Core and corona structure of mixed polymeric micelles

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Core and Corona Structure. ^{1}H NMR spectra of the individual polymers were recorded at 298K on a Bruker AMX-400 spectrometer, operating at 400 MHz. ^{1}H NMR spectra of the micellar solutions were recorded at 298 K on a Bruker AMX-500 spectrometer, operating at 500 MHz, located at the Wageningen NMR Centre. For the 2D NOESY spectrum 976 experiments of 2048 data points were recorded, consisting of 16 scans per *T1* value, using standard Bruker software. The mixing time was varied in the range of 200-1000 ms. The time domain data were multiplied with a phase-shifted sine-square window. Phase-sensitive Fourier transformation, resulting in a data set of 1024 X 512 complex points, was followed by polynomial baseline corrections in both directions. The spectra obtained with different mixing times are essentially the same, but the contour plot from the mixing time of 200 ms is clearest (Figure S1). Tables S1 and S2 list all the intra- and intermolecular NOE interactions.

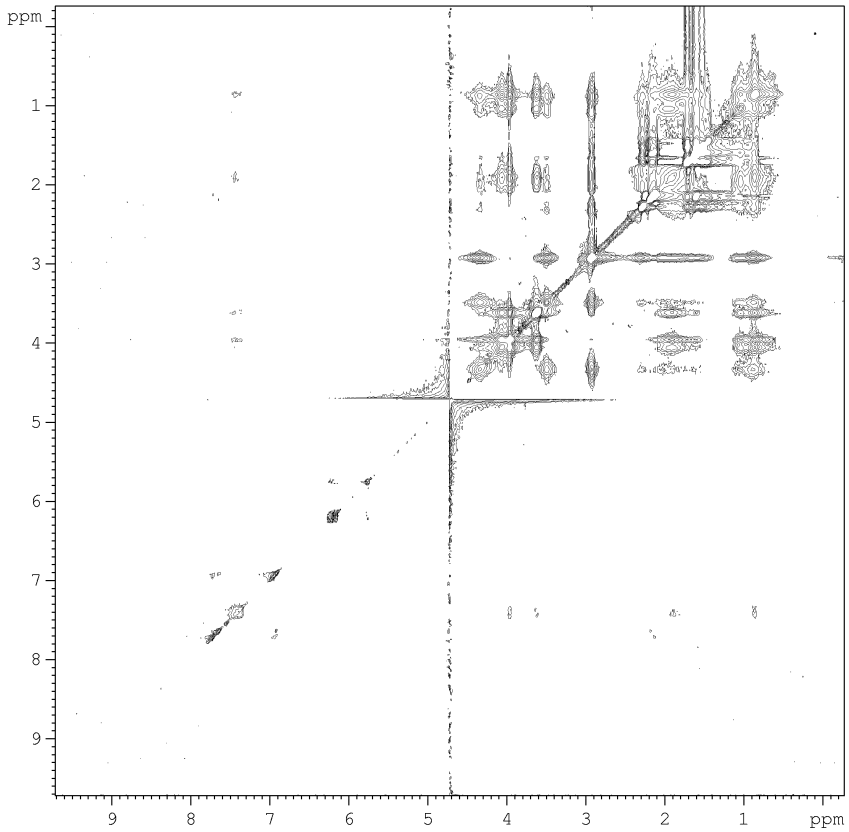

Figure S1. High resolution plot of the original 2D ^{1}H NMR NOESY contour plot of complex coacervate core micelles of PDMAEMA$_{45}$-*b*-PGMA$_{90}$ and PAA$_{42}$-*b*-PAAm$_{417}$ (1 mM $NaNO_3$, pH = 6.7, 25 ºC, f_+ = 0.5, C_p = 10 g/l) in D_2O.

Table S1. Intramolecular NOE interactions in complex coacervate core micelles of $PDMAEMA_{45}$-*b*-$PGMA_{90}$ and PAA_{42}-*b*-$PAAm_{417}$ (1 mM $NaNO_3$, pH = 6.7, 25 ºC, f_+ = 0.5, C_p = 10 g/l) in D_2O. Numbers 1-14 correspond to protons as assigned in the main body of the text (see Figure 2,3).

Intramolecular NOE interactions

Core/core	PAA	11-12 (i.e. all)
	PDMAEMA	2-5[a] (i.e. all)
Core/corona	PAA/PAAm	11-14 (i.e. all)
	PDMAEMA/PGMA	2,3 of PDMAEMA with 7-10; 4,5 of PDMAEMA with 7,10 but not with 8,9[b]
Corona/corona	PAAm	13-14 (i.e. all)
	PGMA	7-10[b] (i.e. all)

[a]NOE interactions with proton 1 are not determined due to overlap with proton 6

[b]NOE interactions with proton 6 are not determined due to overlap with proton 1

Table S2. Intermolecular NOE interactions in complex coacervate core micelles of $PDMAEMA_{45}$-*b*-$PGMA_{90}$ and PAA_{42}-*b*-$PAAm_{417}$ (1 mM $NaNO_3$, pH = 6.7, 25 ºC, f_+ = 0.5, C_p = 10 g/l) in D_2O. Numbers 1-14 correspond to protons as assigned in the main body of the text (see Figure 2,3).

Intermolecular NOE interactions

Core/core	PAA/PDMAEMA	12 of PAA with 2-5[a] 11 of PAA with 2,5 but not with 3,4[a]
Core/corona	PAA/PGMA	11 with none; 12 with 7[c]
	PDMAEMA/PAAm	13 of PAAm with 5,2[c] but not with 3,4[a]; 14 of PAAm with 2[c] but not with 3-5[a]
Corona/corona	PAAm/PGMA	13 of PAAm with 7-10[b]; 14 of PAAm with 7,8 but not with 9,10[b]

[a]NOE interactions with proton 1 are not determined due to overlap with proton 6

[b]NOE interactions with proton 6 are not determined due to overlap with proton 1

[c]maybe a subject of some debate