Supplementary Information

1. NMR Measurements

The NMR spectra for the different copolymers taken in D_2-dichloro methane as solvent.

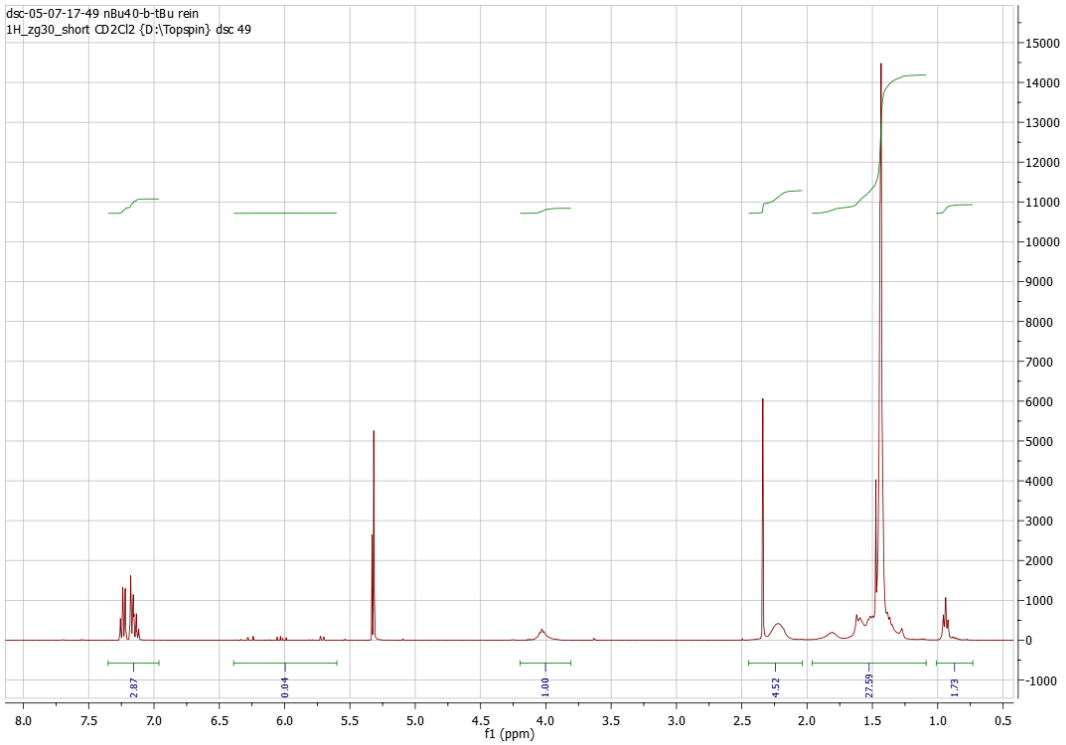


Fig. S 1. NMR Spectrum of *n*Bu68-*b*-tBuA167

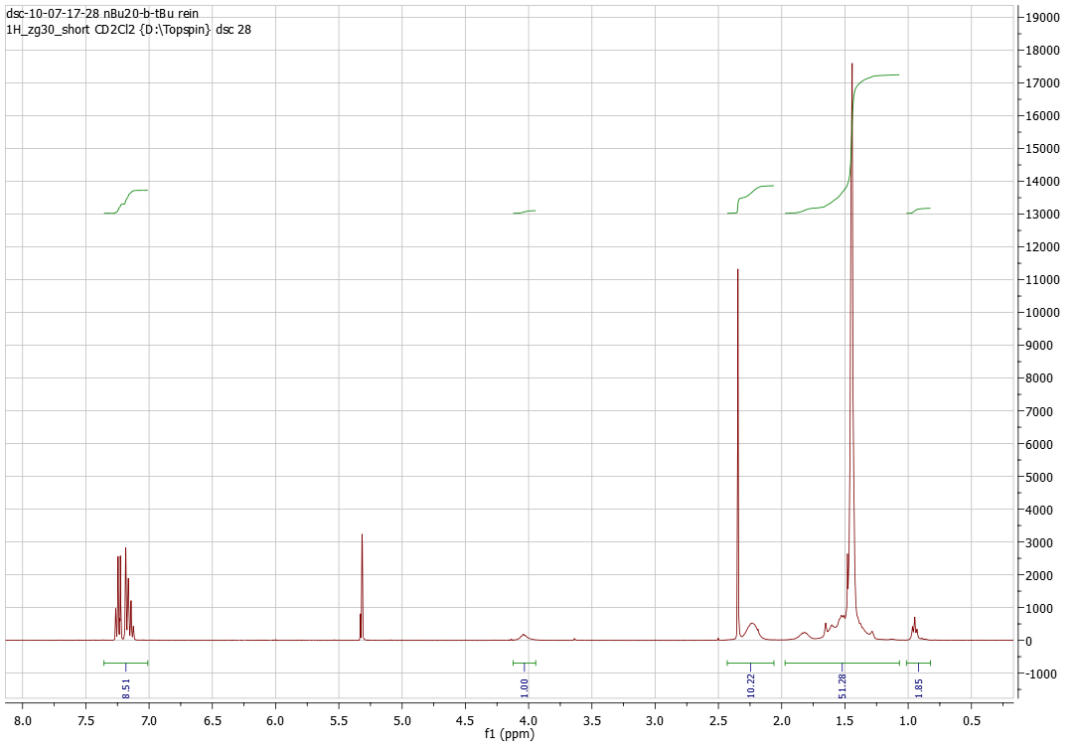


Fig. S 2. NMR Spectrum of *n*Bu40-*b*-tBuA167

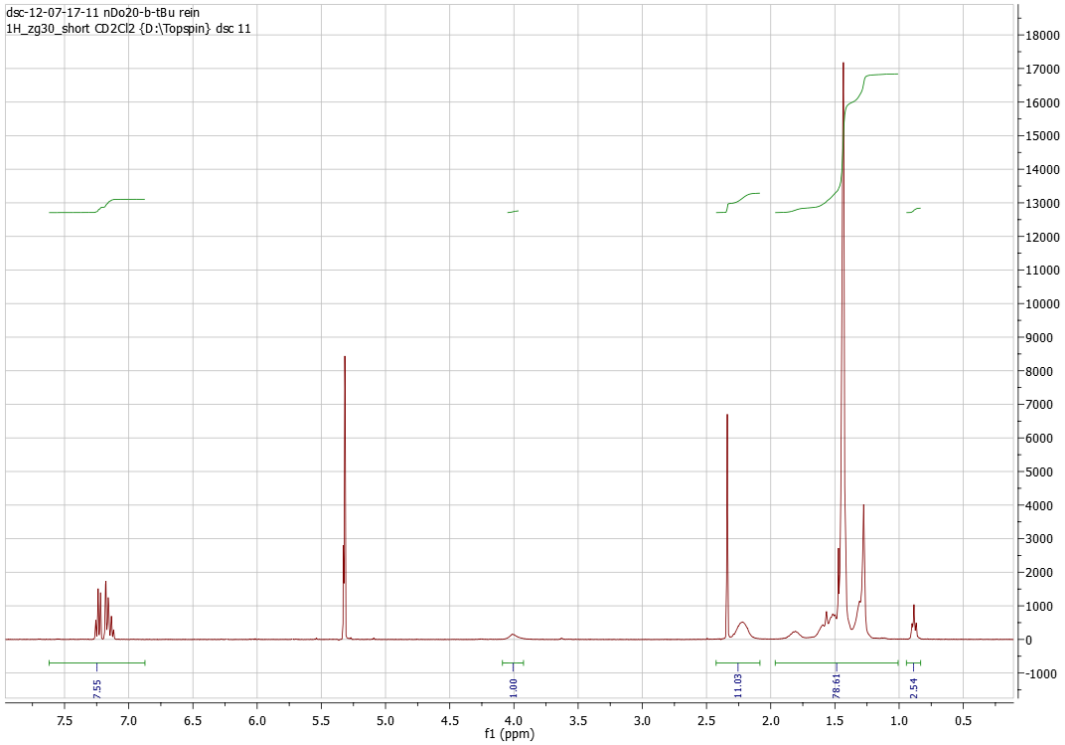


Fig. S 3. NMR Spectrum of *n*Do36-*b*-tBuA127

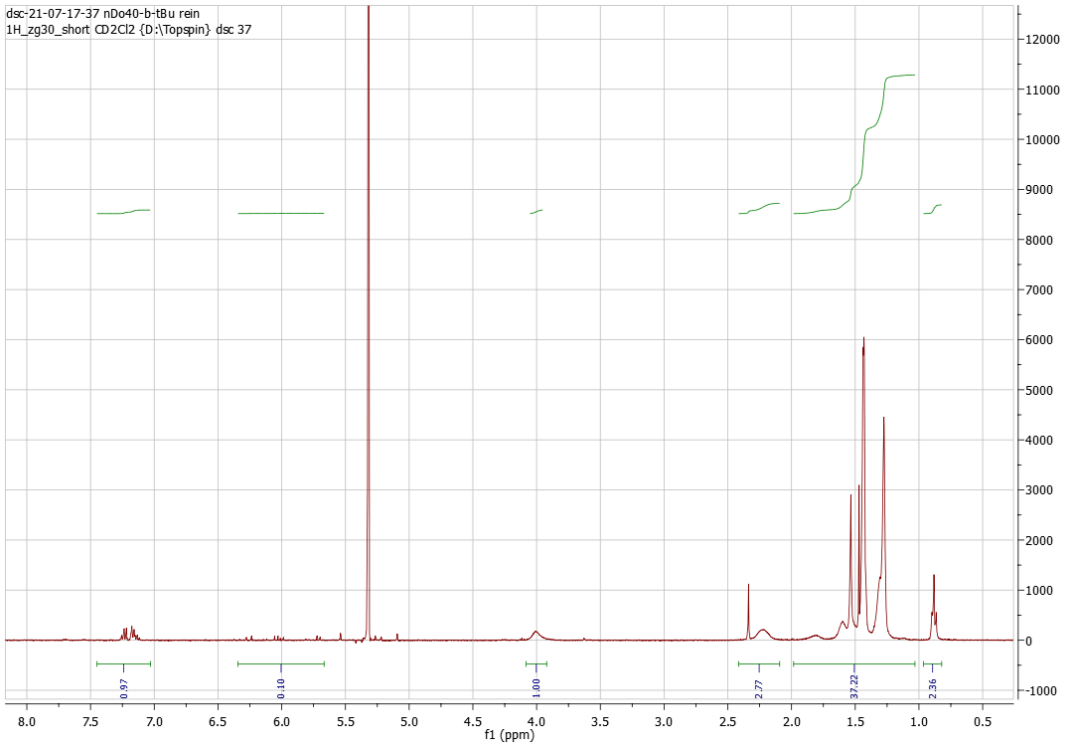


Fig. S 4. NMR Spectrum of *n*Do36-*b*-tBuA71

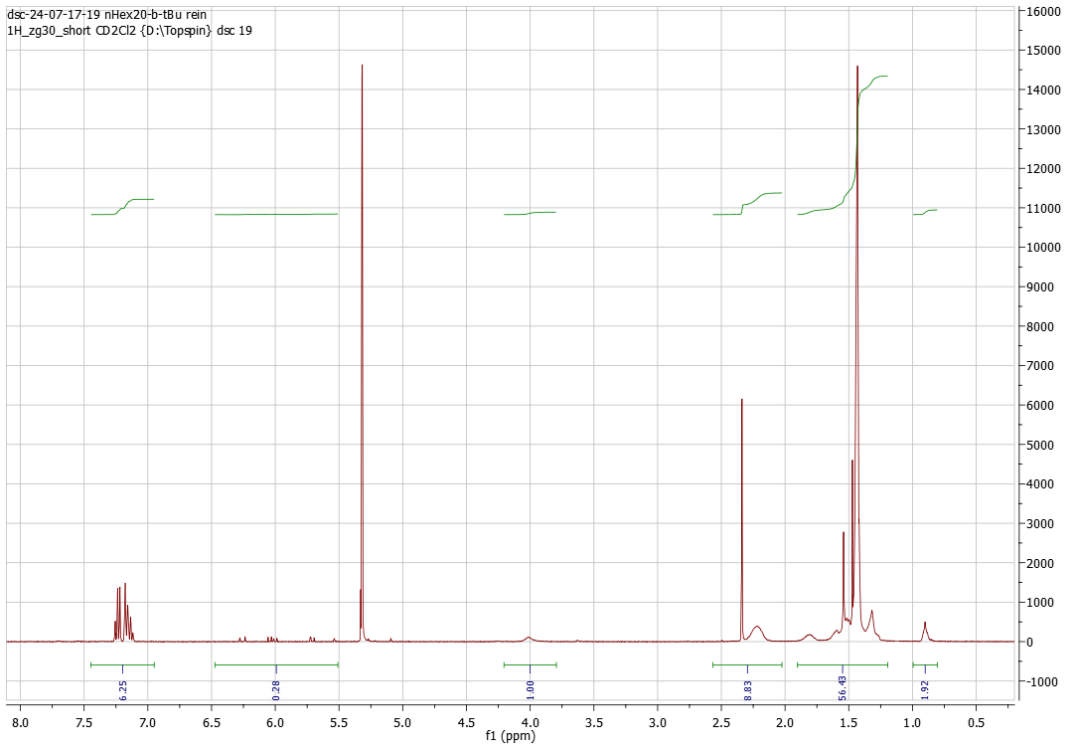


Fig. S 5. NMR Spectrum of *n*Hex37-*b*-tBuA169

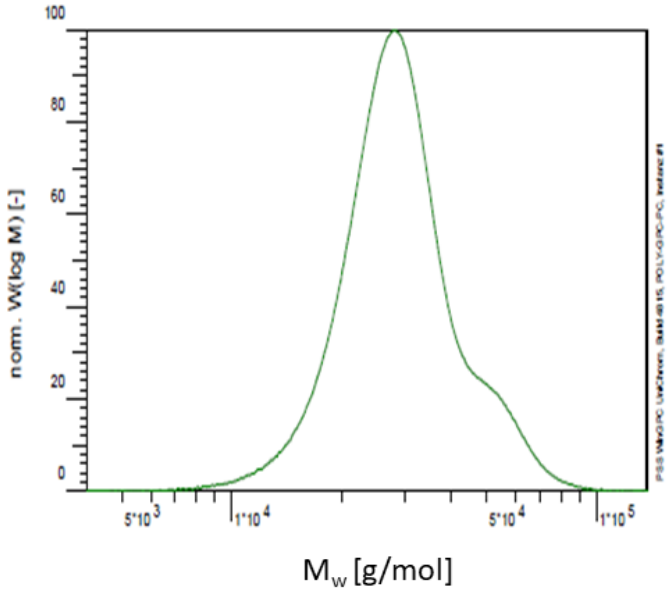
2. Gel Permeation Chromatography (GPC) Measurements

GPC measurements were done in order to determine the molecular weight of the synthesised copolymers and to gain information regarding the pureness of the pureness of the copolymers.

Table S 1. GPC Results of synthesized polymers

Polymer	**M_n [g/mol]**	**M_w [g/mol]**	**PDI**
*n*Bu40-*b*-tBuA167	26700 ± 500	30600 ± 500	1.15
*n*Bu68-*b*-tBuA167	30200 ± 700	36000 ± 800	1.19
*n*Hex37-*b*-tBuA169	27600 ± 1700	30900 ± 1900	1.12
*n*Do36-*b*-tBuA127	25100 ± 2400	30100 ± 2900	1.20
*n*Do36-*b*-tBuA71	18000 ± 500	23000 ± 600	1.28

a)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80
60
40
20
0
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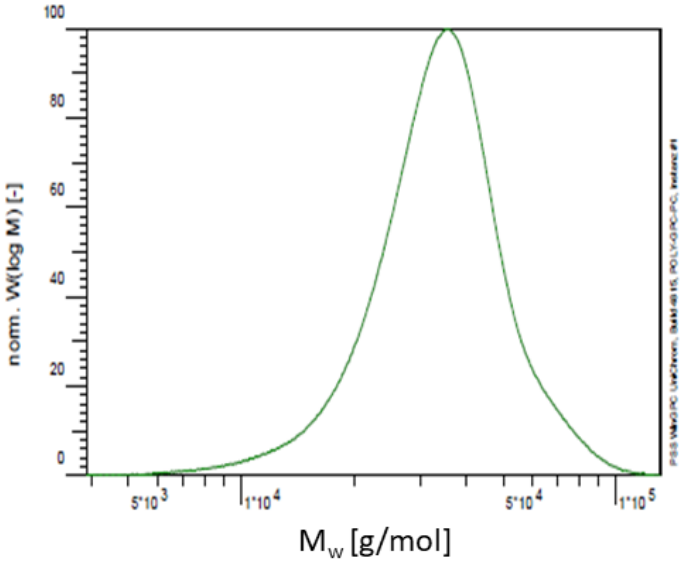
5*10^4
1*10^5
M_w [g/mol]

b)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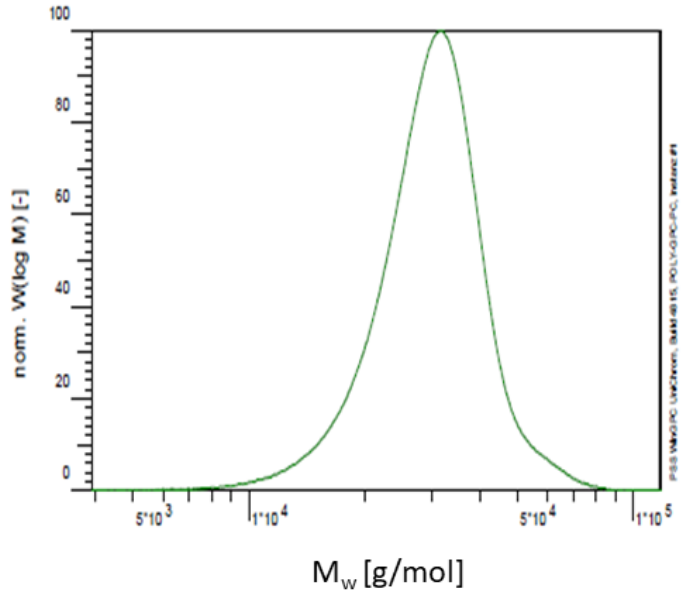
M_w [g/mol]

c)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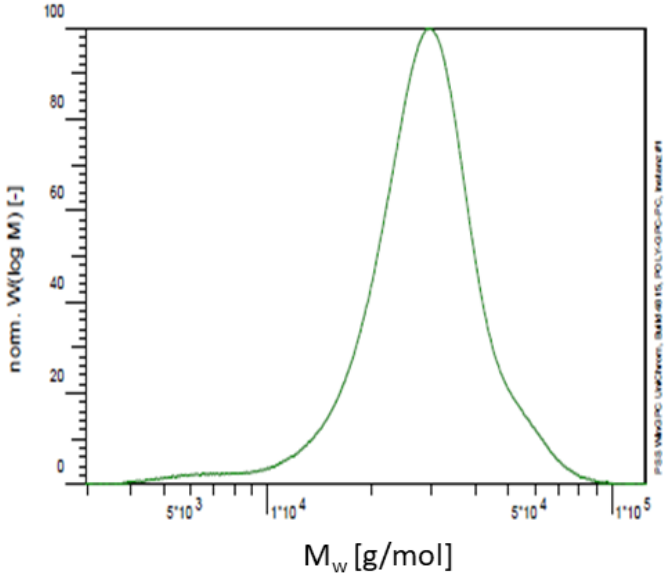
M_w [g/mol]

d)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M_w [g/mol]

e)

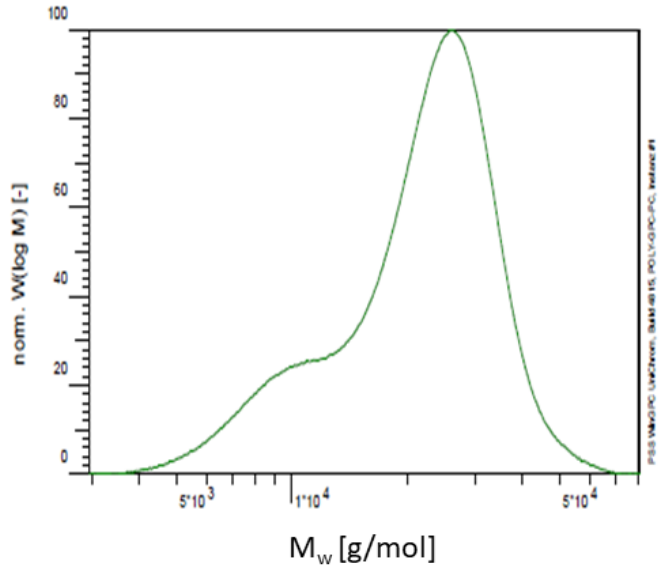


Fig. S 6. GPC chromatograms for a) *n*Bu40-*b*-tBuA167, b) *n*Bu68-*b*-tBuA167, c) *n*Hex37-*b*-tBuA169, d) *n*Do36-*b*-tBuA127, e) *n*Do36-*b*-tBuA71

3. pH-Titration

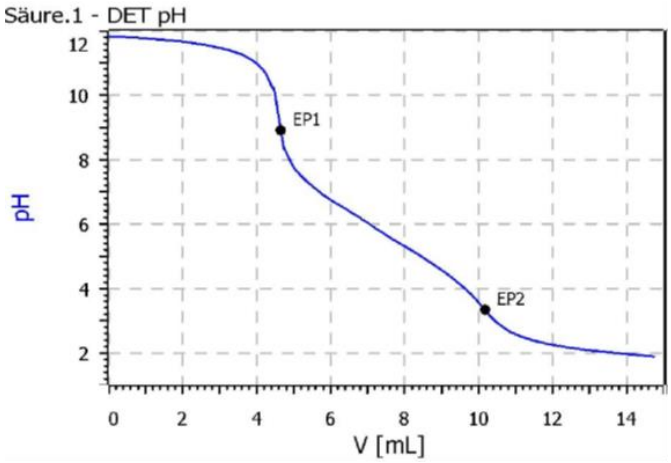


Fig. S 7. Titration curve of *n*Bu$_{40}$-*b*-AA$_{167}$

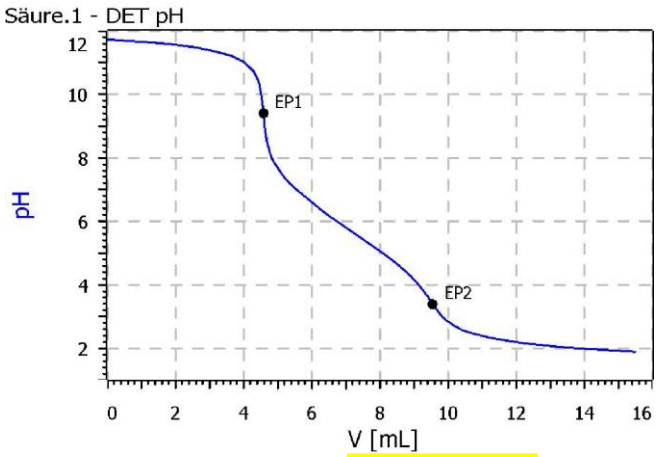


Fig. S 8.Titration curve of *n*Bu$_{68}$-*b*-AA$_{167}$

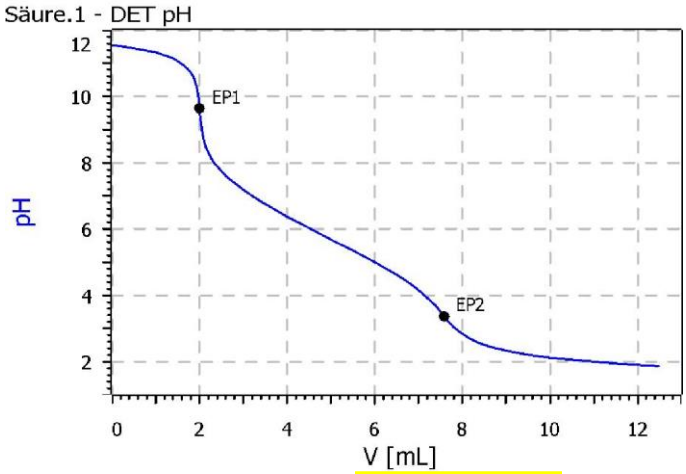


Fig. S 9. Titration curve of *n*Hex$_{37}$-*b*-AA$_{169}$

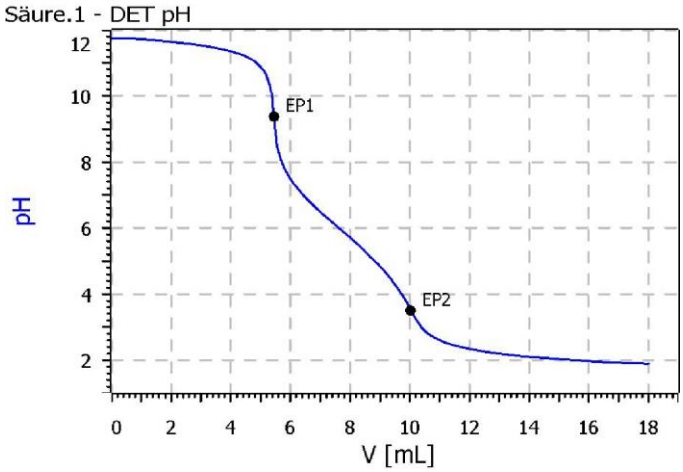


Fig. S 10. Titration curve of *n*Do$_{36}$-*b*-AA$_{127}$

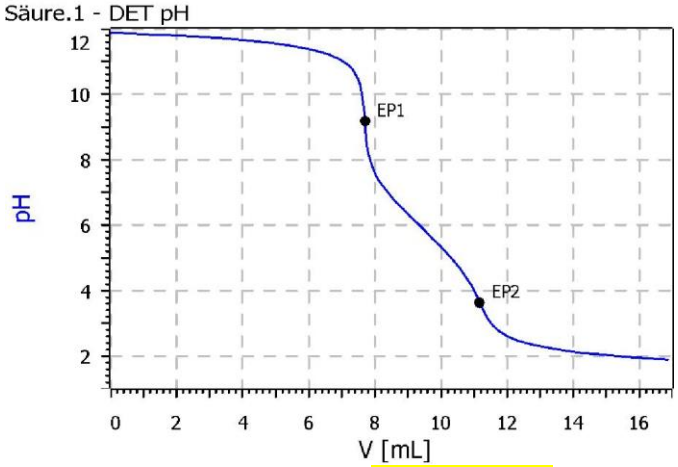


Fig. S 11. Titration curve of *n*Do$_{36}$-*b*-AA$_{71}$

The first equivalence point (EP) from the excess NaOH that was added around the polymer to deprotonate. The base excess is neutralized on this. The second EP (EP2) corresponds to the point at which the acid units are complete again protonated are present. This means that the section between EP1 and EP2 corresponds exactly to the amount of acid units in the polymer.

Consequently represents the difference of the used standard solution between EP1 and EP2 for the evaluation represents important used volumes of the standard solution

$$V(used) = V(EP2) - V(EP1)$$

$$n\,(stock\ Solution)\ =\ n\,(Polymer)$$

$$c * V = \frac{m}{M^{eff}}$$

c: concentration of stock solution

m: the amount of Polymer used for titration

V: determined used volume of stock solution

Table S 2 Effective molecular weights per changed unit as deduced from the pH-titrations and relative molar content of hydrophobic and hydrophilic block according to titration results

Polymer	M^{eff} [g/mol]	Hydrophobic [%]	Hydrophilic [%]
*n*Bu$_{40}$-*b*-AA$_{167}$	92.76	14.74	85.33
*n*Bu$_{68}$-*b*-AA$_{167}$	107.51	22.14	77.86
*n*Hex$_{37}$-*b*-AA$_{169}$	95.16	13.34	86.66
*n*Do$_{36}$-*b*-AA$_{127}$	112.15	14.60	85.40
*n*Do$_{36}$-*b*-AA$_{71}$	149.30	24.56	75.44

The effective block lengths were calculated via percentage of the hydrophobic and hydrophobic part. To do this, the determined relative molar proportions (mol percentages) converted into mass percentages

$$wt(Hydrophilic) = \frac{\%\ Hydrophilic * M(tert.Butylacrylate)}{\%Hydrophilic * M(tert.Butylacylate) + \%Hydrophobic * M(Alkylacrylate)}$$

$$wt(Hydrophobic) = \frac{\%Hydrophobic * M(Alkylacrylate)}{\%Hydrophilic * M(tert.Butylacylate) + \%Hydrophobic * M(Alkylacrylate)}$$

The effective block lengths then result in:

$$Hydrophilic\ Block\ Length = \frac{\big(M(Intermediate\ Product) - M(Macroinitiator)\big) * wt(Hydrophilic\ )}{M(tert.Butylacrylate)}$$

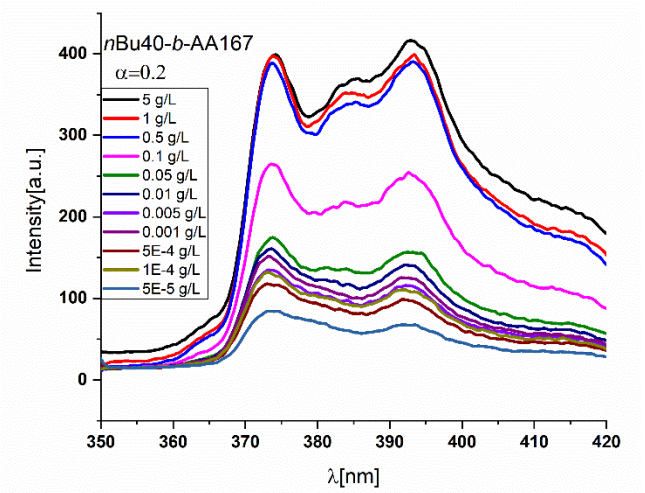
$$Hydrophobic\ Block\ Length = \frac{\big(M(Intermediate\ Product) - M(Macroinitiator)\big) * wt(Hydrophobic\ )}{M(tert.Butylacrylate)}$$

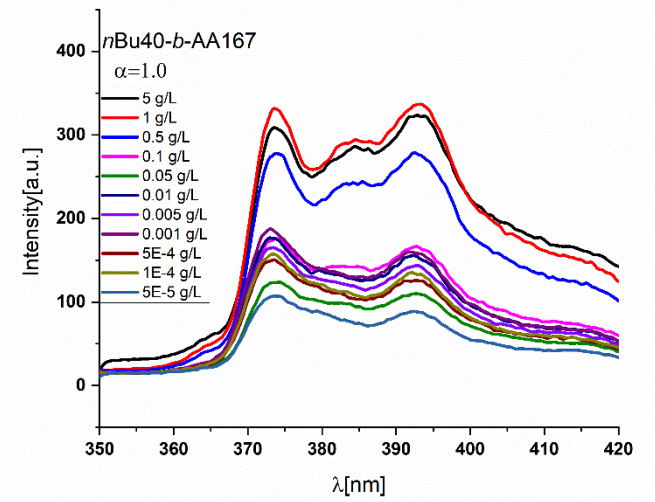
Table S 3. Chain Length of the Hydrophobic and Hydrophilic part of the synthesized polymers calculated from pH-titration

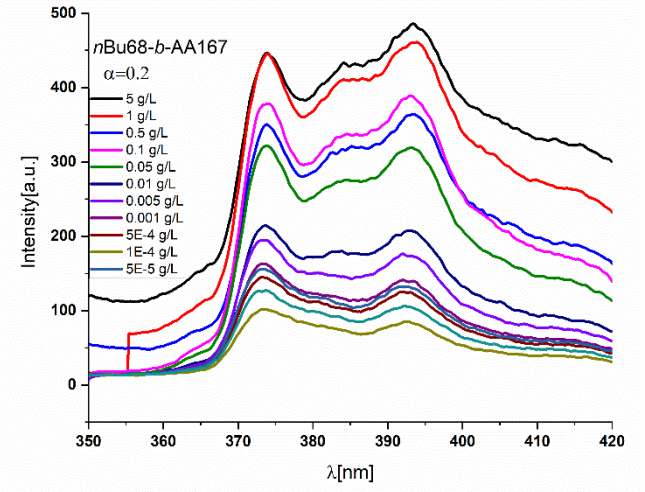
Polymer		**Chain Length**
***n*Bu40-*b*-AA100**	**Hydrophobic**	52
	Hydrophilic	182
	Total	235
***n*Bu20-*b*-AA100**	**Hydrophobic**	30
	Hydrophilic	177
	Total	207
***n*Do20-*b*-AA100**	**Hydrophobic**	25
	Hydrophilic	147
	Total	172
***n*Do40-*b*-AA100**	**Hydrophobic**	28
	Hydrophilic	87
	Total	115
***n*Hex20-*b*-AA100**	**Hydrophobic**	28
	Hydrophilic	180
	Total	208

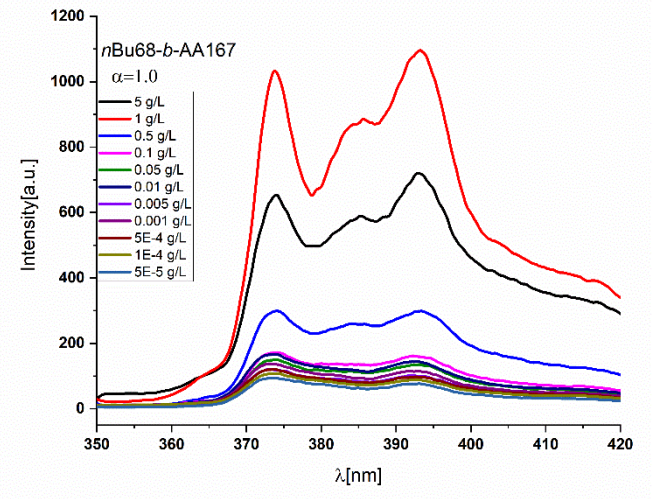
4. Fluorescence Spectra

Fluorescence spectra for the different polymers and for different degrees of ionisation were measured as a function of concentration.









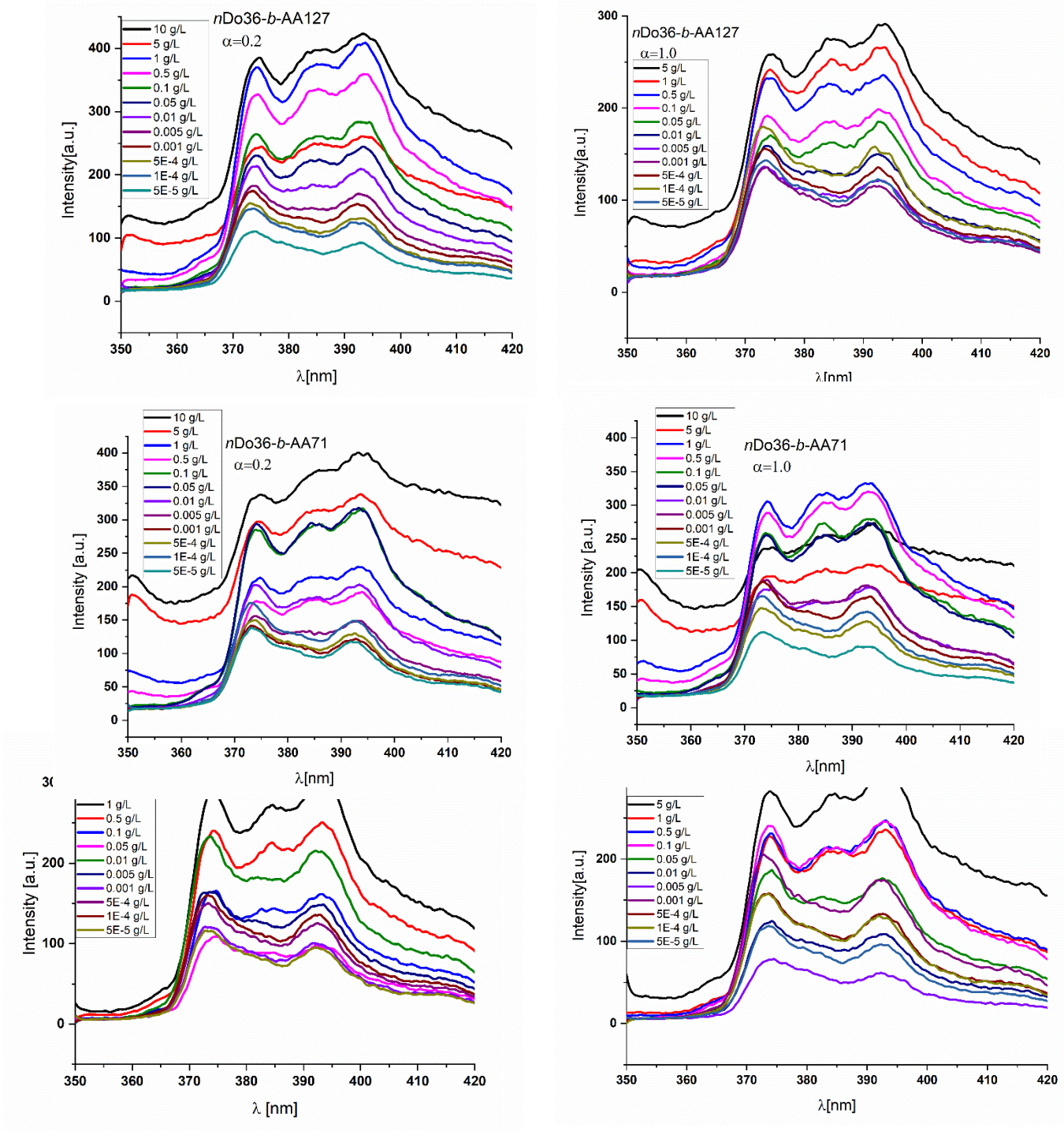


Fig. S 12. Fluorescence spectra of pyrene in water in the presence of an increasing concentration of block copolymer samples. Concentration c of the samples given in the inset in units of g/L.

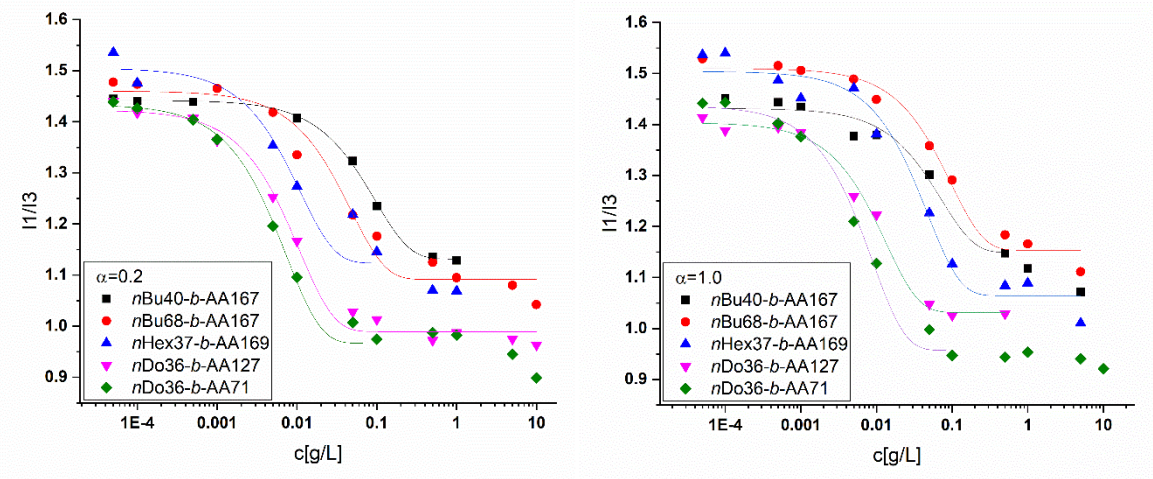


Fig. S 13. Ratio of the first and third maximum of the emission spectrum of pyrene as a function of concentration for different values of degrees of ionisation at room temperature

5. Static Light Scattering

Table S 4. dn/dc values of polymers

	dn/dc [mL/g]	
Polymer	**α= 1.0**	**α= 0.2**
Bu20	0.149	0.145
Bu40	0.154	0.157
Hex20	0.158	0.148
Do20	0.165	0.172
Do40	0.158	0.150

I(0) is the intensity which is extrapolated to zero angle. M_w^{app} is the apparent molecular weight of all scattered object which can be calculated via:

$$M_w^{app} = \frac{I(0)}{c * K}$$

K is the optical contrast and *c* is the concentration of the sample. Here, one can calculate the aggregation number N_{agg}

$$N_{agg} = \frac{M_w^{app}}{M_{w,polymer}}$$

M_w^{core} is the molar mass of the hydrophobic core and calculated via multiplying aggregation number with molecular weight of core.

$$M_w^{core} = N_{agg} * M_{core}$$

Assuming the aggregates as spherical, V_p and then respectively R_{core} are obtained

$$Vp = \frac{M_w^{core}}{\rho * N_{av}}$$

$$R_{core} = \sqrt[3]{\frac{Vp * 3}{4 * \pi}}$$

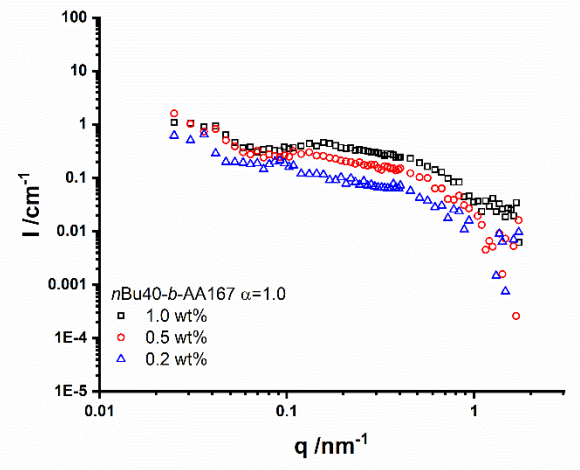
where are V_p the volume of aggregate, ρ the density of solute, N_{av} the Avogadro constant, R_{core} the radius of the hydrophobic core.

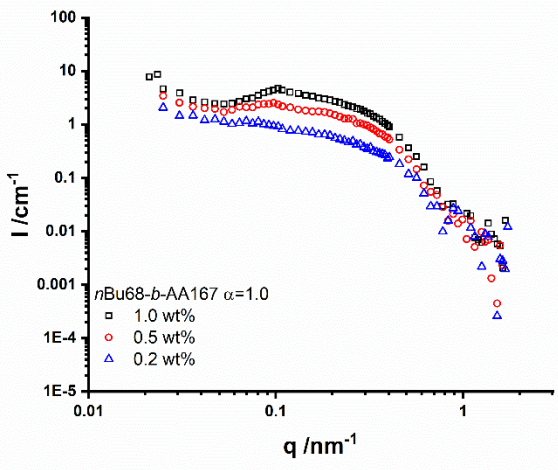
Table S 5. Parameters obtained from the static light scattering experiments.

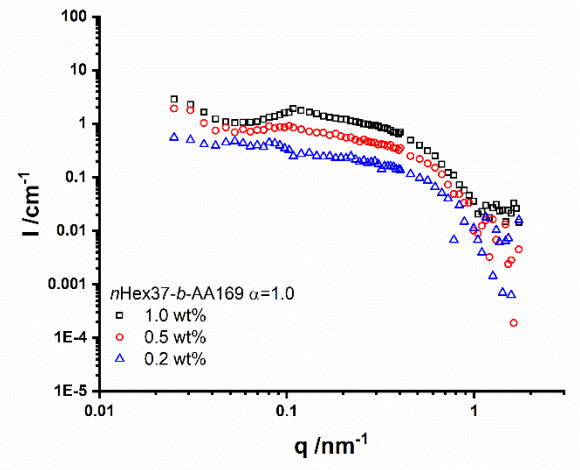
Static Light Scattering (SLS)							
Polymer	**c [g/L]**	**α**	**I(0) [1/cm]**	**M_w^{app} [g/mol]**	**Nagg**	**M_w^{core} [g/mol]**	**R_{core} [nm]**
***n*Bu$_{40}$-*b*-AA$_{167}$**	**1**	**1.0**	9.24E-05	5.74E+05	33.4	1.71E+05	3.95
	2	**1.0**	1.09E-04	3.37E+05	19.6	1.00E+05	3.31
	5	**1.0**	7.02E-04	8.71E+05	50.7	2.60E+05	4.54
	10	**1.0**	3.50E-03	2.17E+06	126.3	6.47E+05	6.15
	5	**0.2**	1.04E-03	1.36E+06	79.0	4.04E+05	5.26
***n*Bu$_{68}$-*b*-AA$_{167}$**	**1**	**1.0**	1.37E-03	8.01E+06	387.4	3.37E+06	10.67
	2	**1.0**	7.64E-04	2.23E+06	108.1	9.41E+05	6.97
	5	**1.0**	1.96E-03	2.29E+06	110.9	9.66E+05	7.03
	10	**1.0**	3.74E-03	2.19E+06	105.7	9.20E+05	6.92
	5	**0.2**	4.64E-03	5.22E+06	252.2	2.20E+06	9.25
***n*Hex$_{37}$-*b*-AA$_{169}$**	**1**	**1.0**	5.76E-04	3.18E+06	177.3	1.02E+06	7.17
	2	**1.0**	3.87E-04	1.07E+06	59.5	3.43E+05	4.98
	5	**1.0**	3.85E-04	4.26E+05	23.7	1.37E+05	3.67
	10	**1.0**	5.69E-04	3.15E+05	17.5	1.01E+05	3.32
	5	**0.2**	1.2E-03	9.77E+05	54.4	3.14E+05	4.84
***n*Do$_{36}$-*b*-AA$_{127}$**	**1**	**1.0**	1.84E-03	9.35E+06	523.4	4.52E+06	11.77
	2	**1.0**	4.28E-04	1.09E+07	610.6	5.28E+06	12.39
	5	**1.0**	7.51E-04	7.64E+05	42.8	3.70E+05	5.11
	10	**1.0**	1.37E-02	7.01E+06	392.4	3.39E+06	10.69
	5	**0.2**	8.65E-03	8.07E+06	452.0	3.91E+06	11.21
***n*Do$_{36}$-*b*-AA$_{71}$**	**1**	**1.0**	4.64E-03	2.56E+07	1833.8	1.58E+07	17.88
	2	**1.0**	4.66E-03	1.30E+07	934.8	8.08E+06	14.28

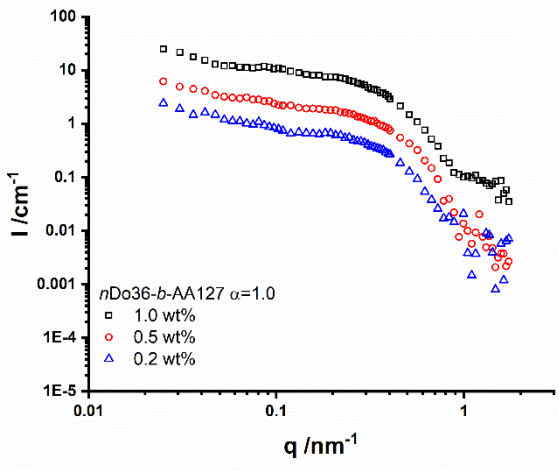
	5	**1.0**	6.70E-03	7.39E+06	529.6	4.58E+06	11.82
	10	**1.0**	8.15E-03	4.49E+06	321.9	2.78E+06	10.01
	5	**0.2**	8.71E-03	1.07E+07	770.1	6.65E+06	13.39

6. Small Angle Neutron Scattering (SANS)









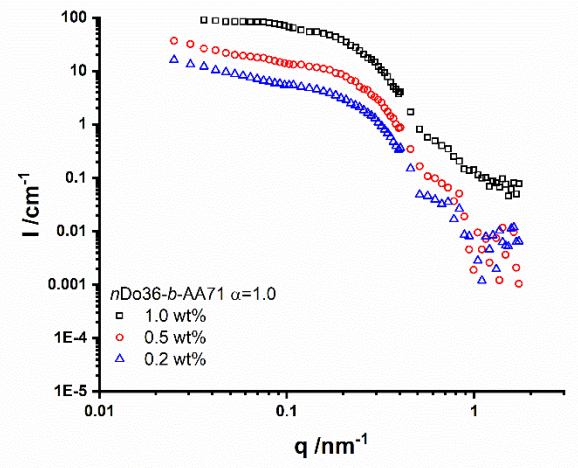


Fig. S 14. SANS intensity, as a function of the magnitude q of the scattering vector for samples with different concentrations and α=1.0.

The hydrophobic volume fraction Φ in the samples was calculated according to the equation below.

$$\phi = x_m\left(\frac{a*\mathrm{V_{block}}}{a*\mathrm{V_{block}} + b*\mathrm{V_{block}}}\right)$$

with x_m the mass fraction of the polymer, a the length of the hydrophobic chain, b the length of the hydrophilic chain, $\mathrm{V_{block}}$ the molecular volume of the corresponding block calculated from SASfit-tools.

Model Free Analysis

Model-free analysis of SANS curves, yielding the extrapolated intensity by Guinier approximation at zero-scattering angle, I(0), the resulting apparent molecular weight $\mathrm{M_w^{app}}$, and the aggregation number $\mathrm{N_{agg}}$ were calculated via:

$$M_w^{app} = \frac{I(0) * d^2 * N_{av}}{c * \Delta SLD^2}$$

$$N_{agg} = \frac{M_w^{app}}{M_w}$$

Table S 6. $\mathrm{M_w^{app}}$, $\mathrm{N_{agg}}$, and R were obtained from model free analysis of SANS data from LLB and HZB which is marked as *. Rg is calculated from a Guinier fit.

SANS [LLB] and *[HZB]						
Polymer	**c [g/L]**	**α**	**$\mathrm{M_w^{app}}$ [g/mol]**	**$\mathrm{N_{agg}}$**	**R [nm]**	**Rg [nm]**
***n*Bu$_{40}$-*b*-AA$_{167}$**	**2**	**1.0**	6.75E+04	3.9	2.89	3.06
	5	**1.0**	1.49E+05	8.7	3.76	3.22

	10	**1.0**	2.61E+04	1.5	2.10	3.07
	5	**0.2**	4.07E+05	23.7	5.26	4.07
	5*	**0.5**	2.90E+05	16.9	4.69	3.73
***n*Bu$_{68}$-*b*-AA$_{167}$**	**2**	**1.0**	4.19E+05	20.3	5.31	5.17
	5	**1.0**	3.50E+05	16.9	5.00	5.23
	10	**1.0**	1.41E+06	68.1	7.95	5.47
	5	**0.2**	7.44E+05	36.0	6.43	6.33
	5	**0.5**	3.61E+05	17.4	5.05	5.58
***n*Hex$_{37}$-*b*-AA$_{169}$**	**2**	**1.0**	1.35E+05	7.5	3.64	3.48
	5	**1.0**	1.60E+05	8.9	3.85	3.86
	10	**1.0**	1.48E+05	8.3	3.76	4.01
	5	**0.2**	3.49E+05	19.4	4.99	4.95
	5	**0.5**	2.45E+05	13.6	4.44	4.34
***n*Do$_{36}$-*b*-AA$_{127}$**	**2**	**1.0**	3.67E+05	20.5	5.08	4.59
	5	**1.0**	4.19E+05	23.4	5.31	4.53
	10	**1.0**	7.85E+05	43.9	6.55	4.73
	5	**0.2**	1.01E+06	56.8	7.13	5.80
	5	**0.5**	5.42E+05	30.4	5.79	4.87
***n*Do$_{36}$-*b*-AA$_{71}$**	**2**	**1.0**	2.85E+06	204.3	10.06	7.67
	5	**1.0**	2.47E+06	177.3	9.60	7.61
	10	**1.0**	1.96E+06	140.6	8.88	8.56
	5	**0.2**	6.05E+06	433.3	12.93	9.27
	5	**0.5**	3.13E+06	224.2	10.38	8.02

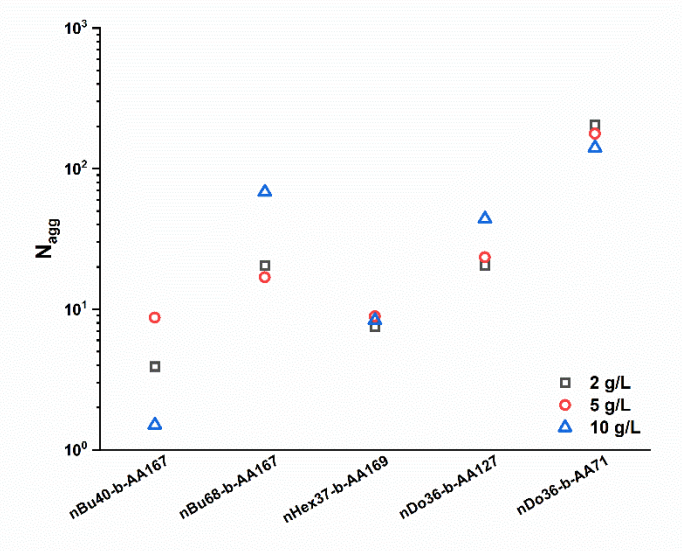


Fig. S 15. Aggregation Number as a function of the concentration for the different polymers studied (T = 25 °C, α = 1.0).

SANS- Simple spherical model						
Polymer	**c [g/L]**	**α**	Φ	fp/ Φ	R_m	Nagg
***n*Do$_{36}$-*b*-AA$_{127}$**	**2**	**1.0**	0.00059	0.546	4.85	36.5
	5	**1.0**	0.00148	0.836	4.46	28.5
	10	**1.0**	0.00479	0.832	4.58	30.7
	5	**0.2**	0.00148	0.770	5.55	54.8
	5	**0.5**	0.00148	0.731	4.75	34.4
***n*Do$_{36}$-*b*-AA$_{71}$**	**2**	**1.0**	0.00086	0.696	7.87	156.5
	5	**1.0**	0.00214	0.732	7.89	157.4
	10	**1.0**	0.00622	1.122	7.56	138.7
	5	**0.2**	0.00214	0.799	9.33	260.8
	5	**0.5**	0.00214	0.788	8.46	194.1

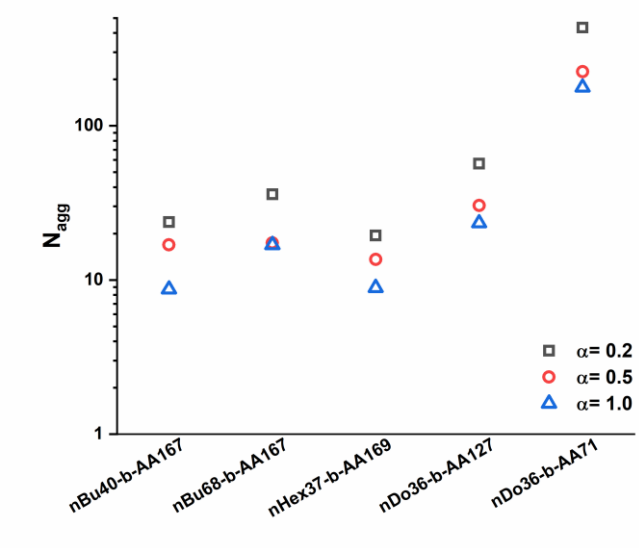


Fig. S 16. Aggregation Number as a function of the degree of ionisation α for the different polymers studied (T = 25 °C, c = 5 g/L).

Table S 7. Parameters calculated from a spherical model for the samples. Φ is the calculated volume fraction (eq S 1) of the hydrophobic core, fp the volume fraction from the fit, R_m the radius of the hydrophobic core and Nagg the aggregation number of hydrophobic core.

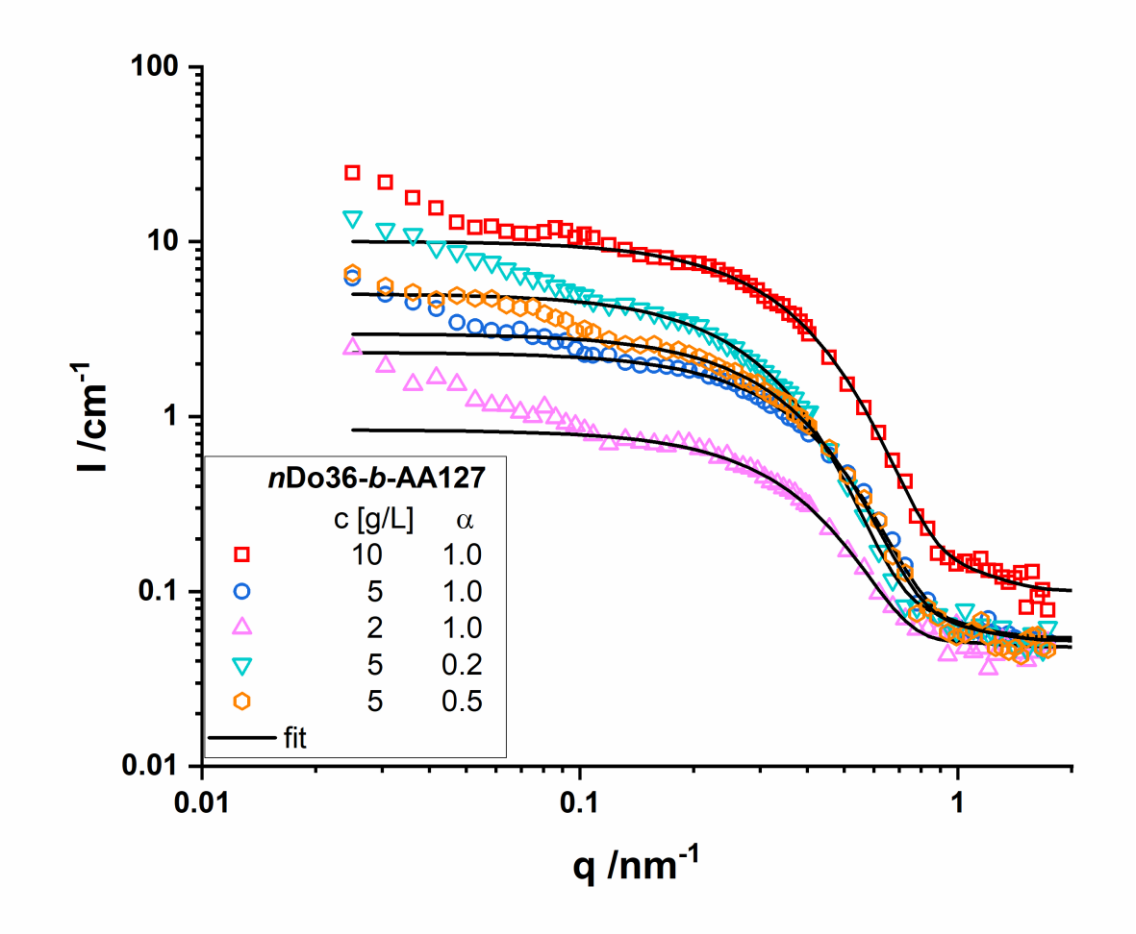


Fig. S 17a. SANS intensity as a function of the magnitude q of the scattering vector for the polymer *n*Do$_{36}$-*b*-AA$_{127}$ together with the fits for the q-range above 0.1 nm^{-1}.

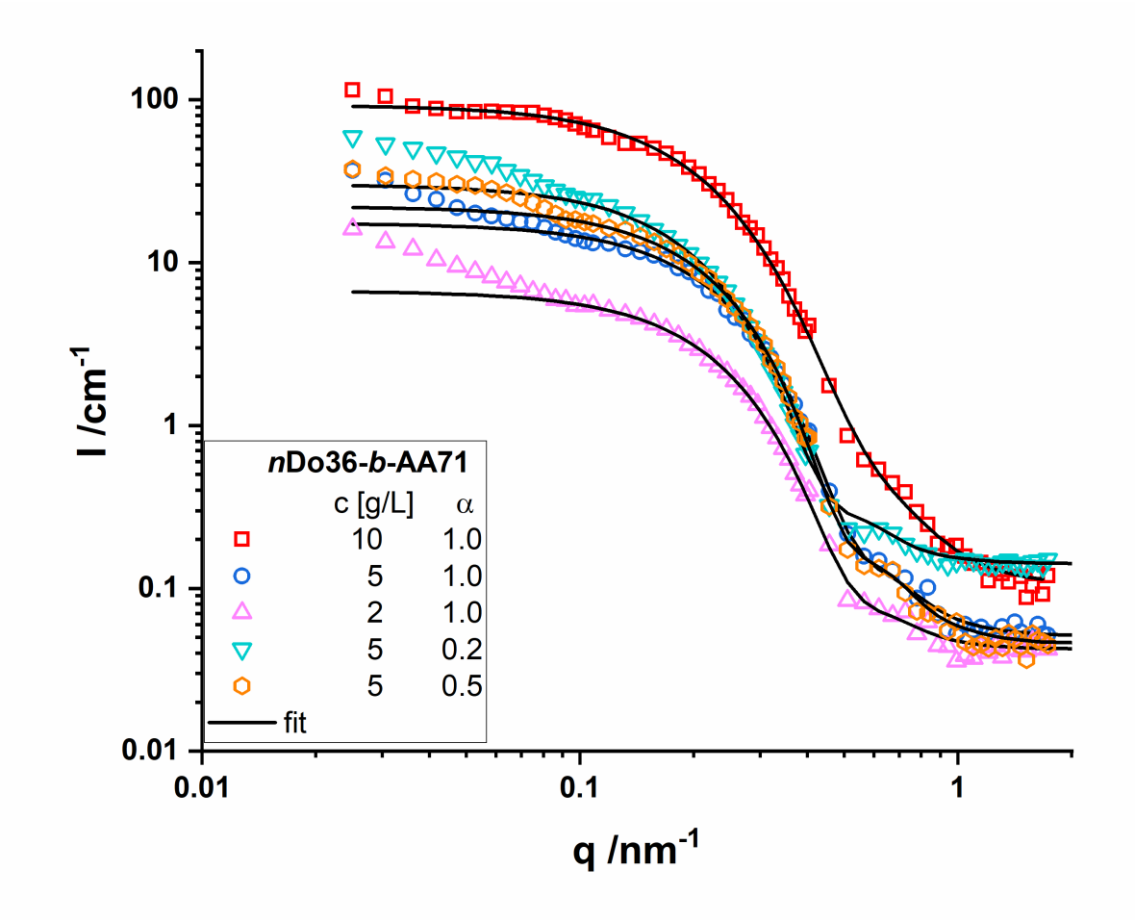


Fig. S 17b. SANS intensity as a function of the magnitude q of the scattering vector for the polymer *n*Do$_{36}$-*b*-AA$_{71}$ together with the fits for the q-range above 0.1 nm^{-1}.