APPENDIX

A. FTIR and ^{1}H-NMR spectra

PEG$_{2000}$-*b*-PDAP-(B)

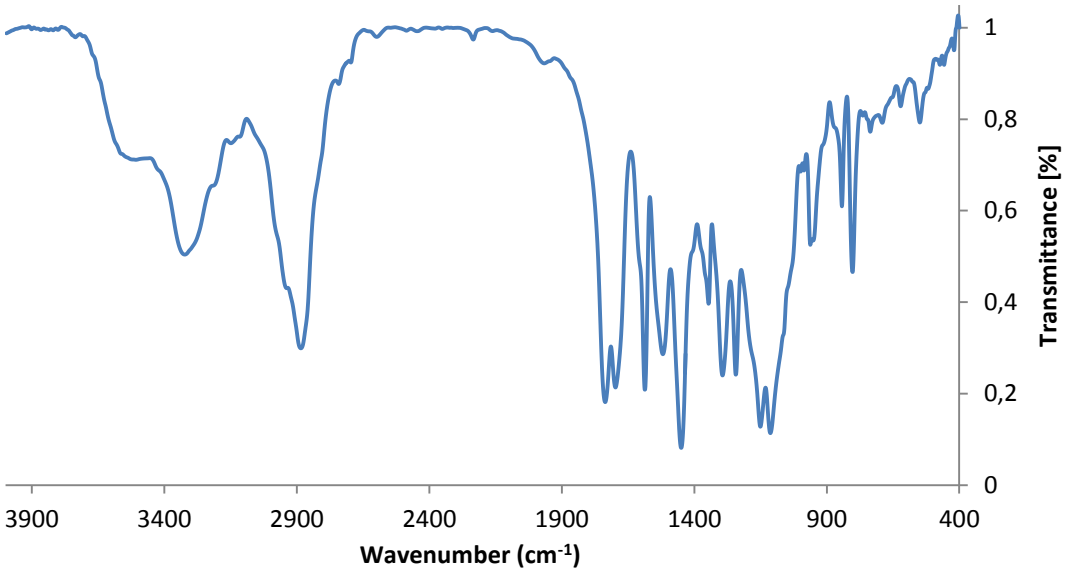


Fig. A.1. PEG$_{2000}$-*b*-PDAP-(B) FTIR spectrum (KBr)

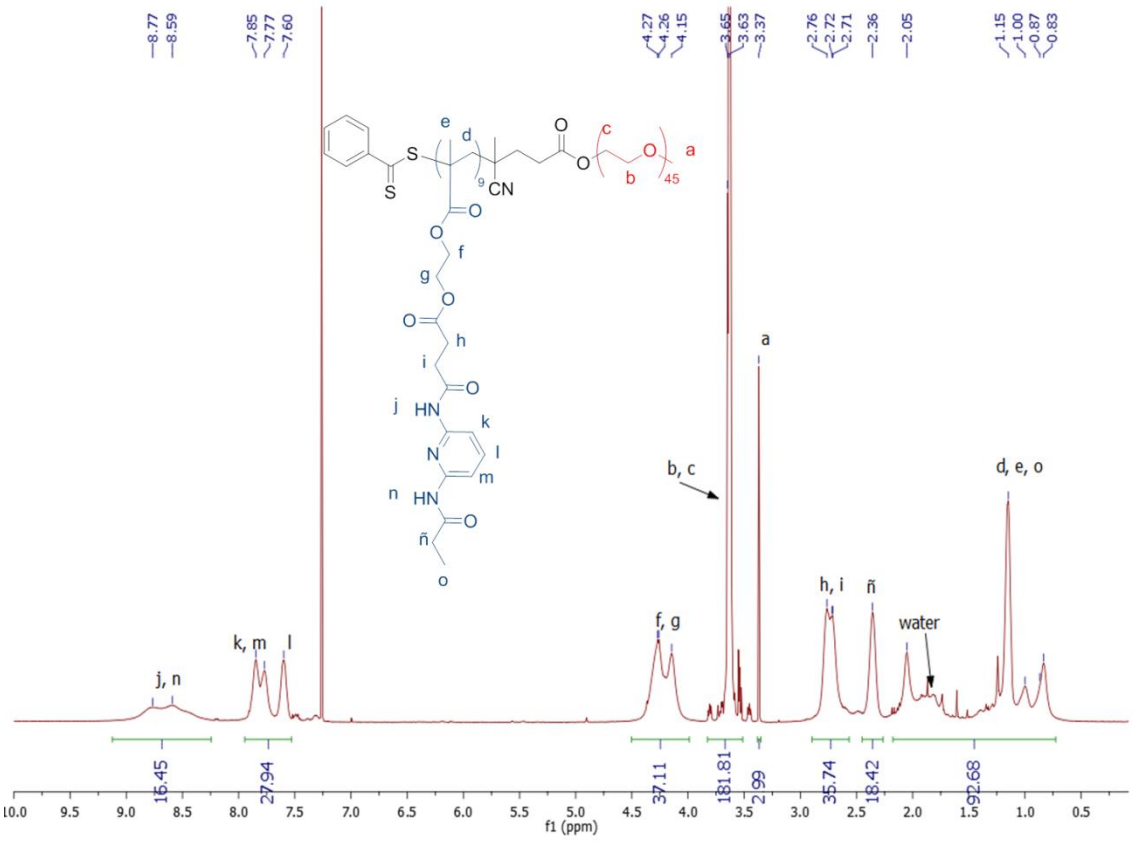


Fig. A.2. PEG$_{2000}$-*b*-PDAP-(B) ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) δ (ppm)

PEG$_{10000}$-*b*-PDAP-(B)

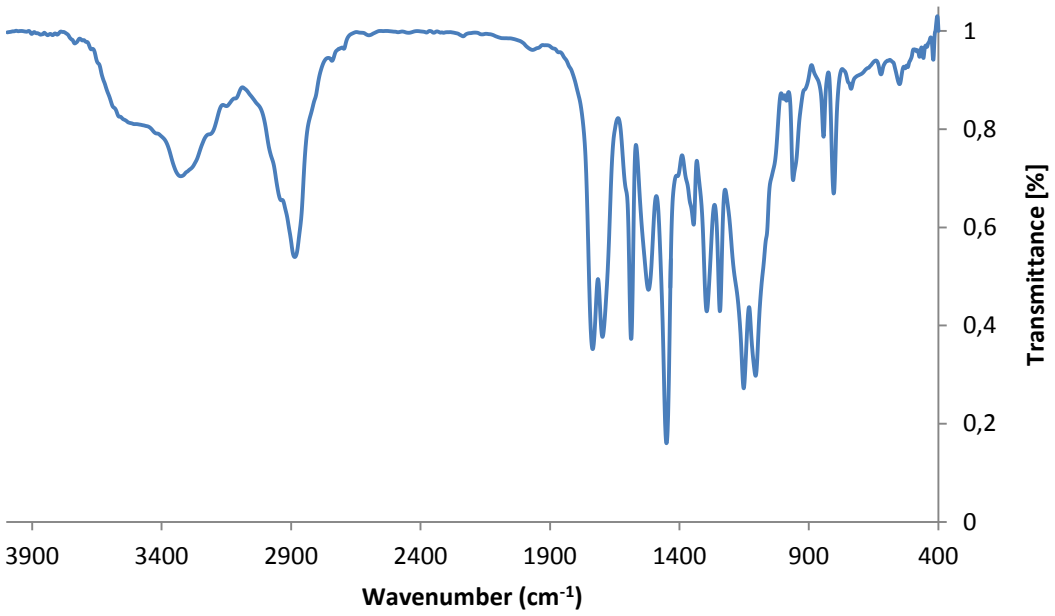


Fig. A.3. PEG$_{10000}$-*b*-PDAP-(B) FTIR spectrum (KBr)

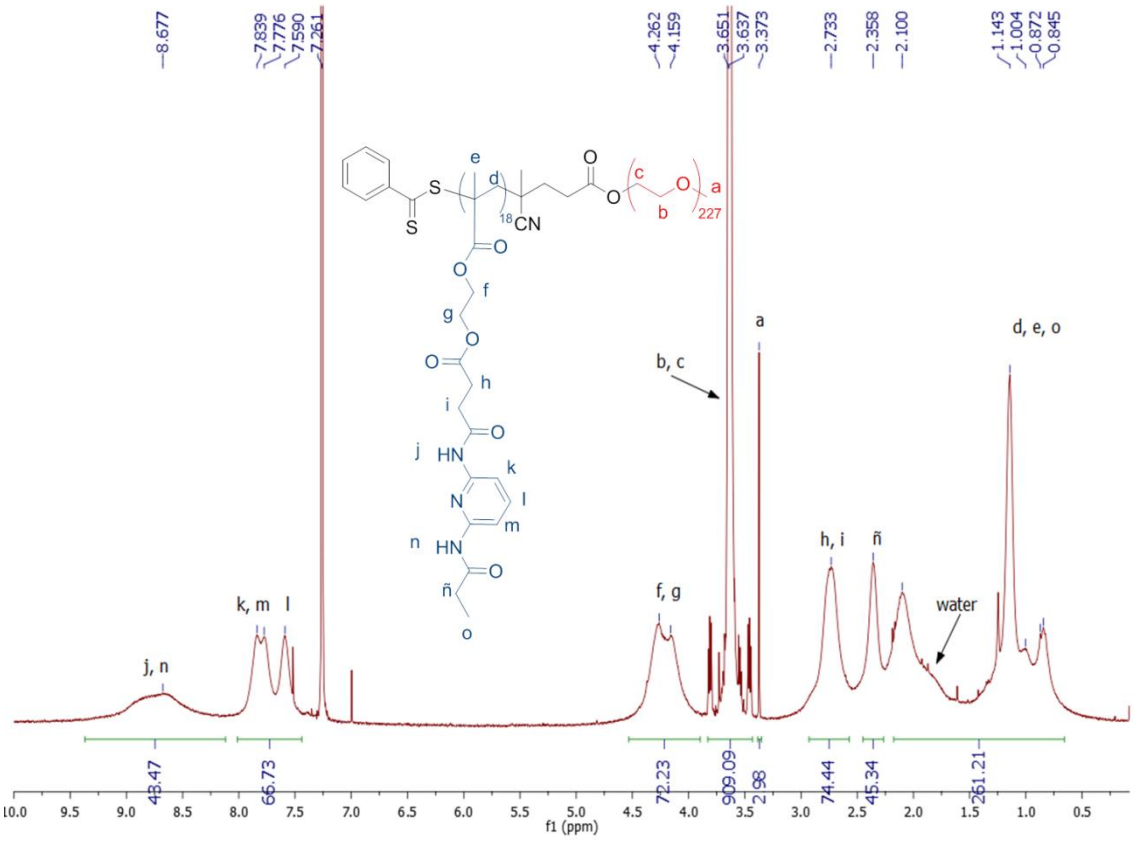


Fig. A.4. PEG$_{10000}$-*b*-PDAP-(B) ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) δ (ppm)

PEG$_{10000}$-*b*-PDAP-(C)

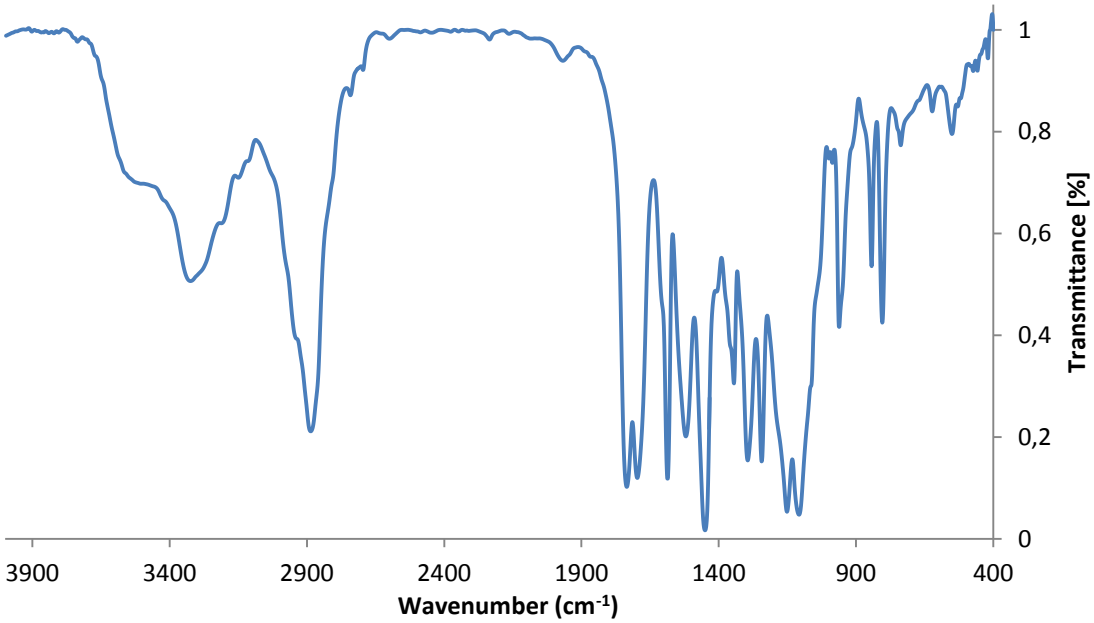


Fig. A.5. PEG$_{10000}$-*b*-PDAP-(C) FTIR spectrum (KBr)

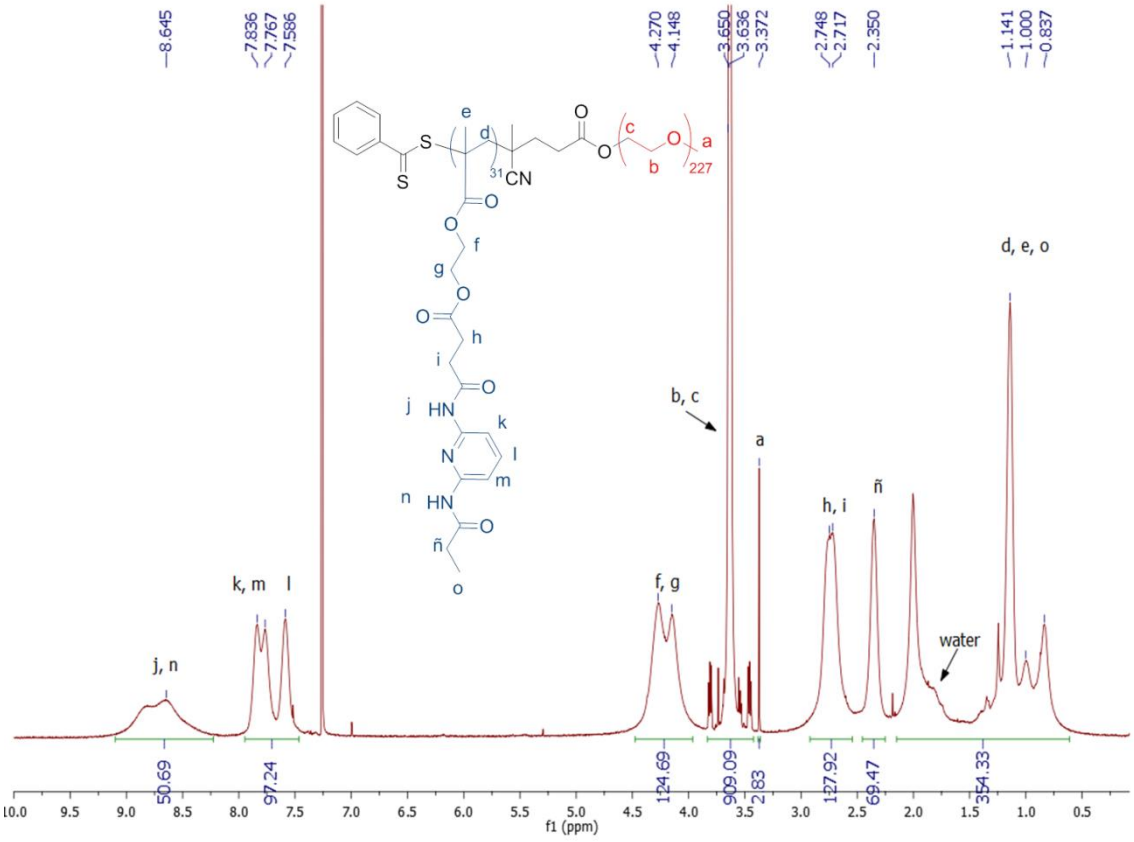


Fig. A.6. PEG$_{10000}$-*b*-PDAP-(C) ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) δ (ppm)

B. Gel permeation chromatography (GPC)

PEG$_{2000}$-*b*-PDAP-(B)

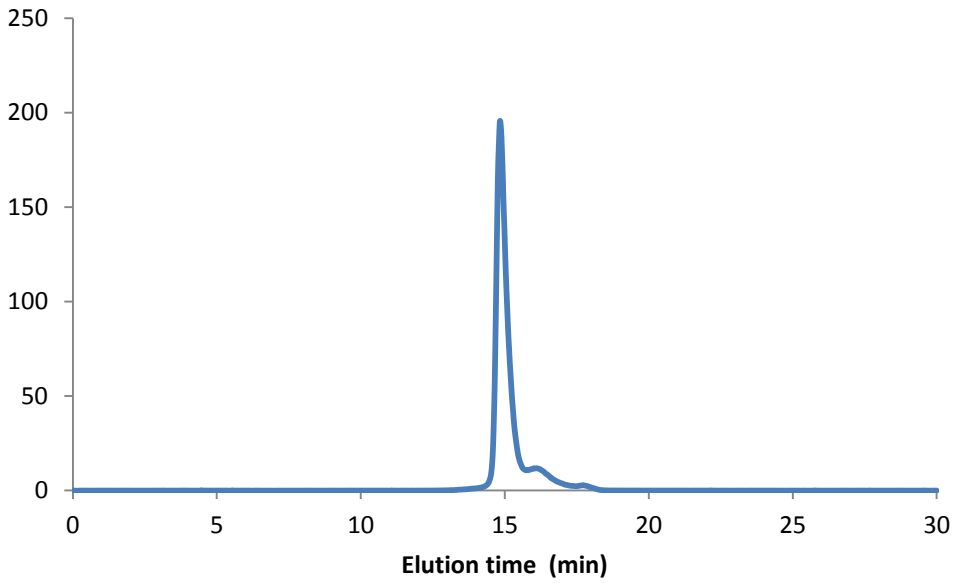


Fig. B.1. PEG$_{2000}$-*b*-PDAP-(B) GPC chromatogram

PEG$_{10000}$-*b*-PDAP-(B)

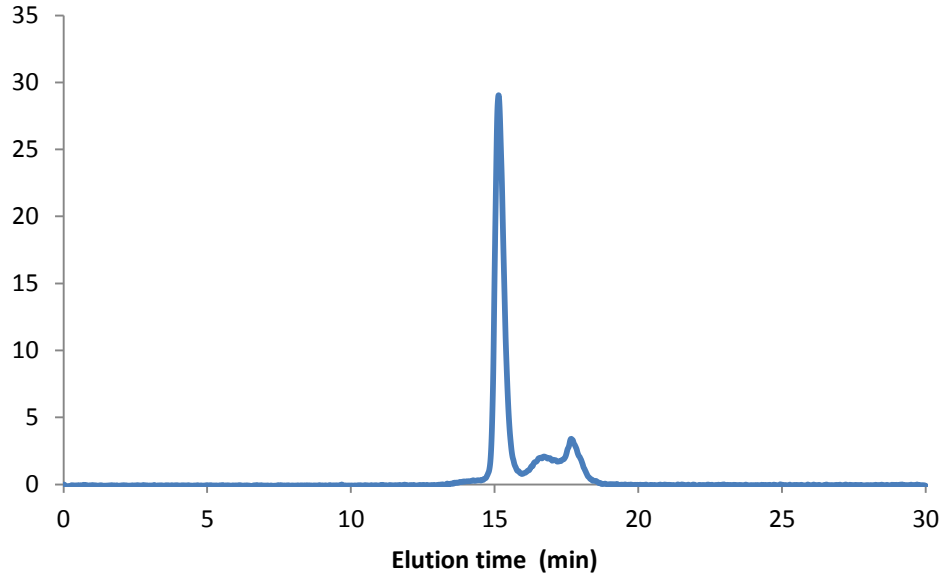


Fig. B.2. PEG$_{10000}$-*b*-PDAP-(B) GPC chromatogram

PEG$_{10000}$-*b*-PDAP-(C)

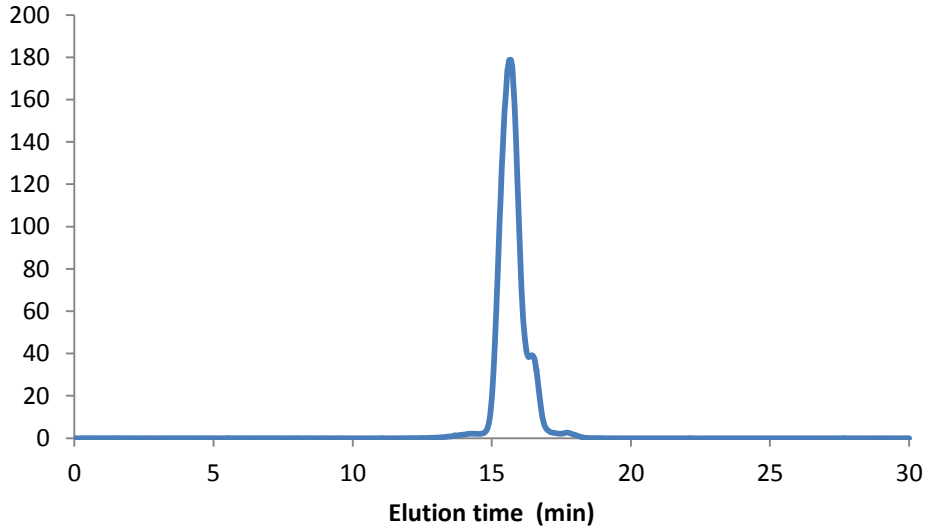


Fig. B.3. PEG$_{10000}$-*b*-PDAP-(C) GPC chromatogram

C. Hydrogen bond study

C.1. FTIR spectra

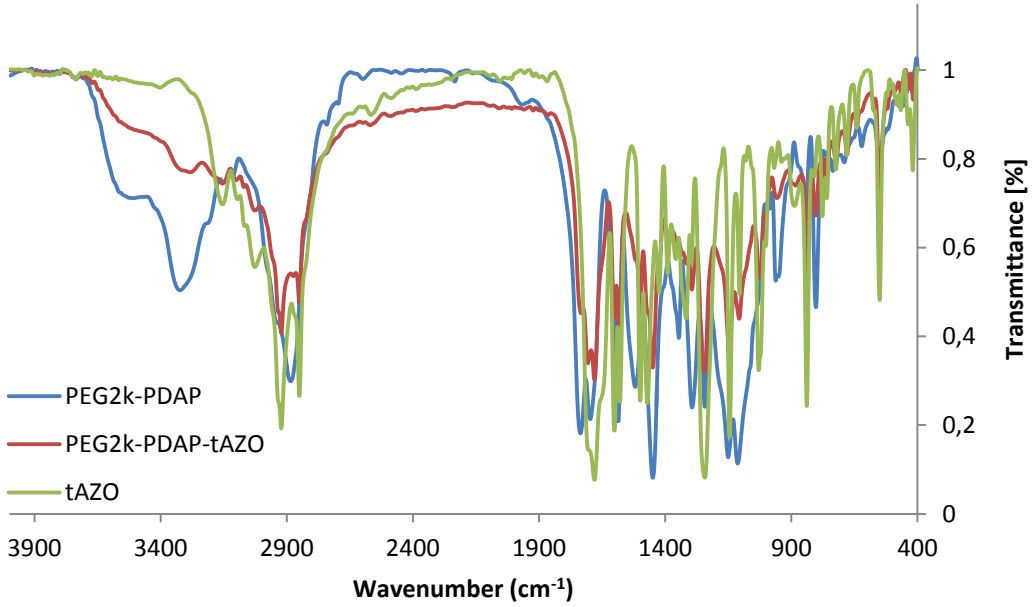


Fig. C.1.1. PEG_{2000}-*b*-PDAP-(A)·tAZO and their starting materials (PEG_{2000}-*b*-PDAP-(A) and tAZO) FTIR spectrum.

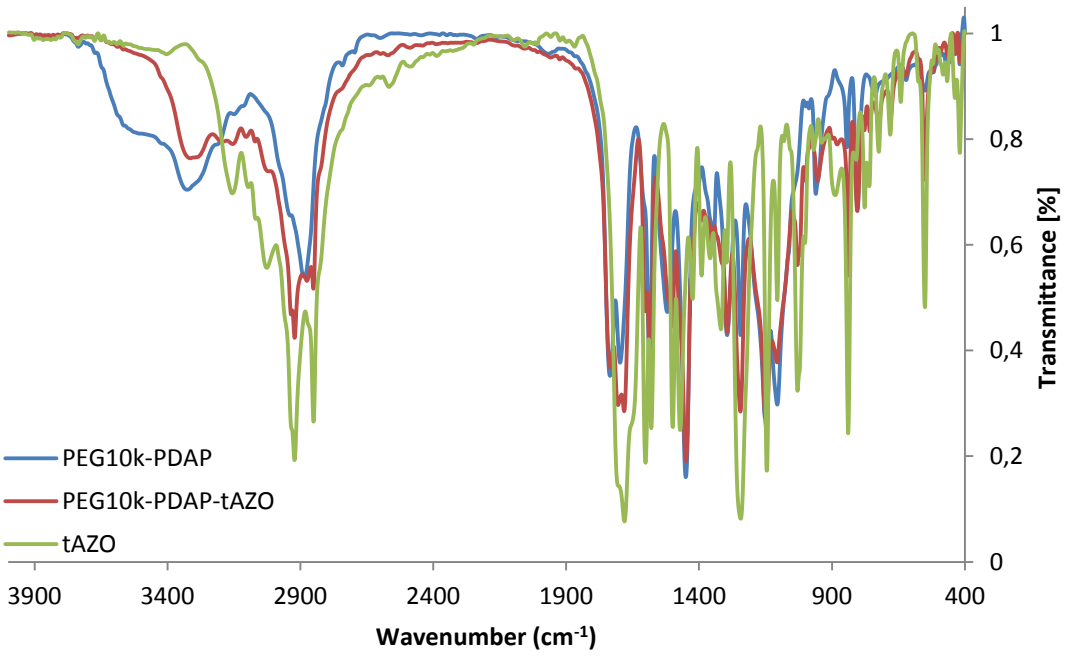


Fig. C.1.2. PEG_{10000}-*b*-PDAP-(A)·tAZO and their starting materials (PEG_{10000}-*b*-PDAP-(A) and tAZO) FTIR spectrum.

C.2. ^{1}H-NMR spectra

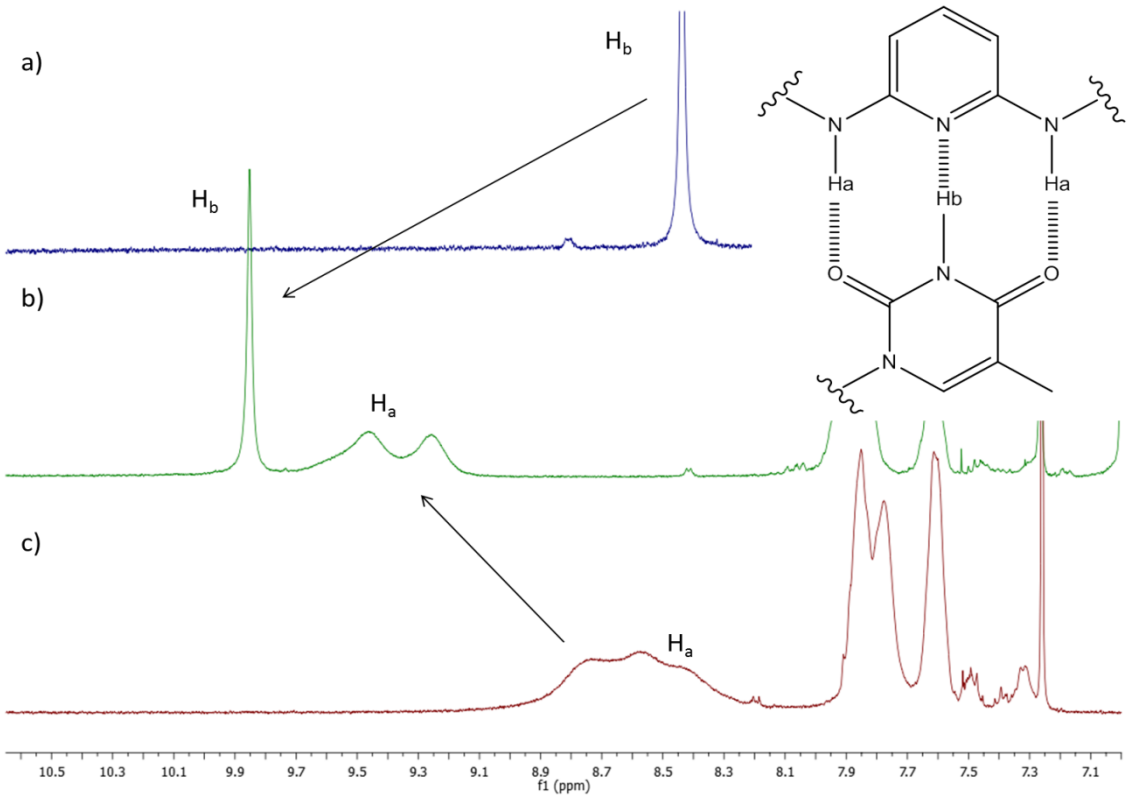


Fig. C.2.1.^{1}H-NMR spectra ($CDCl_3$, 400 MHz) [10.6-7.1 ppm] of: tAZO (a, blue), PEG_{2000}-*b*-PDAP-(A)·tAZO (b, green) and PEG_{2000}-*b*-PDAP-(A) (c, red).

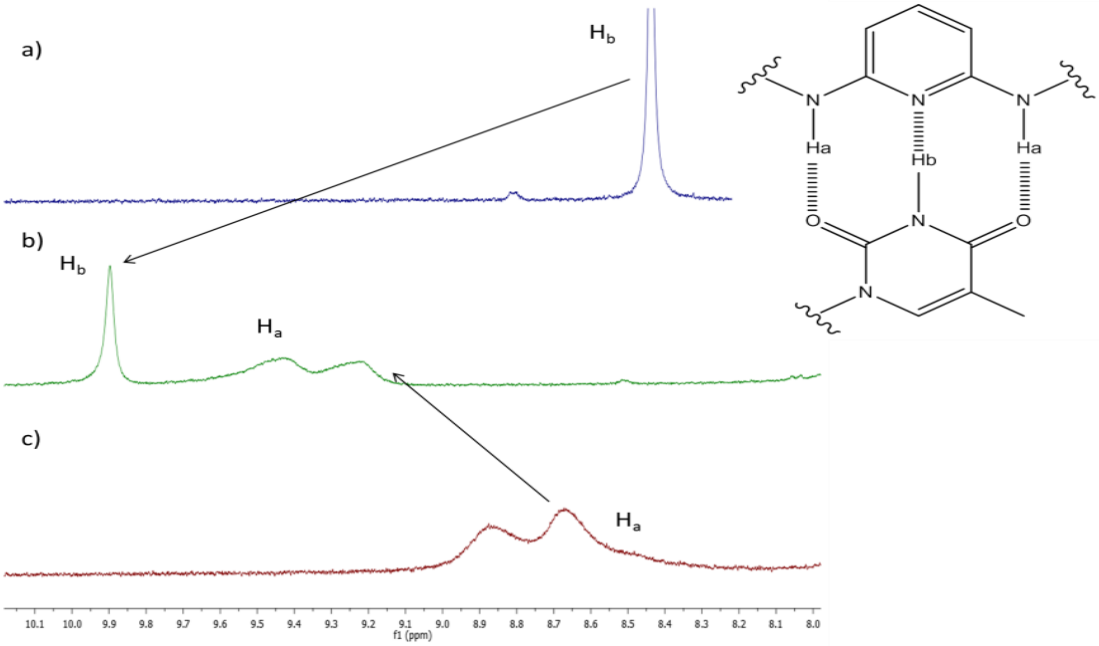


Fig. C.2.2. ^{1}H-NMR spectra ($CDCl_3$, 400 MHz) [10.2-8.0 ppm] of: tAZO (a, blue), PEG_{10000}-*b*-PDAP-(A)·tAZO (b, green) and PEG_{10000}-*b*-PDAP-(A) (c, red).

C.3. ^{1}H-NMR titrations

C.3.1. H-bond study in THF

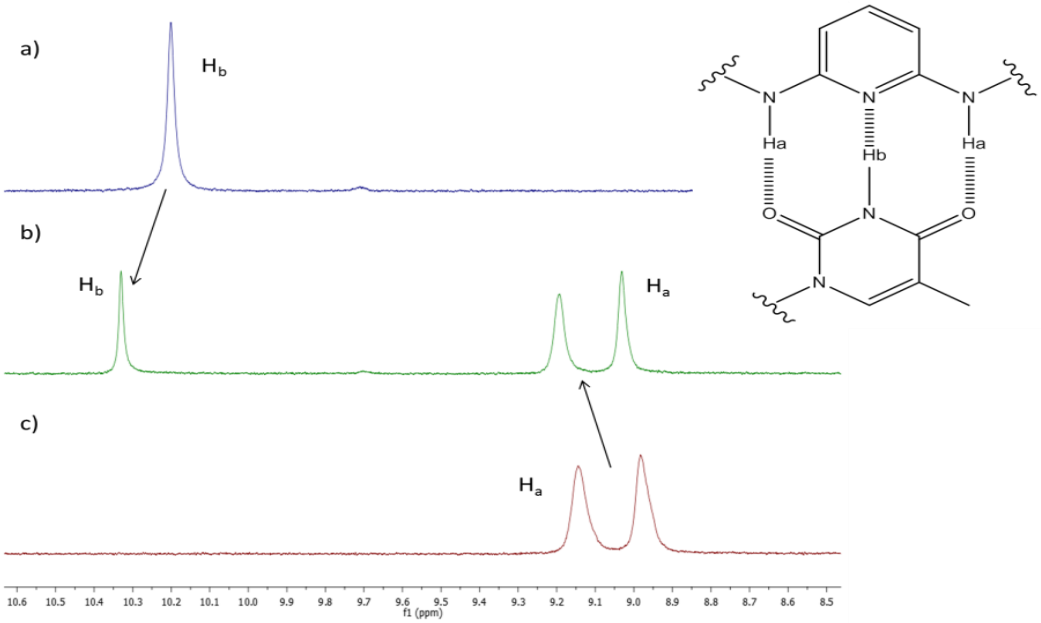


Fig. C.3.1.1. ^{1}H-NMR spectra (THF-d^{6}, 400 MHz) [10.6-8.5 ppm] of: tAZO (a, blue), PEG$_{10000}$-*b*-PDAP-(A)·tAZO (b, green) and PEG$_{10000}$-*b*-PDAP-(A) (c, red).

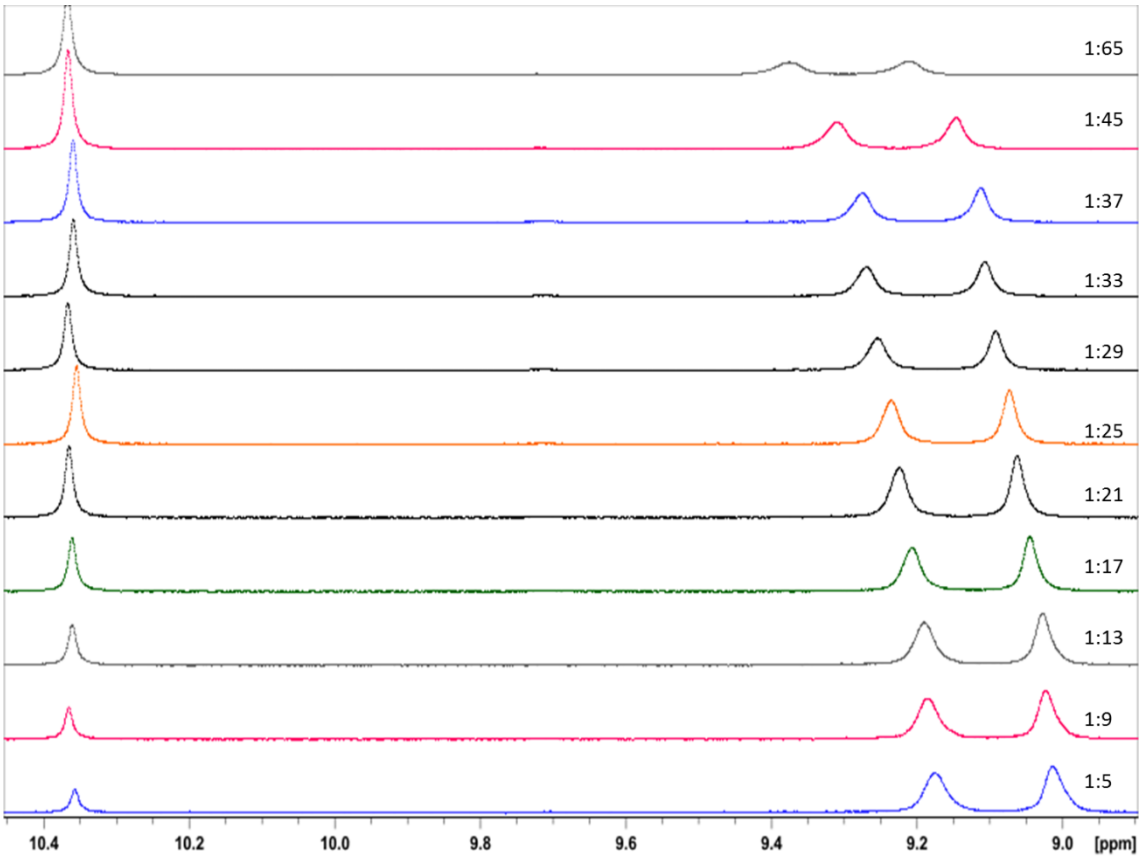


Fig. C.3.1.2. ^{1}H-NMR titration spectra(THF-d^{6}, 400 MHz) [10.5-8.9 ppm] of PEG$_{10000}$-*b*-PDAP-(A)

Table C.3.1. Amounts employed in ^{1}H-NMR titration.

proportions		amounts (mg)		concentrations (mM)		Δδ (ppm)
BC	tAZO	BC	tAZO	BC	tAZO	
1	5	7.0	1.2	0.83	4.17	0.030
1	9	7.0	2.1	0.83	7.50	0.039
1	13	7.0	3.1	0.83	10.84	0.044
1	17	7.0	4.0	0.83	14.17	0.062
1	21	7.0	4.9	0.83	17.51	0.080
1	25	7.0	5.9	0.83	20.84	0.090
1	29	7.0	6.8	0.83	24.18	0.109
1	33	7.0	7.7	0.83	27.51	0.124
1	37	7.0	8.7	0.83	30.85	0.129
1	45	7.0	10.6	0.83	37.52	0.163
1	65	7.0	15.3	0.83	54.19	0.231

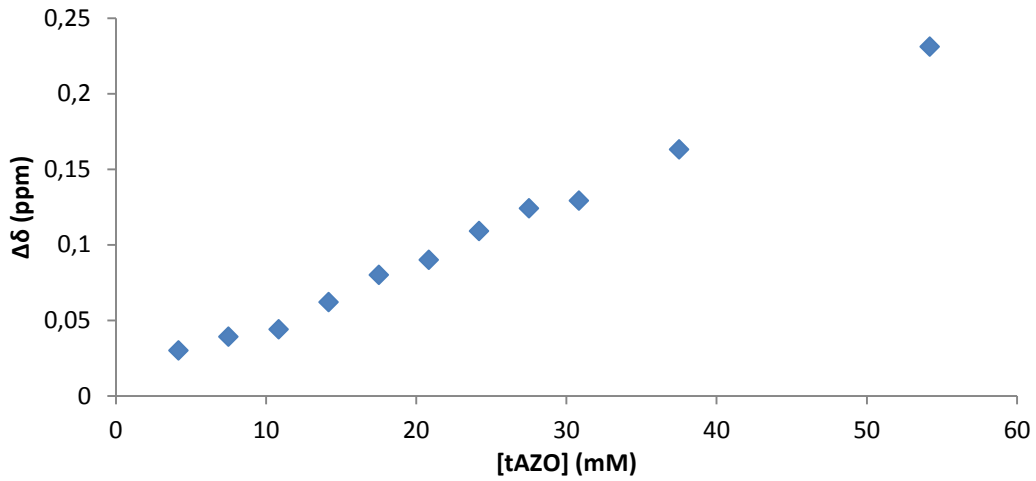


Fig. C.3.1.3. Chemical shift changes of DAP protons (H_a) upon addition of tAZO.

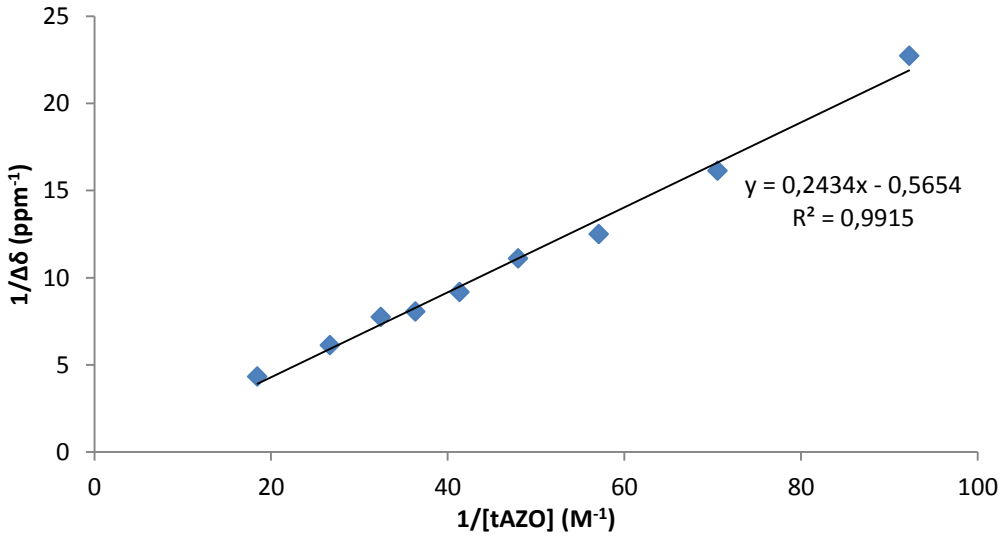


Fig. C.3.1.4. Benesi-Hildebrand Plot for K_a calculation.

C.3.2. H-bond study in $CHCl_3$.

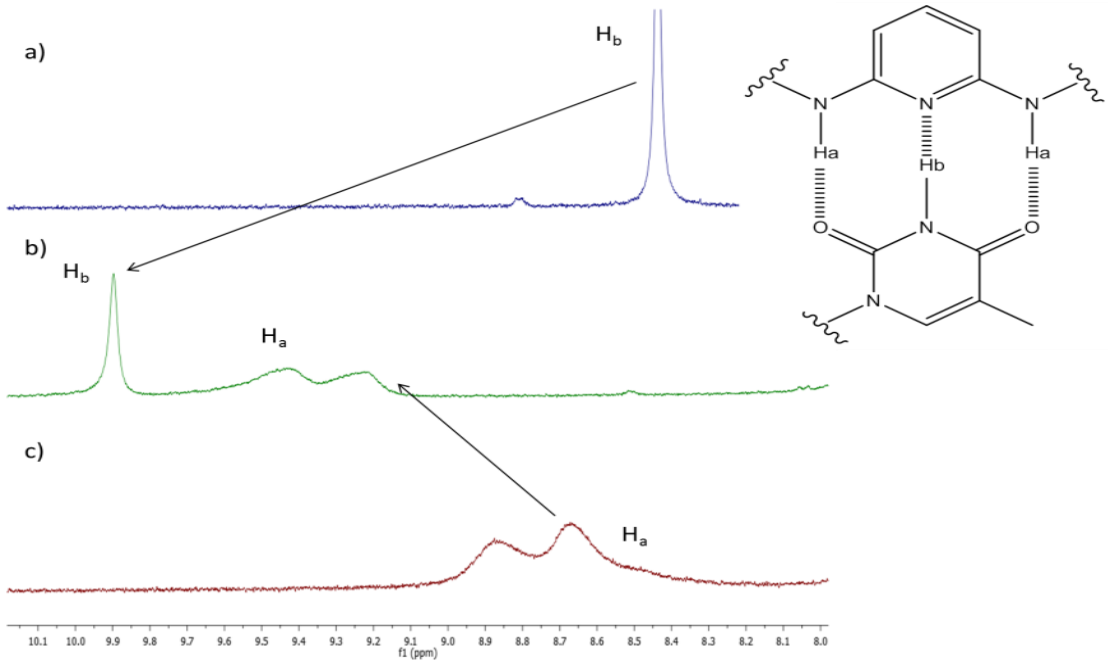


Fig. C.3.2.1. ^{1}H-NMR spectra ($CDCl_3$, 400 MHz) [10.2-8.0 ppm] of: tAZO (a, blue), PEG_{10000}-*b*-PDAP-(A)·tAZO (b, green) and PEG_{10000}-*b*-PDAP-(A) (c, red).

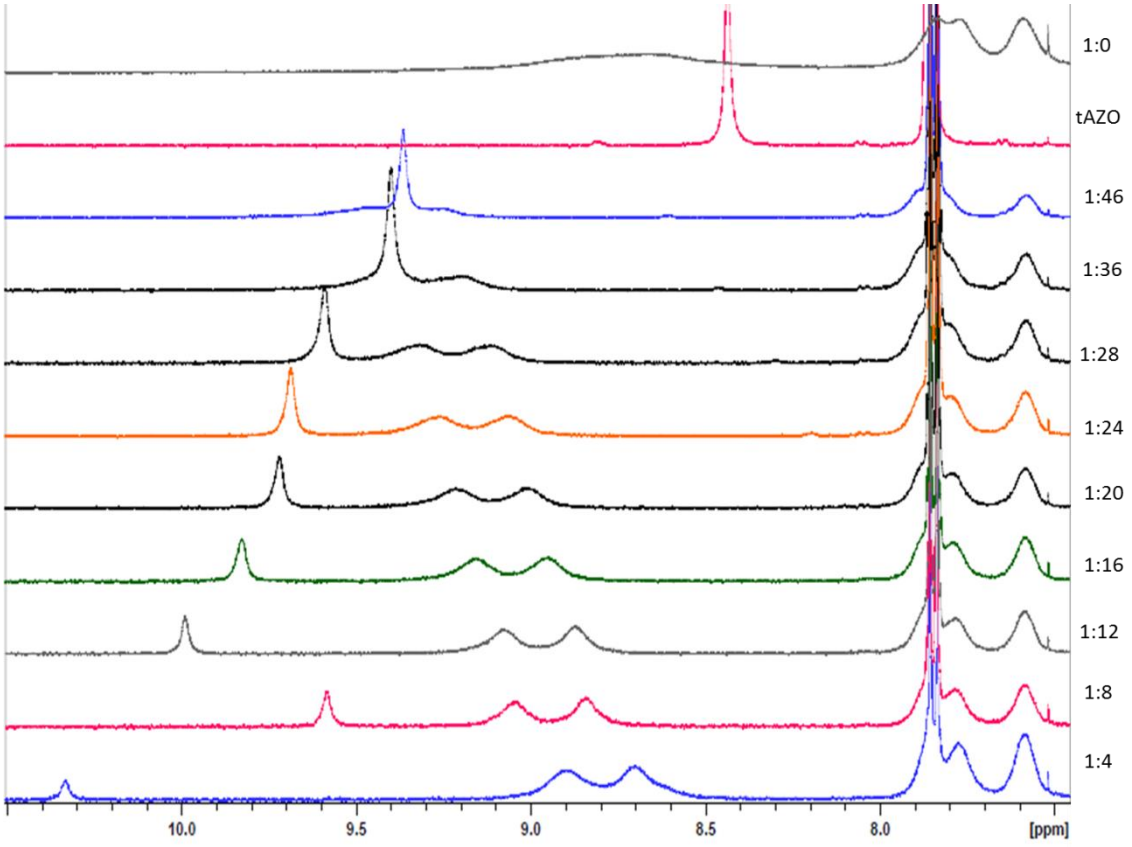


Fig. C.3.2.2. ^{1}H-NMR titration spectra ($CDCl_3$, 400 MHz) [10.5-7.5 ppm] of PEG_{10000}-*b*-PDAP-(B)

Table C.3.2. Amounts employed in ^{1}H-NMR titration.

Proportions		amounts (mg)		concentrations (mM)		Δδ (ppm)
BC	AZO	BC	AZO	BC	AZO	
1	4	6.0	0.8	0.71	2.84	0.025
1	8	6.0	1.7	0.71	6.04	0.165
1	12	6.0	2.5	0.71	8.88	0.198
1	16	6.0	3.3	0.71	11.73	0.273
1	20	6.0	4.1	0.71	14.57	0.331
1	24	6.0	4.9	0.71	17.41	0.386
1	28	6.0	5.7	0.71	20.26	0.436
1	36	6.0	7.3	0.71	25.94	0.520
1	46	6.0	9.2	0.71	32.70	0.572

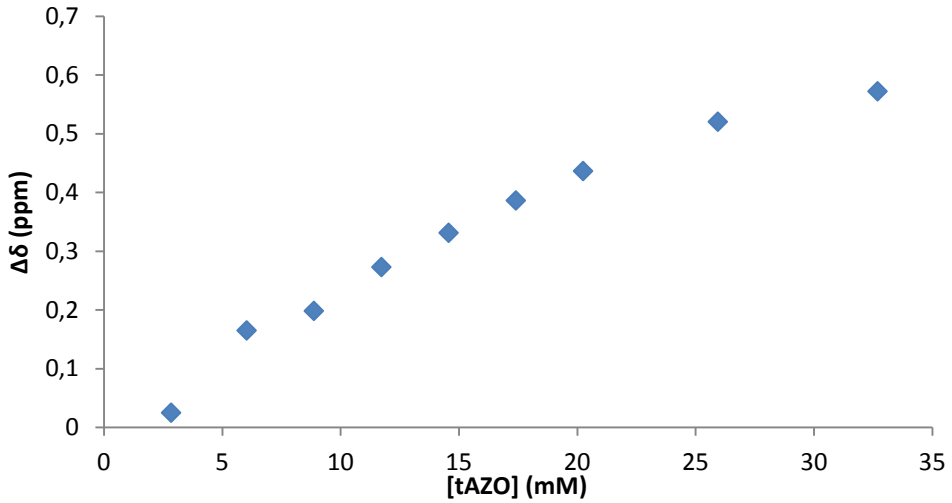


Fig. C.3.2.3. Chemical shift changes of DAP protons (H_a) upon addition of tAZO.

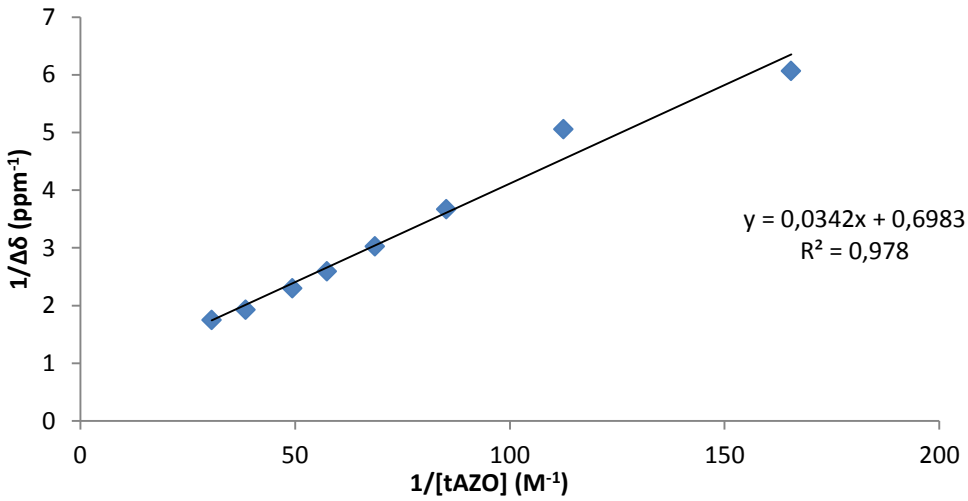


Fig. C.3.2.4. Benesi-Hildebrand Plot for K_a calculation.

D. Preparation of polymeric nanoparticles by microfluidics

Table D.1. Samples and their characterization data prepared using THF/H_2O.

Number of samples	Polymer	Flow (ml/min)	% aqueous phase	DLS diameter (intensity) (nm)	DLS diameter (number) (nm)	TEM diameter
1	PEG10k-b-PDAP	0.4	60	72	37	---
1	PEG10k-b-PDAP	0.4	80	110	30	---
1	PEG10k-b-PDAP	2	60	68	37	---
1	PEG10k-b-PDAP	2	80	120	38	---
2	PEG10k-b-PDAP	10	60	62	35	25-35
2	PEG10k-b-PDAP	10	70	53	27	<20
2	PEG10k-b-PDAP	10	80	45	28	20-25
2	PEG10k-b-PDAP	10	90	38	25	<20
1	PEG10k-b-PDAP	10	95	31	22	<20
1	PEG10k-b-PDAP	50	60	58	32	25-30
1	PEG10k-b-PDAP	50	70	65	26	---
1	PEG10k-b-PDAP	50	80	43	24	20
1	PEG10k-b-PDAP	50	90	---	---	---
1	PEG10k-b-PDAP · tAZO	2	60	---	---	---
1	PEG10k-b-PDAP · tAZO	2	80	---	---	---
1	PEG10k-b-PDAP · tAZO	10	60	---	---	---
2	PEG10k-b-PDAP · tAZO	10	70	---	---	---
3	PEG10k-b-PDAP · tAZO	10	80	----	---	---
7	PEG10k-b-PDAP · tAZO	10	90	50	32	25-30
3	PEG10k-b-PDAP · tAZO	10	95		29	<25
1	PEG10k-b-PDAP · tAZO	50	60	---	---	---
1	PEG10k-b-PDAP · tAZO	50	80	---	---	---
3	PEG10k-b-PDAP · tAZO	50	90	48	31	25
2	PEG2k-b-PDAP	10	60	105	44	110
2	PEG2k-b-PDAP	10	70	95	35	20 100
5	PEG2k-b-PDAP	10	80	100	50	75-180
2	PEG2k-b-PDAP	10	90	34	19	15-30
2	PEG2k-b-PDAP	10	95	23	20	18
1	PEG2k-b-PDAP	50	70	37	21	---

1	PEG2k-b-PDAP	50	80	105	68	75-95
2	PEG2k-b-PDAP	50	90	40	21	---
1	PEG2k-b-PDAP · tAZO	10	70	---	---	---
1	PEG2k-b-PDAP · tAZO	10	80	---	---	----
5	PEG2k-b-PDAP · tAZO	10	90	145	80	25-30 120-200
2	PEG2k-b-PDAP · tAZO	10	95	120	60	40 90
1	PEG2k-b-PDAP · tAZO	50	70	---	----	---
1	PEG2k-b-PDAP · tAZO	50	80	---	---	----
4	PEG2k-b-PDAP · tAZO	50	90	140	85	25-30 100

--- : sample precipitated so the characterization techniques were not carried out.

Table D.2. Samples and their characterization data prepared using $CHCl_3/H_2O$.

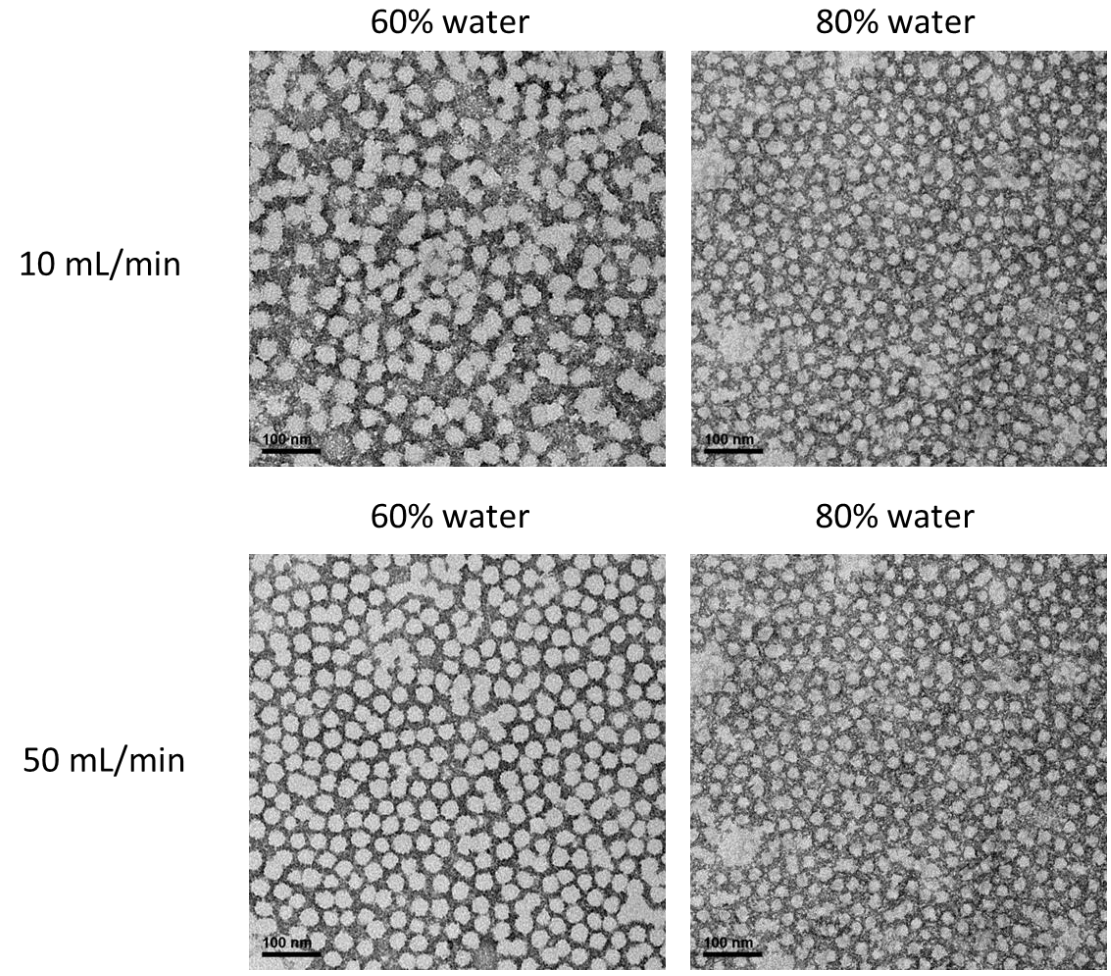
Number of samples	Polymer	Flow (ml/min)	% aqueous phase	DLS diameter (intensity) (nm)	DLS diameter (number) (nm)	TEM diameter
5 **2***	PEG10k-b-PDAP	50	90	190-350; 100-190*	50-340; 85*	40-400; 25-50*
1 **1***	PEG10k-b-PDAP	50	95	248; 202*	78; 100*	50-80; 50-100*
1 **1***	PEG10k-b-PDAP·tAZO	50	90	230-960 965*	160 950*	50 60-130*
1 **1***	PEG10k-b-PDAP·tAZO	50	95	404 141-668*	165 105-400*	150-600 20-100*
1 **1***	PEG2k-b-PDAP	50	90	168 154*	44 68*	---
1 **1***	PEG2k-b-PDAP	50	95	100-597 261*	44 25*	---
1 **1***	PEG2k-b-PDAP·tAZO	50	90	412 85-687*	190 90*	---
1 **1***	PEG2k-b-PDAP·tAZO	50	95	110-424 115-474*	68 100*	---

*: sonicated samples

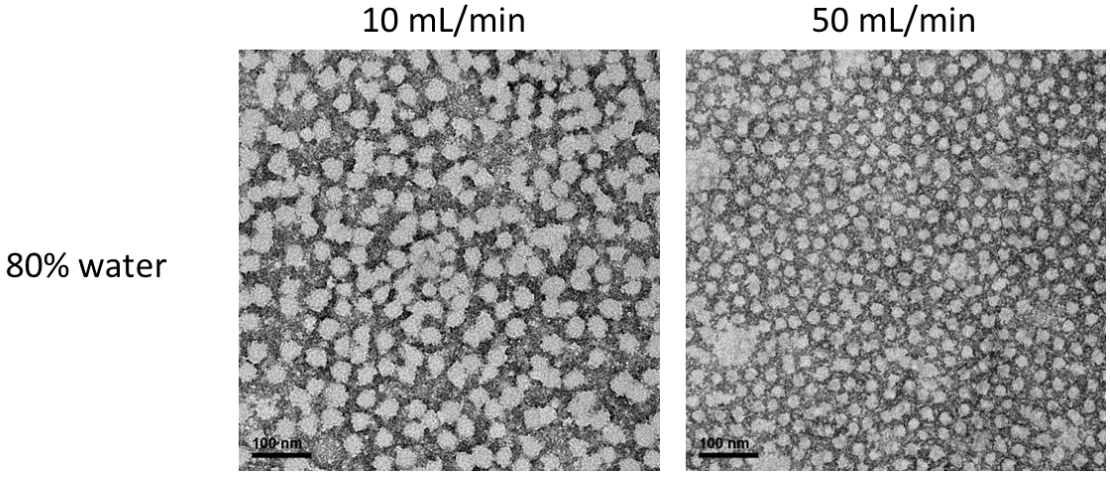
--- : sample precipitated so the characterization techniques were not carried out.

D.1. Comparison between 10 and 50 mL/min flows in THF/water system TEM images

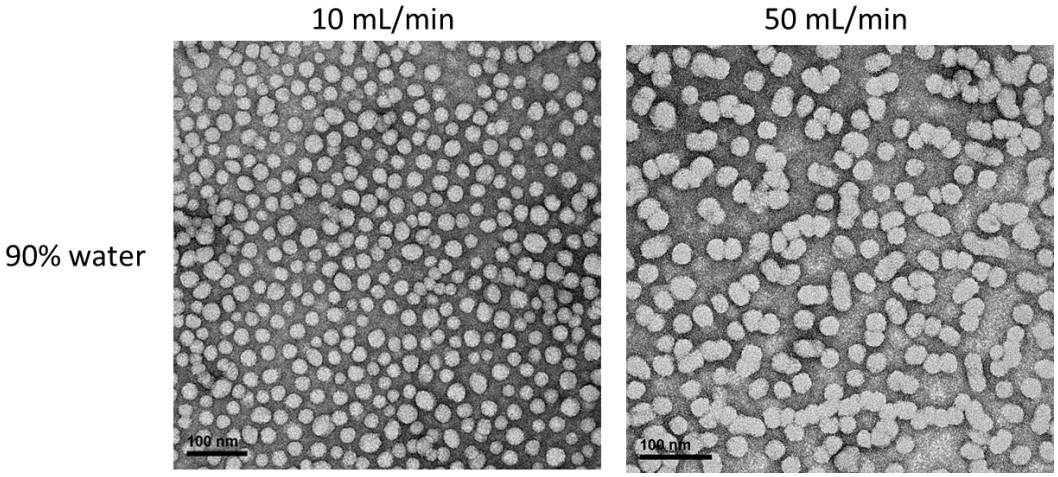
- PEG_{10000}-*b*-PDAP-(A and B)



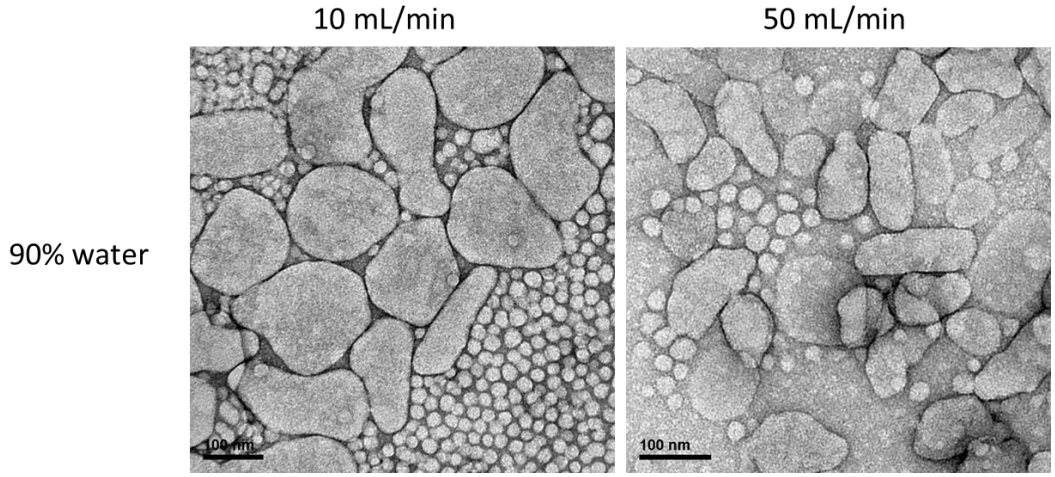
- PEG_{2000}-*b*-PDAP-(A)



- PEG_{10000}-*b*-PDAP-(A)·tAZO



- PEG_{2000}-*b*-PDAP-(A)·tAZO



E. Instruments and techniques

Infrared Spectroscopy (FTIR).

FTIR spectroscopy was performed with a Bruker Vertex 70. Samples were prepared in KBr pellets (2% wt).

Nuclear Magnetic Resonance (^{1}H-NMR)

Most of the ^{1}H-NMR spectra were recorded using a Bruker AV-400 (400 MHz) equipment. Both $CDCl_3$ and THF-d^6 have been used as solvent.

Gel Permeation Chromatography (GPC).

GPC was carried out using a Waters Alliance 2695 HPLC with an evaporative light scattering detector Waters 2420 and Styragel® Water columns (7.8 mm ID x 300 mm) HR2 and HR4, using THF as eluent (flow 1mL/min). Calibration was made with poly(methyl methacrylate) standards. Samples were prepared by dissolving 2 mg of product in 2 mL of THF (HPLC) and filtering them using a 0.2 micron PTFE filter.

Microfluidics

Self-assemblies preparation was carried out using two Harvard PHd Plus syringe pumps and a commercial slit interdigital microstructured mixer from IMM (Institut für Mikrotechnik Mainz GmbH, Germany).

Sonication

A Digital Sonifier 450 (Branson, USA) was employed with a sonotrode for low volumes of aqueous or organic solutions (12 mm of diameter).

Ultraviolet-visible spectroscopy (UV-vis)

For UV irradiation studies, an ATI Unicam UV4-200 spectrophotometer and quartz short path length cuvettes were employed.

Transmission Electron Microscopy (TEM)

TEM studies were performed at the "Servicio de Microscopía Electrónica de Materiales" from the "Servicios Generales de Apoyo a la Investigación-SAIs de la Universidad de Zaragoza". A high resolution transmission electron microscope JEOL-2000 FXII was employed operating at 200 kV.

Sample solution (10 μL) is deposited in a copper grid with carbon film (CF400-Cu) and after 30 s, excess of water and non-deposited sample is removed by capillarity. The sample adhered on the copper grid surface is dyed using uranyl acetate (10 μL) and after 30 s, excess of dye is removed by capillarity. The prepared samples stay 24 h under vacuum to dry before measurement.

Dynamic Light Scattering (DLS)

DLS measurements were carried out in a Malvern Instrument Nano ZS using a He-Ne laser with a 633 nm wavelength and a detector angle of 173^{o} at 25^{o}C, with polystyrene cuvettes. Samples are diluting in Milli-Q water to reach a concentration of 200 μg/mL.