Supplementary Material (ESI) for *Soft Matter*.

Supplementary Information

SANS, SAXS and Light Scattering Investigations of pH-Responsive Dynamic Combinatorial Mesophases

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Synthesis of Dynablocks

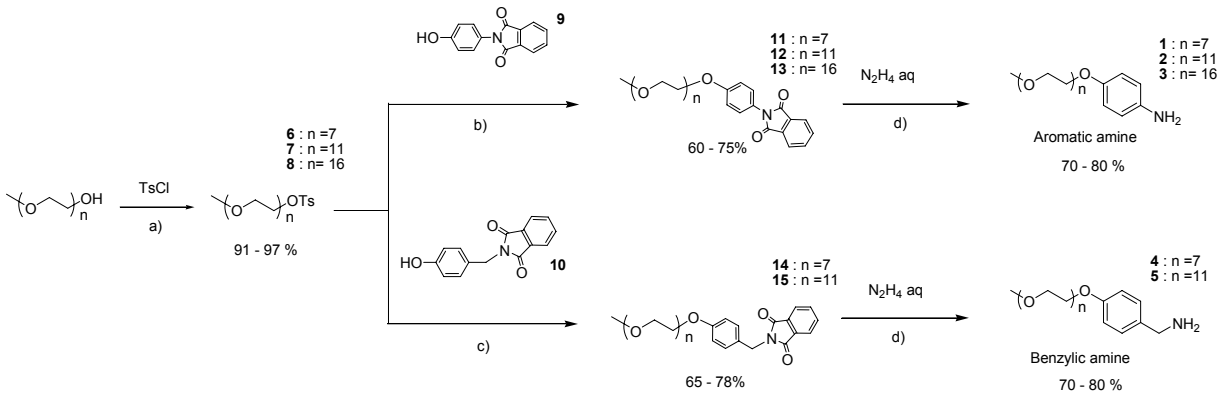

Fig. S 1 General synthesis of amine functionalized peg.

a) PEG_nOH (1.0 equiv.), *p*-toluenesulfonyl chloride (1.2 equiv.), pyridine, 0 °C, 4 – 8 h

b) PEG_nOTs **6-8** (1.0 equiv.), **9** (2.5 equiv.), K_2CO_3 (3.5 equiv.), CH_3CN, reflux, 6 – 8 h

c) PEG_nOTs **6-7** (1.0 equiv.), 10 (2.0 equiv.), K_2CO_3 (3.0 equiv.), CH_3CN, reflux, 6 – 8 h

d) Compounds **11-15** (1.0 equiv.), $N_2H_{4\,aq}$ (45 equiv.), THF, r.t., 4 - 8 h.

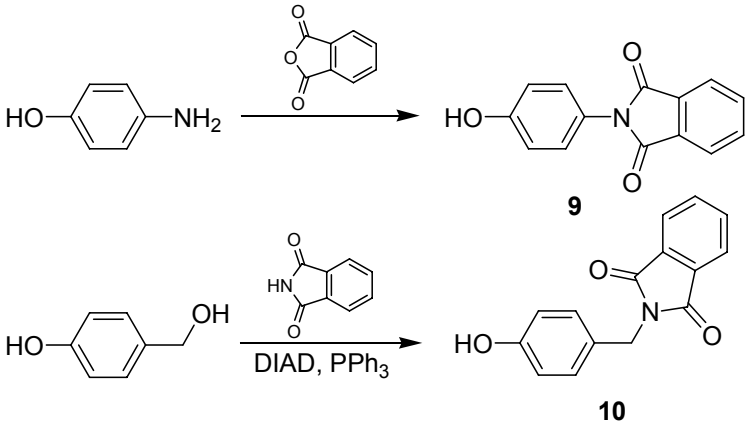

Fig. S 2 Synthesis of aromatic phtalimid 9 and benzylic phtalimid 10.

2-(4-hydroxyphenyl)isoindoline-1,3-dione **9:** *p*-aminophenol (1.0 equiv.), phtalic anhydride (1.0 equiv.), DMF, 90°C, 6 h, **9**: 90%.

2-(4-hydroxybenzyl)isoindoline-1,3-dione **10:** 4-hydroxybenzylalcohol (1,0 equiv), Phtalimide (1.2 equiv.), PPh_3 (1.5 equiv.), DIAD (1.2 equiv.), THF, 8 h, **10:** 54%.

Description of chemical products 1-15

1: ^{1}H NMR in $CDCl_3$: 6.75 (d, ^3J = .0 Hz, 2H), 6.62 (d, ^3J = 8.0 Hz, 2H), 4.04 (t, ^3J = 4.8 Hz, 2H), 3.80 (t, ^3J = 4.6 Hz, 2H), 3.64 (m, 22H), 3.54 (m, 2H), 3.37 (s, 3H); ESI-MS: calcd $C_{21}H_{37}NO_8$ 432.26 $[M+H]^+$; found 432.51.

2: ^{1}H NMR in $CDCl_3$: 6.73 (d, ^3J = 8.0 Hz, 2H), 6.62 (d, ^3J = 8.0 Hz, 2H), 4.05 (t, ^3J = 4.8 Hz, 2H), 3.80 (t, ^3J = 4.8 Hz, 2H), 3.65 (m, 40H), 3.37 (s, 3H.

3: ^{1}H NMR in $CDCl_3$: 6.74 (d, ^3J = 8.0 Hz, 2H), 6.64 (d, ^3J = 8.0 Hz, 2H), 4.05 (t, ^3J = 4.4 Hz, 2H), 3.81 (t, ^3J = 4.4 Hz, 2H), 3.65 (m, 60H), 3.37 (s, 3H).

4: ^{1}H NMR in $CDCl_3$: 7.19 (d, ^3J = 8.4 Hz, 2H), 6.87 (d, ^3J = 8.4 Hz, 2H), 4.10 (t, ^3J = 4.8 Hz, 2H), 3.83 (m, 2H), 3.79 (s, 2H), 3.65 (m, 24H), 3.36 (s, 3H); ^{13}C NMR in $CDCl_3$: 159.97, 157.47, 128.24, 113.61, 70.87, 69.51, 58.01, 29.61; ESI-MS: calcd $C_{22}H_{39}NO_8$ 446.27 $[M+H]^+$; found 446.52.

5: ^{1}H NMR in $CDCl_3$: 7.21 (d, ^3J = 8.4 Hz, 2H), 6.88 (d, ^3J = 8.4 Hz, 2H), 4.10 (t, ^3J = 4.8 Hz, 2H), 3.84 (t, ^3J = 4.8 Hz, 2H), 3.79 (s, 2H), 3.64 (m, 40H), 3.37 (s, 3H).

6: ^{1}H NMR in $CDCl_3$: 7.76 (d, ^{3}J = 8.4 Hz, 2H), 7.31 (d, ^{3}J = 8.3 Hz, 2H), 4.12 (t, ^{3}J = 4.8 Hz, 2H), 3.66 (t, ^{3}J = 5.0 Hz, 2H), 3.58 (brm, 26H), 3.34 (s, 3H), 2.41 (s, 3H); ^{13}C NMR in $CDCl_3$: 144.66, 132.90, 129.70, 127.84, 71.80, 70.60, 70.47, 70.43, 70.37, 69.13, 68.54, 58.88, 21.50. Anal. calcd. for $C_{22}H_{38}O_{10}S$: C 53.42, H 7.74, S 6.48; found C 52.65, H 7.82, S 5.93; ESI-MS: calcd for $C_{22}H_{38}O_{10}S$ 495.22 $[M+H]^+$; found 495,45.

7: ^{1}H NMR in $CDCl_3$: 7.76 (d, ^{3}J = 8.4 Hz, 2H), 7.30 (d, ^{3}J = 8.3 Hz, 2H), 4.12 (t, ^{3}J = 4.8 Hz, 2H), 3.64 (t, ^{3}J = 5 Hz, 2H), 3.62 (m, 6H), 3.60 (m, 24H), 3.57 (m, 4H), 3.54 (m, 4H), 3.51 (m, 2H), 3.34 (s, 3H), 2.41 (s, 3H); ^{13}C NMR in $CDCl_3$: 144.77, 133.02, 129.82, 127.96, 71.92, 70.72, 70.55, 70.49, 69.25, 68.67, 59.01, 21.63; ESI-MS: calcd for $C_{30}H_{54}SO_{14}$ 688.34 $[M+H_2O]^+$; found 688.58.

8: ^{1}H NMR in $CDCl_3$: 7.79 (d, ^{3}J = 8.4 Hz, 2H), 7.33 (d, ^{3}J = 8.3 Hz, 2H), 4.14 (t, ^{3}J = 4.8 Hz, 2H), 3.67 (t, ^{3}J = 4.8 Hz, 2H), 3.64 (m, 6H), 3.62 (m, 44H), 3.60 (m, 4H), 3.56 (m, 4H), 3.53 (m, 2H), 3.37 (s, 3H), 2.44 (s, 3H); ^{13}C NMR in $CDCl_3$: 144.78, 133.05, 129.83, 127.99, 71.94, 70.75, 70.57, 70.51, 69.25, 68.69, 59.04, 21.66; ESI-MS: calcd for $C_{40}H_{74}SO_{19}$ 908.47 $[M+H_2O]^+$; found 908.90.

9: ^{1}H NMR in $CDCl_3$: 7.94 (m, 2H), 7.78 (m, 2H), 7.30 (d, ^{3}J = 8.8 Hz, 2H), 6.95 (d, ^{3}J = 8.8 Hz, 2H); ^{1}H NMR in DMSO: 9.77 (s, 1H), 7.93 (m, 2H), 7.88 (m, 2H), 7.21 (d, ^{3}J = 8.7, 2H), 6.88 (d, ^{3}J = 8.7, 2H); ^{13}C NMR in DMSO: 167.43, 157.32, 134.64, 131.61, 128.84, 123.31, 122.85, 115.42; Anal. calcd. for $C_{14}H_9NO_3$: C 70.29, H 3.79, N 5.86; found C 67.70, H 4.06, N 5.80.

10: ^{1}H NMR in $CDCl_3$: 7.83 (m, 2H), 7.69 (m, 2H), 7.33 (d, ^{3}J = 8.5 Hz, 2H), 6.76 (d, ^{3}J = 8.5 Hz, 2H), 4.77 (s, 2H), 4.74 (s, 1H); ^{13}C NMR in $CDCl_3$: 168.10, 155.20, 133.94, 132.15, 130.37, 128.82, 123.30, 115.42, 41.02; Anal. calcd. for $C_{15}H_{11}NO_3$: C 71.14, H 4.38, N 5.53; found C 70.71, H 4.45, N 5.68; HRMS (ESI-TOF): calcd for $C_{15}H_{11}NO_3$ 260.089 $[M+Li]^+$; found 260.090.

11: ^{1}H NMR in $CDCl_3$: 7.94 (m, 2H), 7.78 (m, 2H), 7.32 (d, ^{3}J = 9.2 Hz, 2H), 7.03 (d, ^{3}J = 9.2 Hz, 2H), 4.17 (t, ^{3}J = 5.2 Hz, 2H), 3.87 (t, ^{3}J = 5.2 Hz, 2H), 3.73 (m, 2H), 3.64 (m, 20H), 3.54 (m, 2H), 3.37 (s, 3H); ^{13}C NMR in $CDCl_3$: 167.54, 158.42, 134.31, 131.82, 127.90, 124.56, 123.68, 115.17, 71.95, 70.92, 70.67, 70.59, 69.65, 67.72, 59.07; ESI-MS: calcd $C_{29}H_{39}NO_{10}$ 579.27 $[M+H_2O]^+$; found 579.60.

12: ^{1}H NMR in $CDCl_3$: 7.94 (m, 2H), 7.78 (m, 2H), 7.32 (d, ^{3}J = 9.2 Hz, 2H), 7.03 (d, ^{3}J = 9.2 Hz, 2H), 4.17 (t, ^{3}J = 5.2 Hz, 2H), 3.87 (t, ^{3}J = 5.2 Hz, 2H), 3.73 (m, 2H), 3.64 (m, 36H), 3.54 (m, 2H), 3.37 (s, 3H); ^{13}C NMR in $CDCl_3$: 167.54, 158.47, 134.31, 131.84, 127.91, 124.57, 123.68, 115.18, 71.94, 70.88, 70.65, 70.57, 69.65, 67.74, 59.05; ESI-MS: calcd $C_{37}H_{55}NO_{14}$ 755.38 $[M+H_2O]^+$; found 755.75.

13: ^{1}H NMR in $CDCl_3$: 7.94 (m, 2H), 7.78 (m, 2H), 7.33 (d, ^{3}J = 9.0 Hz, 2H), 7.02 (d, ^{3}J = 9.0 Hz, 2H), 4.18 (t, ^{3}J = 5.2 Hz, 2H), 3.87 (t, ^{3}J = 5.0 Hz, 2H), 3.73 (m, 2H), 3.68 (m, 56H), 3.54 (m, 2H), 3.37 (s, 3H); ^{13}C NMR in $CDCl_3$: 167.54, 158.46, 134.33, 131.83, 127.90, 124.56, 123.68, 115.15, 71.96, 70.87, 70.57, 69.65, 67.73, 59.07.

14: ^{1}H NMR in $CDCl_3$: 7.82 (m, 2H), 7.69 (m, 2H), 7.35 (d, ^{3}J = 8.8 Hz, 2H), 6.83 (d, ^{3}J = 8.8 Hz, 2H), 4.77 (s, 2H), 4.07 (t, ^{3}J = 4.0 Hz, 2H), 3.81 (t, ^{3}J = 5.0 Hz, 2H), 3.62 (m, 22H), 3.53 (m, 2H), 3.36 (s, 3H); ^{13}C NMR in

$CDCl_3$: 168.09, 158.41, 133.94, 132.09, 130.11, 128.70, 123.27, 114.75, 71.96, 70.82, 70.65, 70.57, 69.71, 67.42, 59.06, 41.09.

15: ^{1}H NMR in $CDCl_3$: 7.83 (m, 2H), 7.69 (m, 2H), 7.35 (d, ^3J = 8.4 Hz, 2H), 6.84 (d, ^3J = 8.8 Hz, 2H), 4.77 (s, 2H), 4.08 (t, ^3J = 4.0 Hz, 2H), 3.81 (t, ^3J = 4.8 Hz, 2H), 3.63 (m, 38H), 3.55 (m, 2H), 3.37 (s, 3H); ^{13}C NMR in $CDCl_3$: 165.88, 157.36, 132.87, 131.14, 129.05, 127.8, 122.29, 113.70, 70.93, 69.56, 58.02, 40.18; ESI-MS: calcd $C_{38}H_{57}NO_{14}$ 769.39 $[M+H_2O]^+$; found 769.72.

Detail of fitting procedures for Dynablocks and for competitive exchanges.

For all the experimental data the fitting procedure is based on a core-shell model with different form factors: spherical or cylindrical micelles. In some cases we observe coexistence between different shapes, thus the total scattering intensity $I_{tot}(q)$ can be described as a sum of contributions from the different objects: $I(q)=I_1(q)+I_2(q)+I_3(q)$.

In the Supplementary Information we detailed the fits when coexistences of shapes are involved. Figures S3, S4 and S5 present the SANS curves of Dynablocks **3A**, **4A** and **5A**. To fit the data, we used a combination of spheres form factor and vesicle form factor for **3A** and **5A** and a combination of cylinder and vesicle for **4A**. For each case we added the form factor of rigid chain to account the behavior at high q.

Figures S6 and S7 detail the fits for exchange **2A-5A** at pD=8.1 and 9 (S6) and for exchange **3A-4A** at all pD (S7).

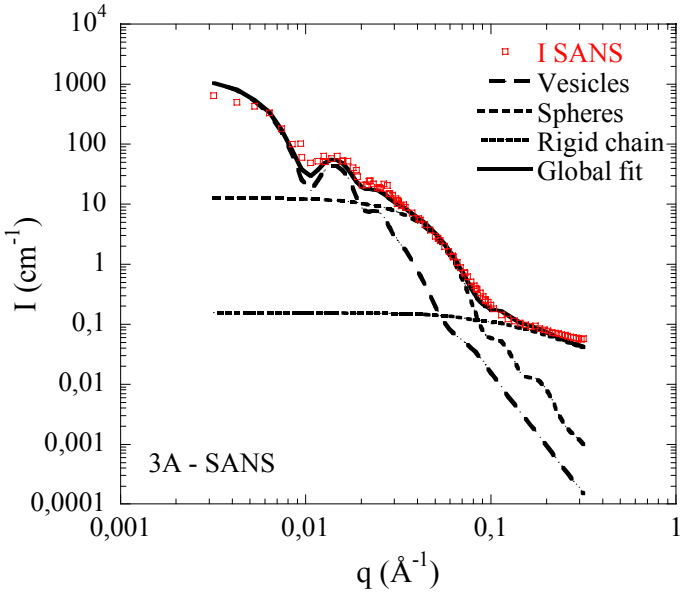

Fig. S 3 SANS spectra of Dynablock 3A: the best fit (black solid line) is obtained by a combination of vesicle (--), sphere (--) and rigid chain (....) form factors.

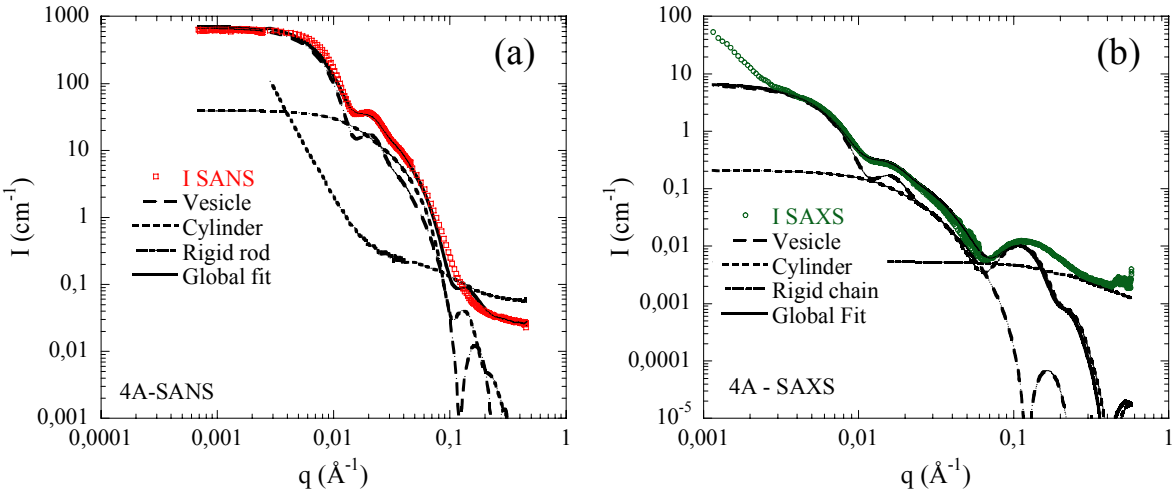

Fig. S 4 Scattering spectra of Dynablock **4A**: the best fit (black solid line) is obtained by a combination of vesicle (--), cylinder (--) and rigid chain (....) form factors. (a) SANS, (b) SAXS.

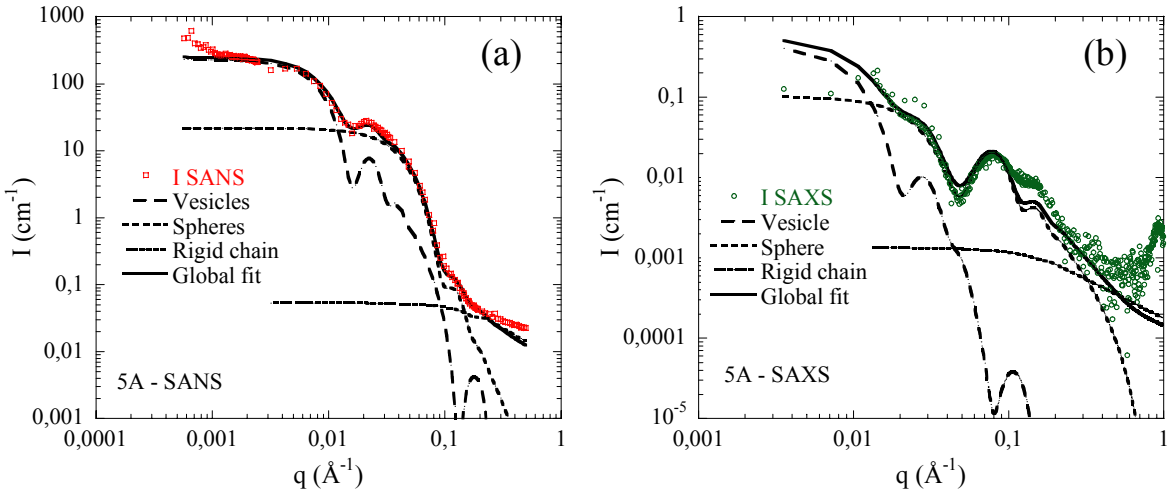

Fig. S 5 Scattering spectra of Dynablock **5A**: the best fit (black solid line) is obtained by a combination of vesicle (--), sphere (--) and rigid chain (....) form factors. (a) SANS, (b) SAXS.

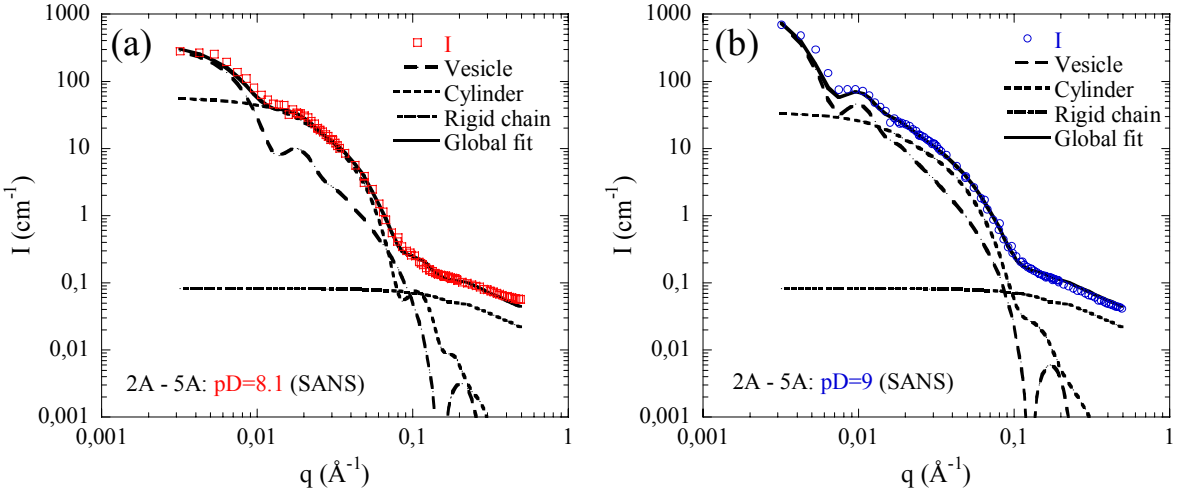

Fig. S 6 Scattering spectra for exchange **2A-5A**: the best fit (black solid line) is obtained by a combination of vesicle (--), cylinder (--) and rigid chain (....) form factors. (a) pD=8.1, (b) pD=9.

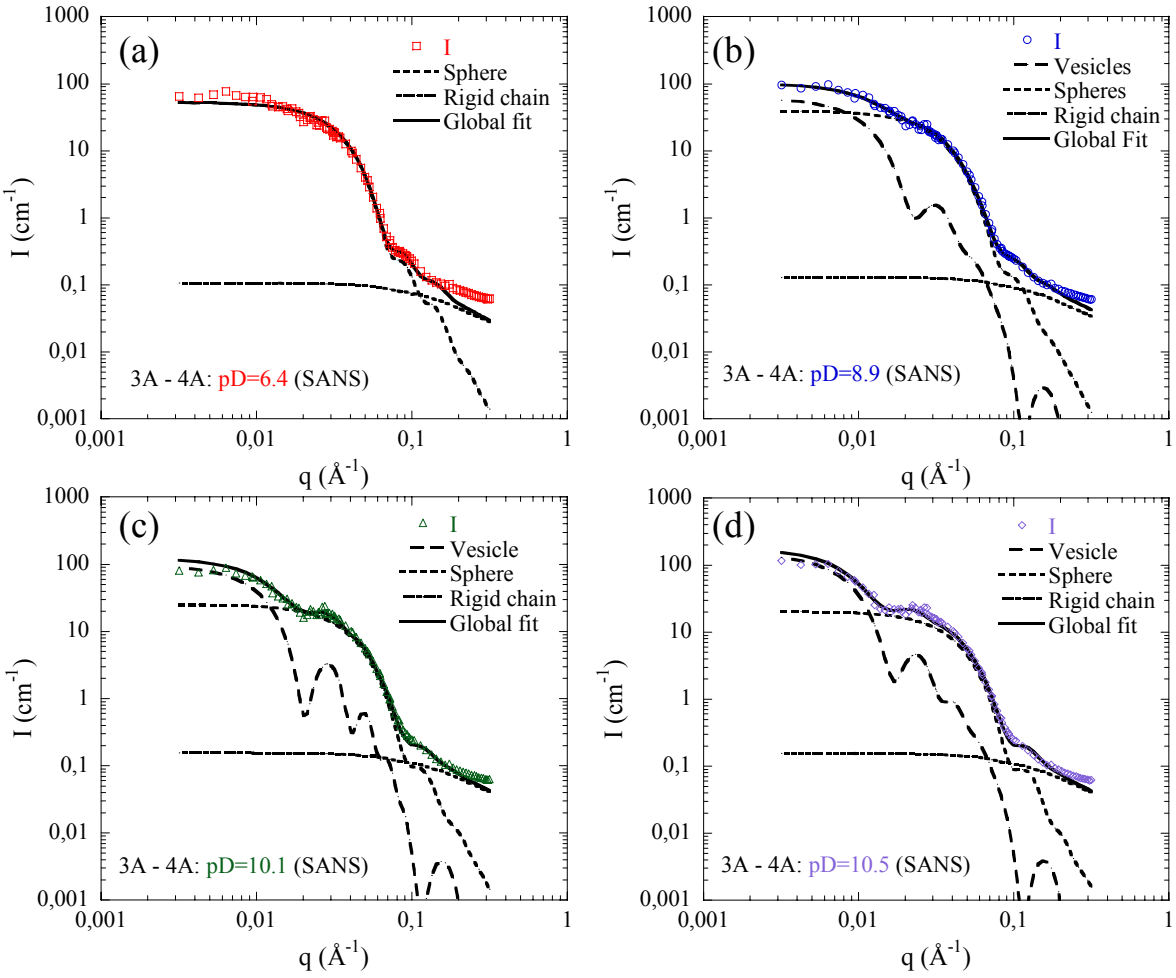

Fig. S 7 Scattering spectra for exchange 3A-4A: the best fit (black solid line) is obtained by a combination of vesicle (--), sphere (--) and rigid chain (....) form factors. (a) pD=6.4, (b) pD=8.9, (c) pD=10.1, (d) pD=10.5.