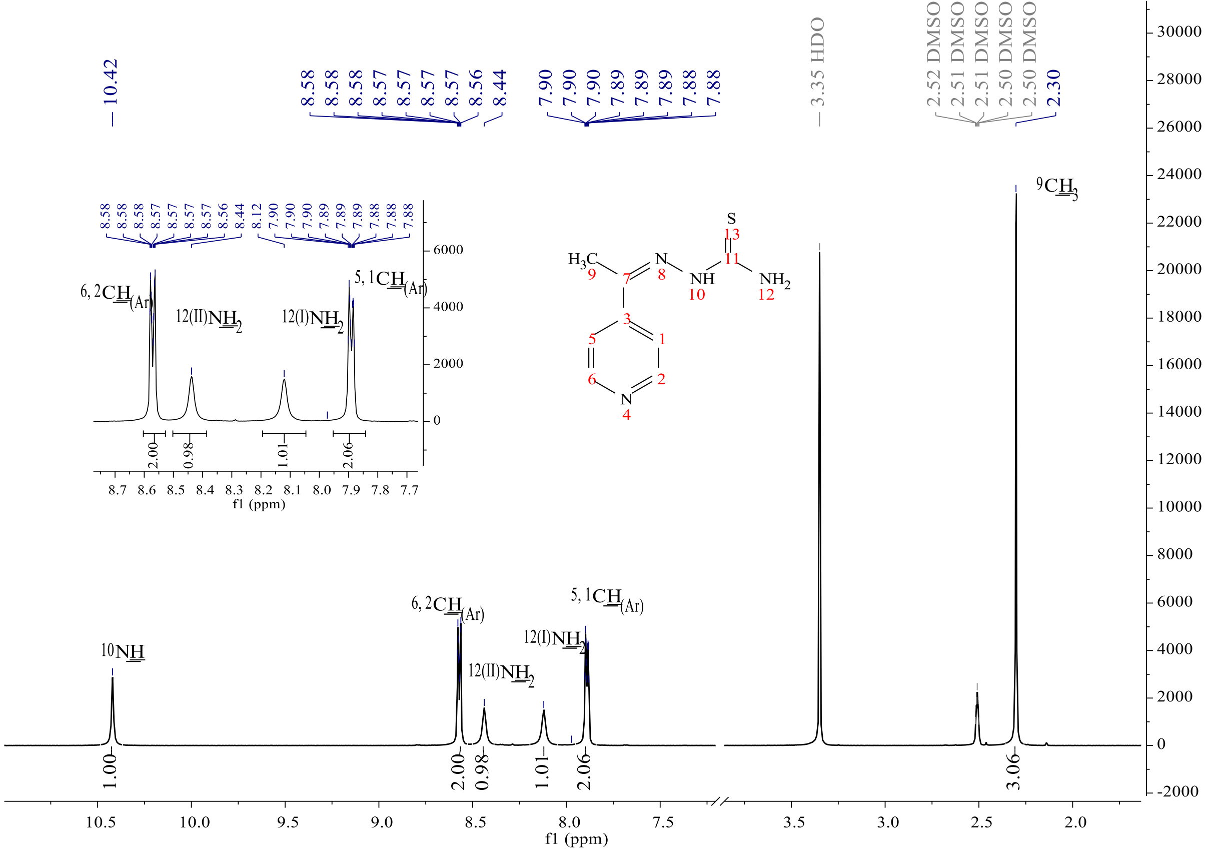


Figure S5 ^{13}C NMR spectrum of **2**

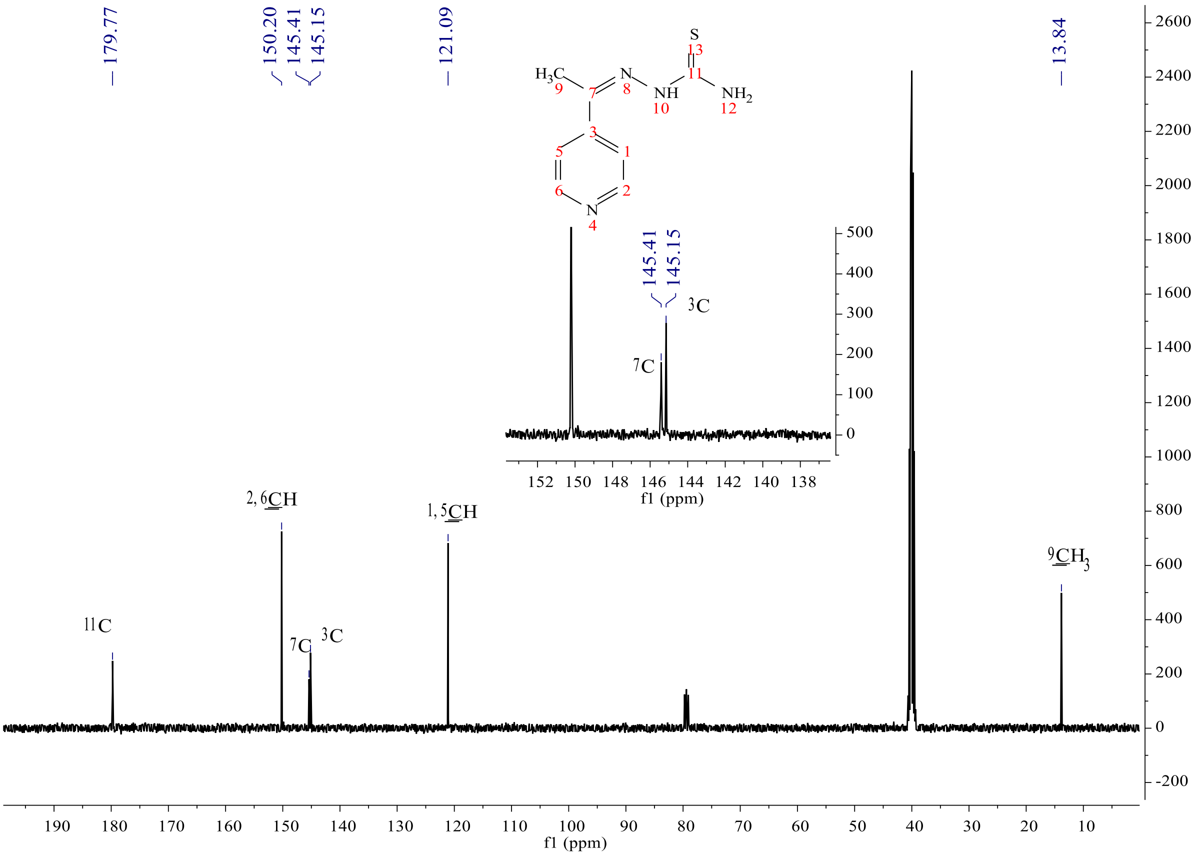


Figure S6 IR spectrum of **2**

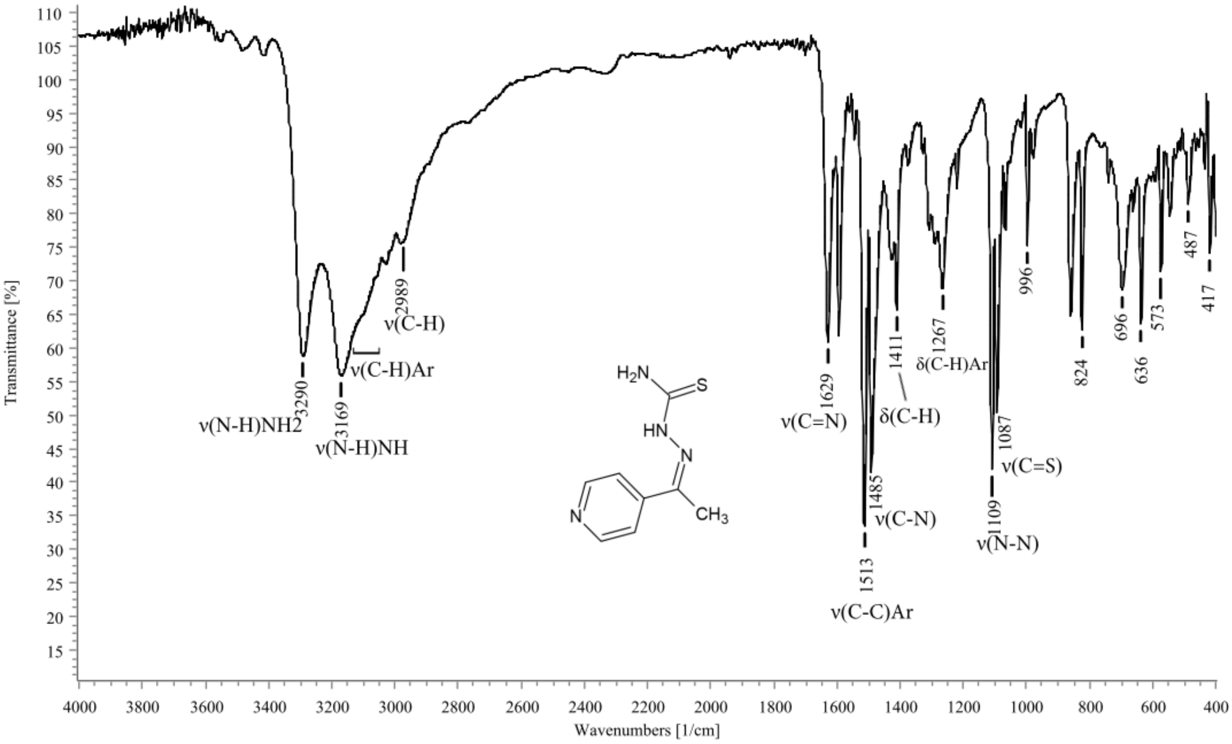


Figure S7 Fragment of IR spectrum of PVP and its hydrolyzed form **3** (in KBr pellet)

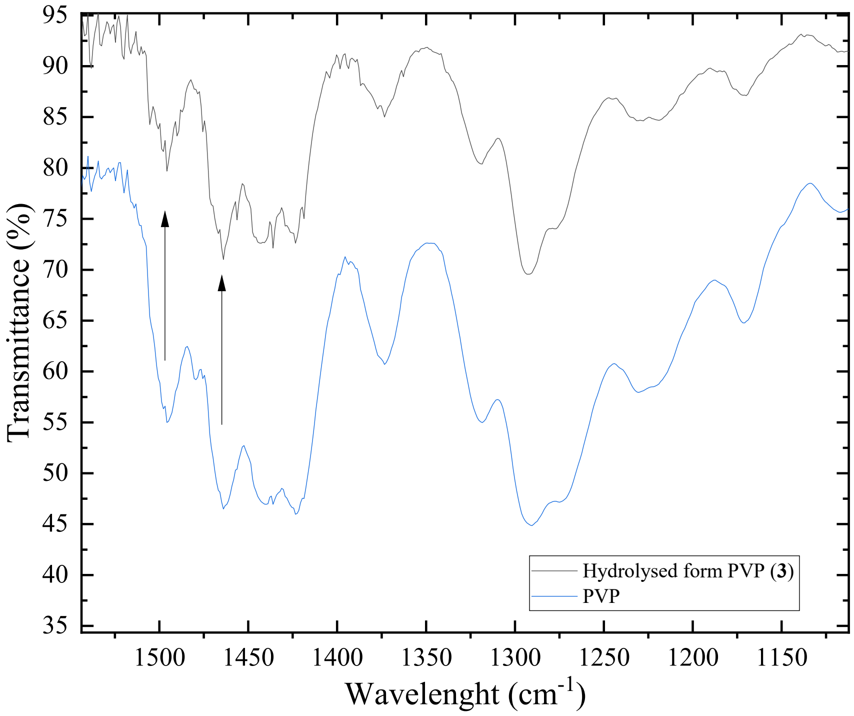


Figure S8 ^{1}H NMR spectrum of **4**

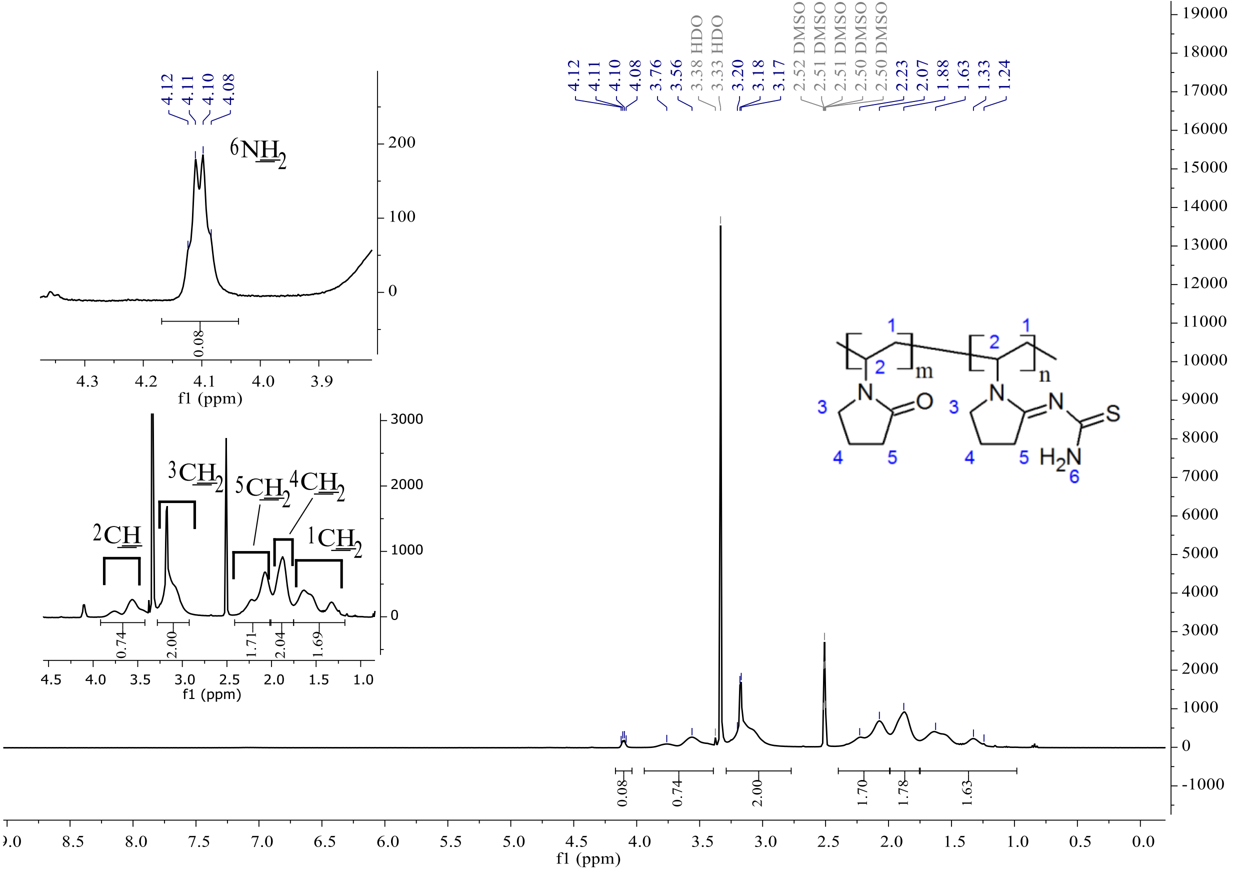


Figure S9 ^{1}H NMR spectrum of **5**