Supporting Information

Continuous flow system for the simple preparation of functionalized polymeric beads from Poly(acrylamide-thiolactone)

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Table SI.1. Effect of the concentration on the gelation time.

Entry	DMF [µL][a]	1 [mol L^{-1}]	Inversion test (time/ min) [b]		
1	92	1.114	L (0)	L (10)	G (20)
2	137	1.026	L (0)	L (10)	G (25)
3	229	0.884	L (0)	L (10)	G (45)
4	275	0.826	L (0)	L (10)	G (50)

[a] 0.25 mL of a polymer solution of 2.34 mmol mL^{-1} (400 mg mL^{-1}) in DMF was added to different volumes of DMF containing the same amount of trimethylamine (121 µL, PAHT (**1**):Et_3N, 1:1.5 molar ratio), 3-(dimethylamino)-1-propylamine (DMAPA, **2,** 55 µL, PAHT:**2**, 1:1.34 molar ratio) and 1,5-diaminopentane (**3**, 7 µL, PAHT:**3**, 5:1 molar ratio). 40 % mol crosslinking. [b] Vial inversion test L: liquid, G: gel, the time for each vial inversion test if provided in brackets.

Table SI.2. Effect of the amount of crosslinking agent on the gelation time.[a]

Entry	2+3:1	1:3	Molar ratio crosslinking	1 [M]	Inversion test (time/ min)[b]		
1	1.49	0.00	0	0.69	L (0)	L (0)	L (24 h)
2	1.64	13.76	15	0.69	L (0)	L (10)	G (24 h)
3	1.69	10.12	20	0.69	L (0)	L (10)	G (24 h)
4	4.49	0.67	299	0.69	G (0)	-	-
5	2.49	2.00	100	0.69	L (0)	G (2)	/
6	2.09	3.34	60	0.69	L (0)	G (3)	/
7	1.90	4.98	40	0.69	L (0)	G (10)	/

[a] To 0.25 mL of a polymer solution of 1.17 mmol mL^{-1} (200 mg mL^{-1}) in DMF was added the same amount of trimethylamine (121 µL, PAHT (**1**):Et_3N, 1:3 molar ratio), 3-(dimethylamino)-1-propylamine (DMAPA, **2,** 55 µL, PAHT (**1**):**2**, 1:1.5 molar ratio) and a variable volume of 1,5-diaminopentane (**3**). [b] Using the vial inversion test L: liquid, G: gel.

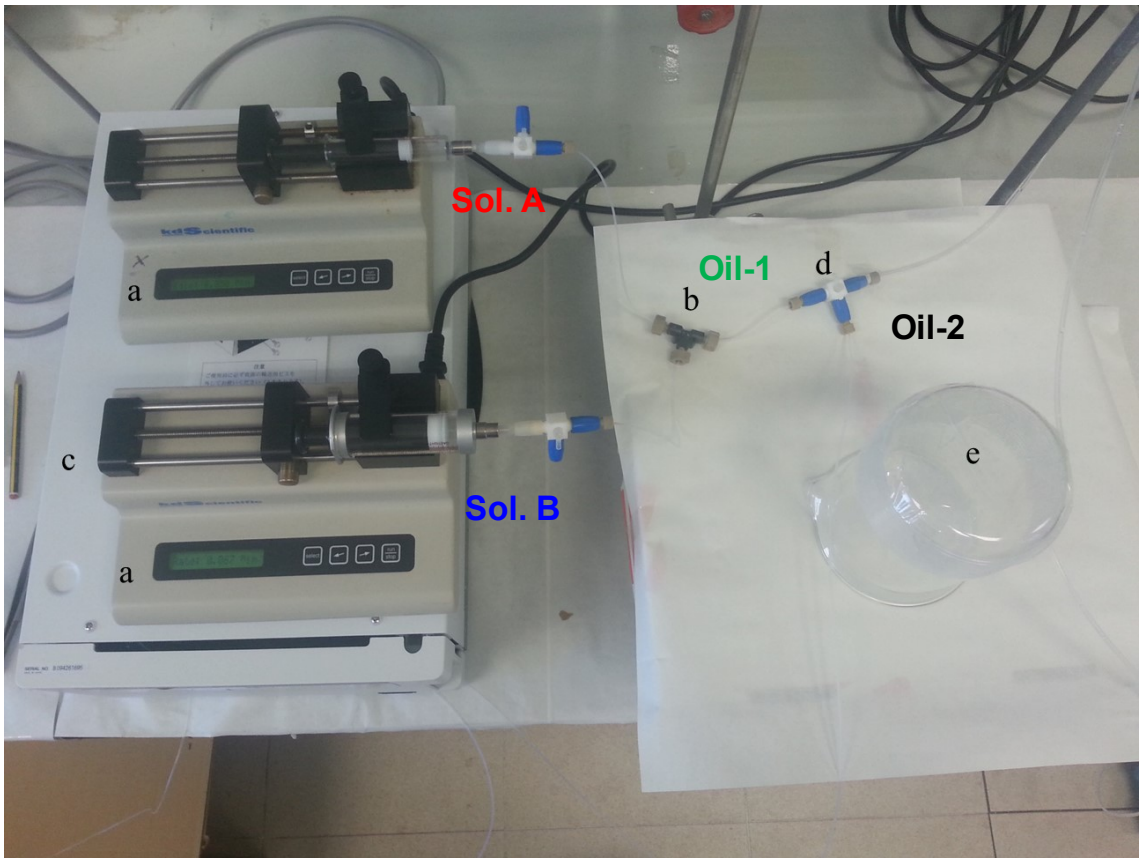


Fig. SI.1. General scheme of reactor for the post-polymerization modification of **1** to obtain beads of polymer **4** in flow. **a:** syringe pumps, **b:** T-piece connection to mix solution A (polymer solution) Solution B (modifiers solutions), **c:** HPLC pump, **d:** generator droplets, **e:** residence unit (reactor).

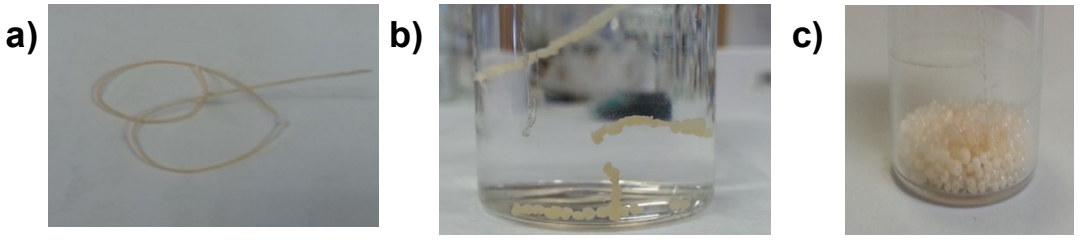
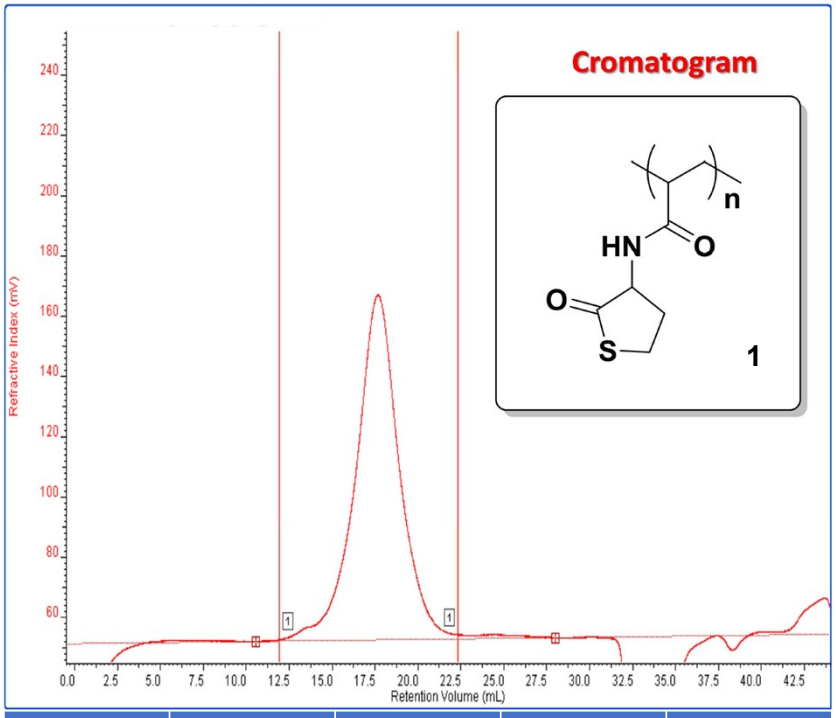


Fig. SI.2. Functional insoluble polymers obtained by post-polymerization modification of **1**. **(a)** Obtained with the conditions reported in Table 1, Entry 3. **(b)** Obtained with the conditions reported in Table 1, Entry 4. **(c)** Obtained with the conditions reported in Table 1, Entry 6.



Sample	Mn (Da)	Mw (Da)	Polydispersity (Mw/Mn)	Volum of retention (mL)
Compound **1**	20669	32709	1.582	17.616

Fig. SI.3. Size exclusion chromatography obtained for **1** in DMF (8 mg/mL) and 0.1% (w/w) of LiBr.

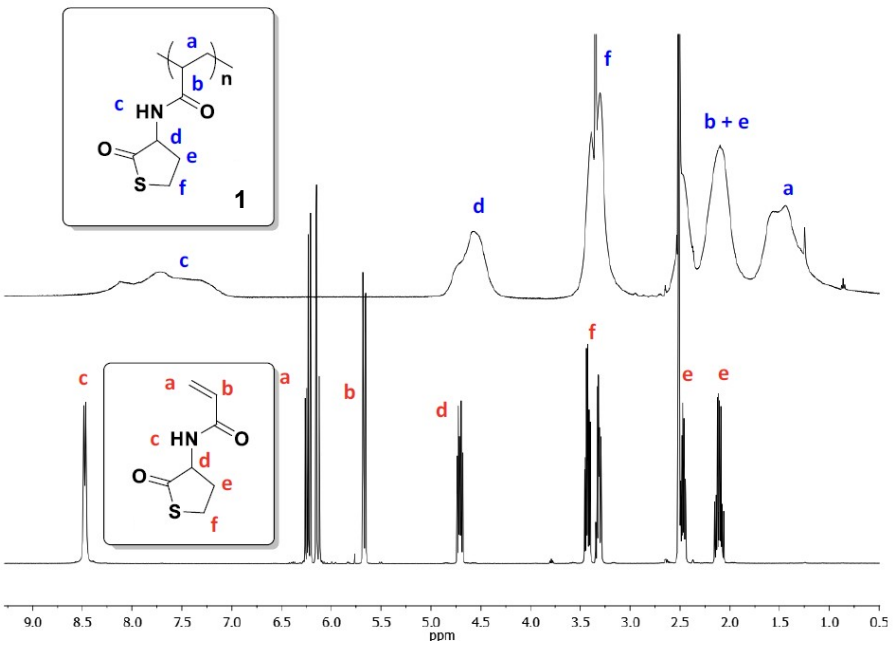


Fig. SI.4. Comparison of the ^{1}H-NMR spectra for the acryloyl homocysteine thiolactone and the related homopolymer **1** obtained by RAFT polymerization.

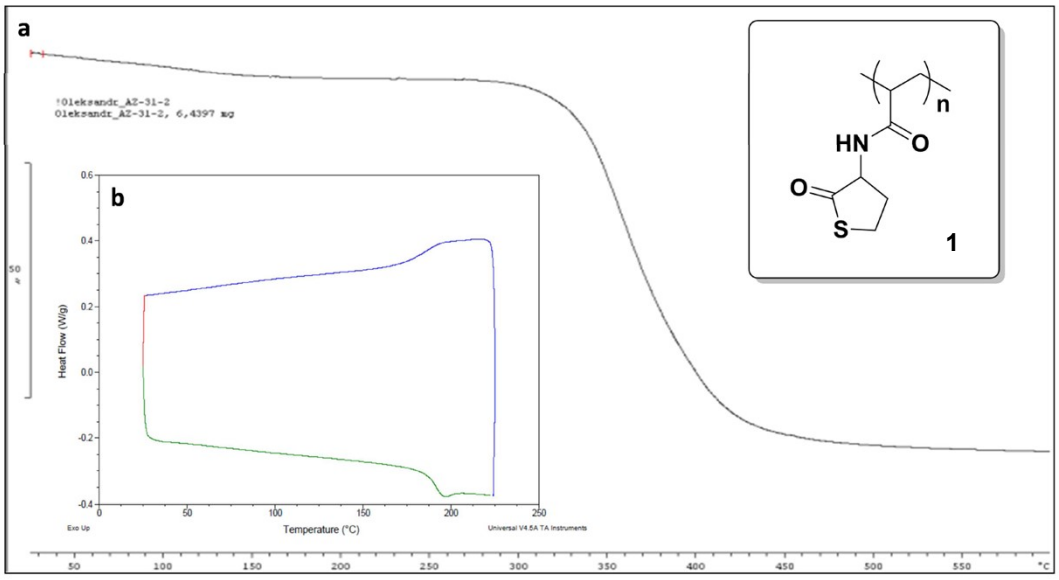


Fig. SI.5. a: TGA spectra obtained from 25 to 600 °C for **1**. **b**: DSC spectra obtained for **1** between 195 and 200 °C.

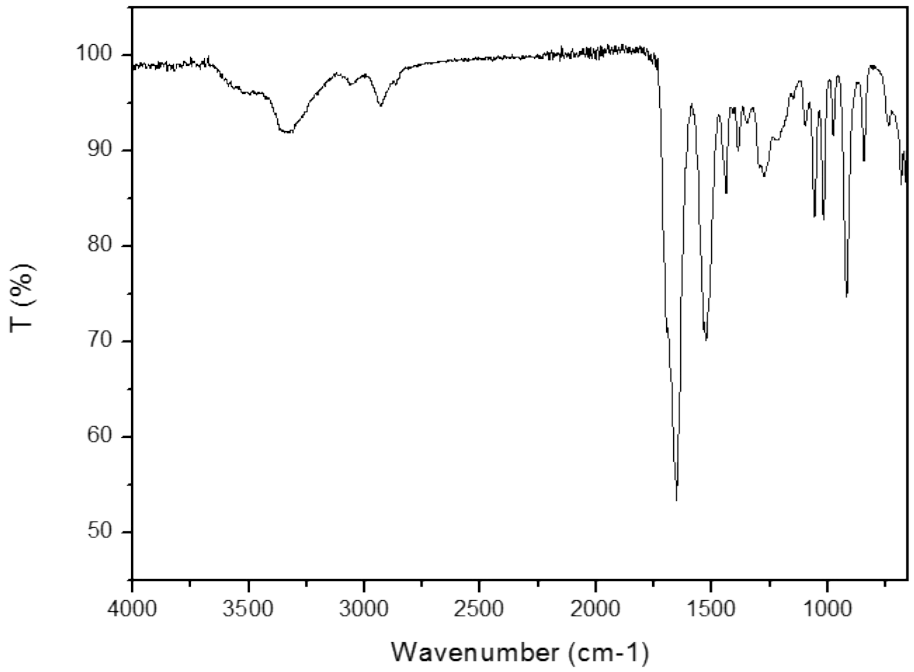


Fig. SI.6. FT-IR-ATR spectra of the polymer **1**.

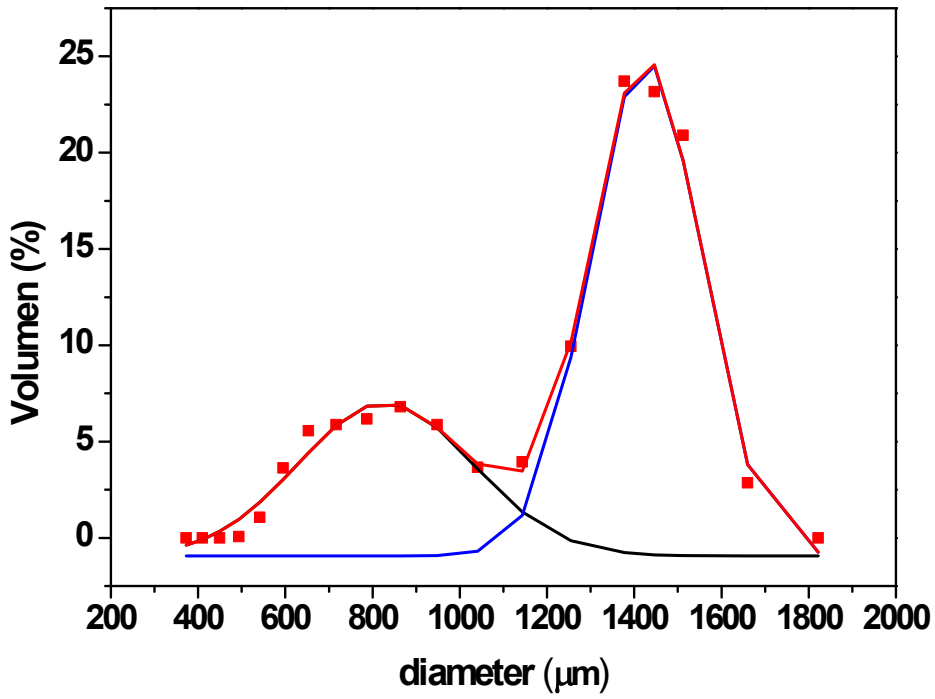


Fig. SI.7. Size distribution of the polymer **4** obtained using a Coulter counter system.

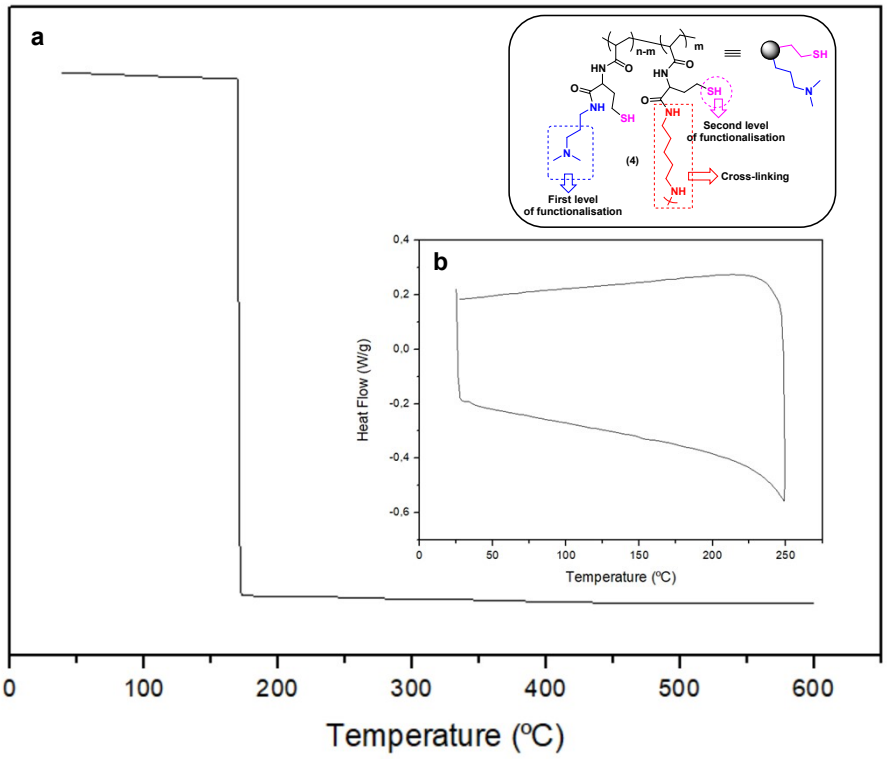


Fig. SI.8. a: TGA spectra obtained from 25 to 600 °C for **4**. **b**: DSC spectra obtained for **4** between 25 and 250 °C.

Syringe method for the swelling test

The swelling properties of the polymers were measured by the syringe method. A syringe was loaded with a known amount (typically 100 mg) of the polymer, and the volume of the dry polymer was recorded (*b* mL). H_2O, MeOH or CH_2Cl_2 was added to the syringe, and the mixture was let to stand at room temperature to reach equilibrium. The extra solvent was removed from the syringe by using a plunger, and the volume of the swollen polymer was recorded (*c* mL). The swelling volume (mL g^{-1}) was estimated as the volume of solvent in the swollen polymer (*c*–*b* mL) divided by the weight of the used polymer.

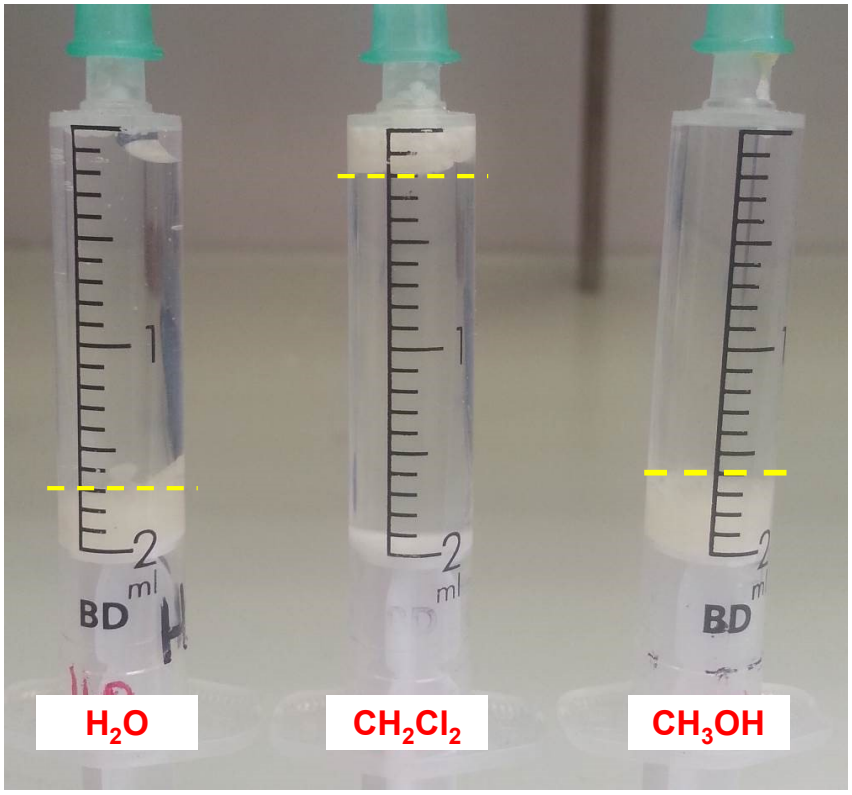


Fig. SI.9. Swelling of the resin **4** in three different solvents.

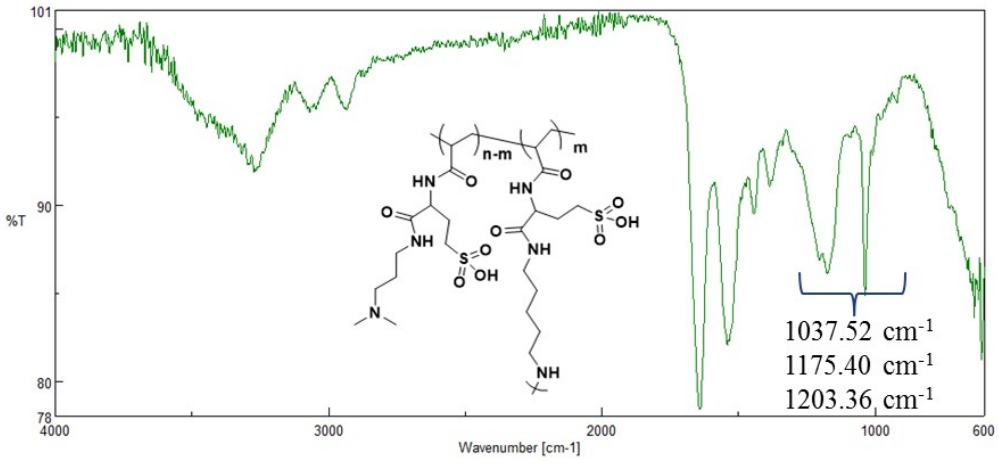


Fig. SI.10. FT-IR-ATR spectra of the polymer **5** obtained by chemical modification of **4**.

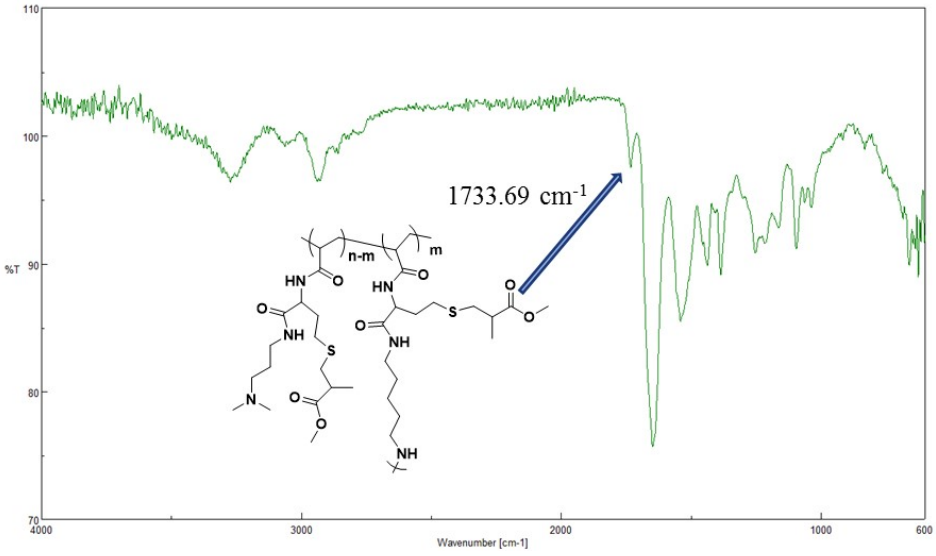


Fig. SI.11. FT-IR-ATR spectra of the polymer **6** obtained by chemical modification of **4**.

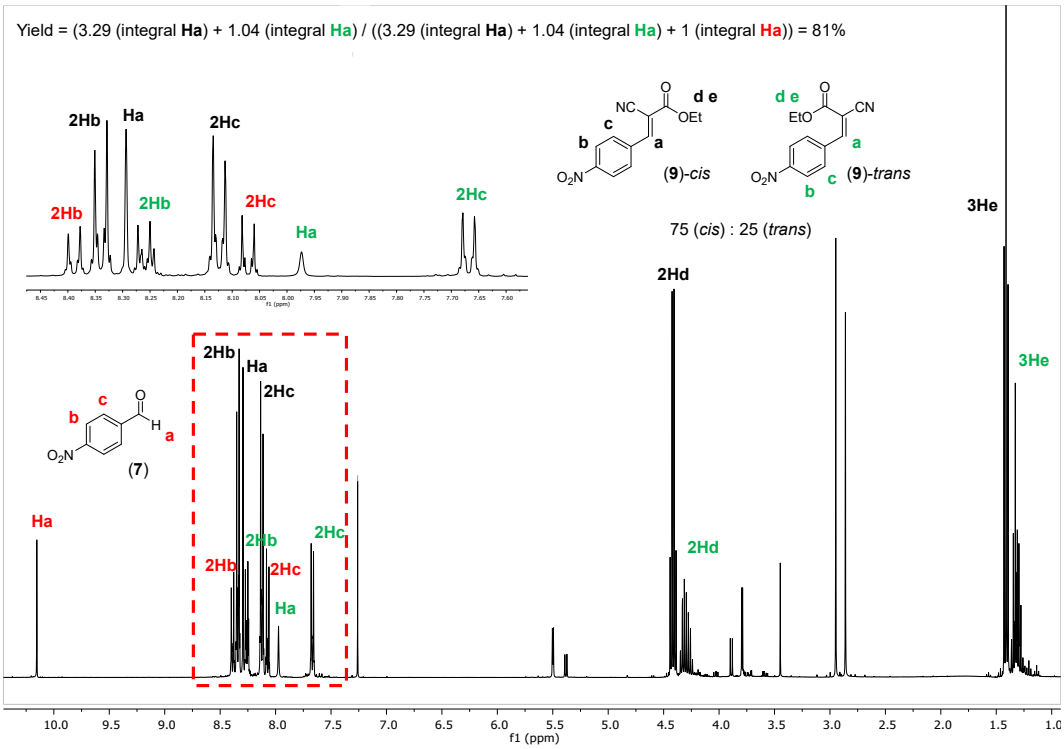


Fig. SI.12. ^{1}H-NMR spectra of the crude Knoevenagel reaction (**9**) in DMC ($CDCl_3$).

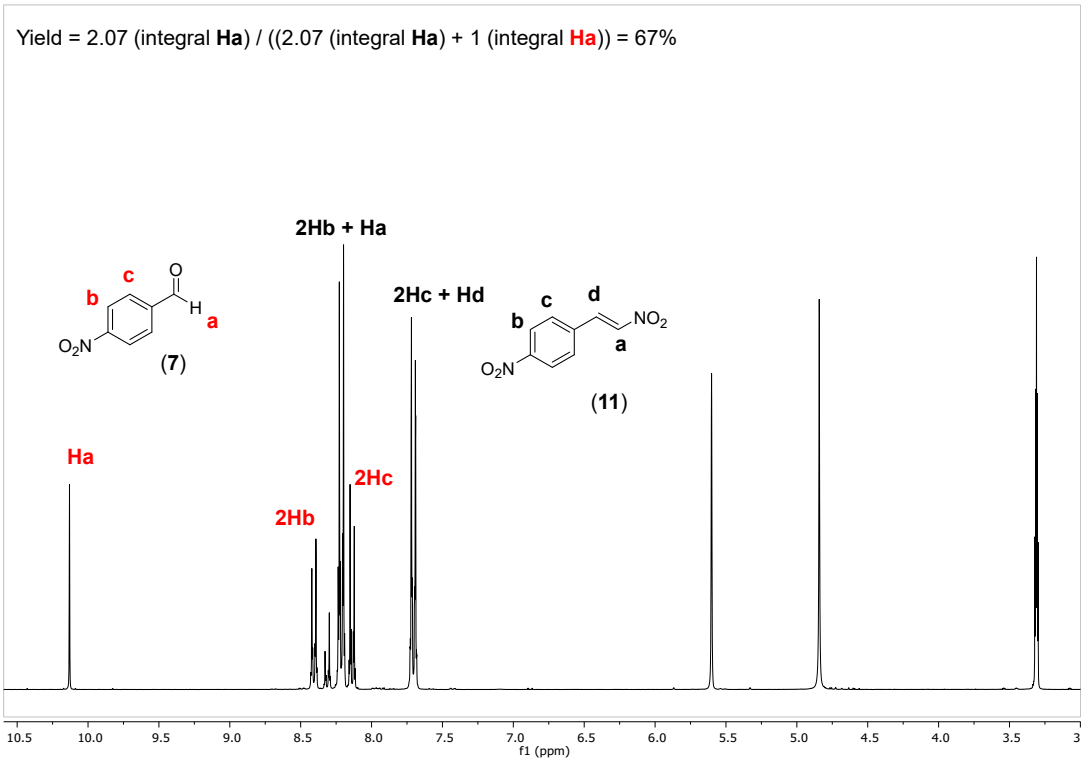


Fig. SI.13. ^{1}H-NMR spectra of the crude Henry reaction (**11**) in DMC (CD_3OD).

Video_SI.V1.mp4

Video_SI.V2.mp4

Video SI.V1. and SI.V2. Droplet generator to afford the corresponding functionalized insoluble polymeric beads (**4**). Droplets generated by the phase-phase system.