Electronic supplementary materials

Tailoring the Amphiphilicity and Self-assembly of Thermosensitive Polymers: End-capped PEG-PNIPAAM Block Copolymers

Zhilong Quan[1,2], Kaizheng Zhu[2], Kenneth D. Knudsen[3], Bo Nyström[2] and Reidar Lund[2]*

[1] College of Materials Science & Engineering, Huaqian University, 361021 Xiamen, P.R.China.

[2] Department of Chemistry, University of Oslo, P.O.Box 1033, Blindern, N-0315 Oslo, Norway.

[3]Department of Physics, Institute for Energy Technology, P. O. Box 40, N-2027 Kjeller, Norway.

* To whom correspondence should be addressed: reidar.lund@kjemi.uio.no

NMR spectra were recorded using a Bruker AVANCE DPX 300 MHz spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C). $CDCl_3$ was used as the solvent and TMS was selected as the reference standard. The D_2O singlet at 4.70 ppm was selected as reference standard when the samples were measured in heavy water. Spectral features are tabulated in the following order: chemical shift (ppm); multiplicity (s – singlet, d – doublet, t – triplet, m – complex multiple).

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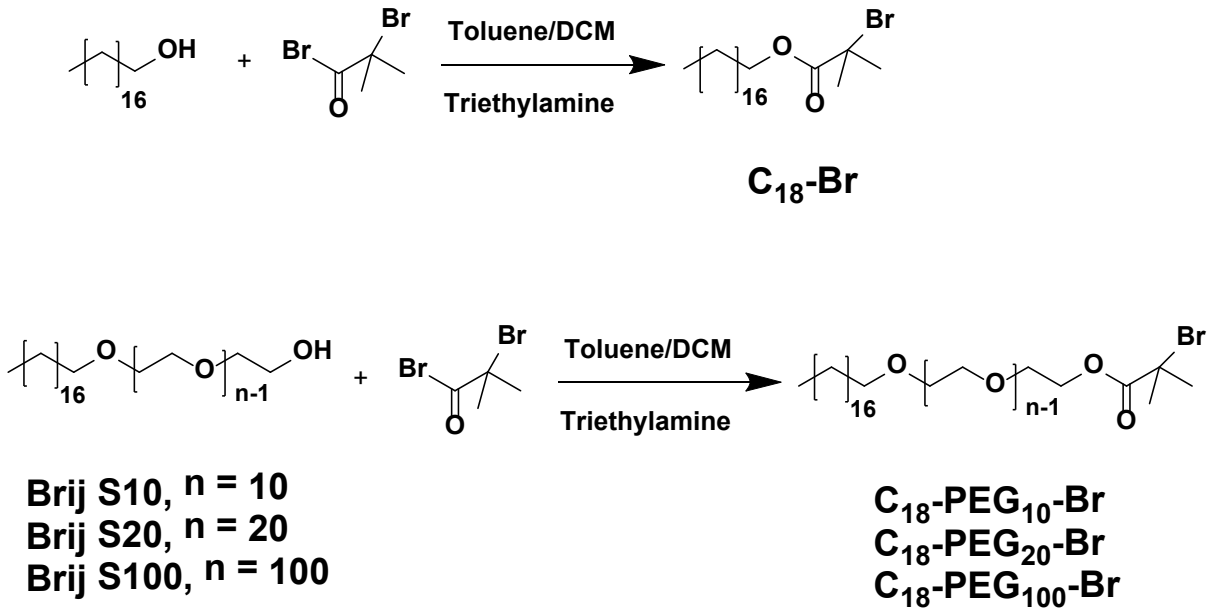

Figure S1 Synthesis of C_{18}-Br and C_{18}-PEG-Br initiator

Synthesis of the octadecyl initiator (C_{18}-Br) and octadecyl-capped poly(ethylene glycol) initiator (C_{18}-PEG$_n$-Br, n= 10, 20 and 100)

The octadecyl-capped initiator (C_{18}-Br) and octadecyl-capped-PEG macroinitiators (C_{18}-PEG-Br) were prepared by reacting octadecanol (C_{18}-OH) or poly(ethylene glycol) octadecyl ether (C_{18}-PEG-OH) with 2-bromoisobutyl bromide in the presence of triethylamine. [1,2,3] The ^{1}H-NMR spectra indicated that the degree of esterification was at least 99 %.

Octadecyl 2-bromoisobutyrate (C_{18}-Br): ^{1}H NMR (300MHz, $CDCl_3$): δ = 0.88 (t, 3H, C***H***$_3$-CH$_2$-), 1.26 (m, 30H, -(C***H***$_2$)$_{15}$-), 1.66 (m, 2H, CH$_3$(CH$_2$)$_{15}$C***H***$_2$CH$_2$O-), 1.95(s, 6H, -COC(C***H***$_3$)$_2$Br), 4.16 (t, 2H, CH$_3$(CH$_2$)$_{16}$C***H***$_2$O-);

^{13}C NMR (75MHz, $CDCl_3$): δ = 172 (***C***=O), 66(-O***C***H$_2$(CH$_2$)$_{16}$CH$_3$), 56(-***C***(CH$_3$)$_2$ Br), 32 (-C(***C***H$_3$)$_2$Br), 23-31 (-OCH$_2$(***C***H$_2$)$_{16}$CH$_3$), 14(-O(CH$_2$)$_{17}$***C***H$_3$).

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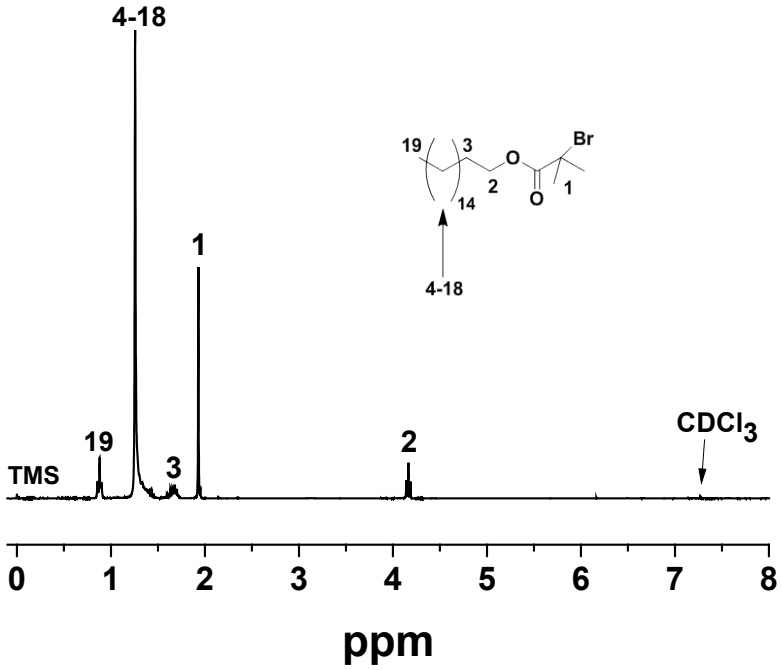

Figure S2 ^{1}H NMR spectrum of C_{18}-Br in $CDCl_3$

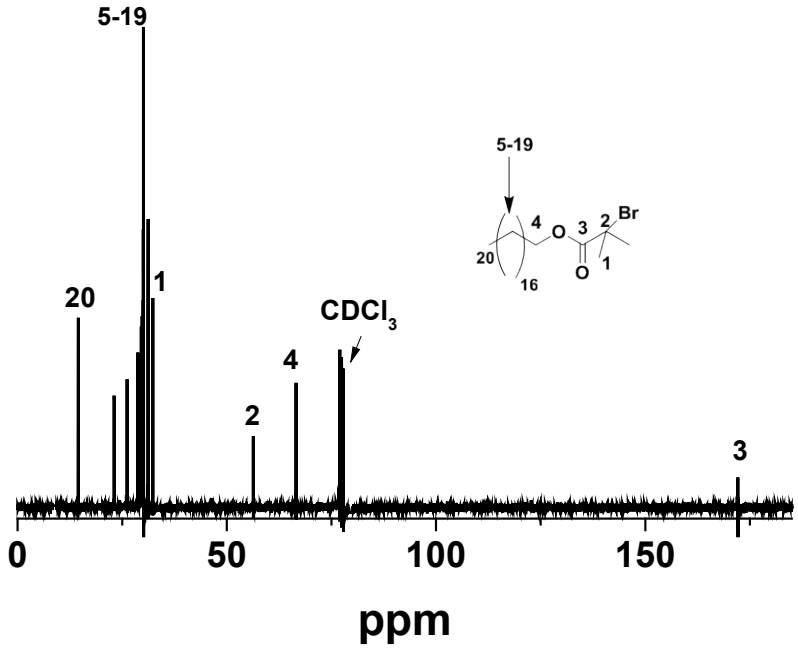

Figure S3 ^{13}C NMR spectrum of C_{18}-Br in $CDCl_3$

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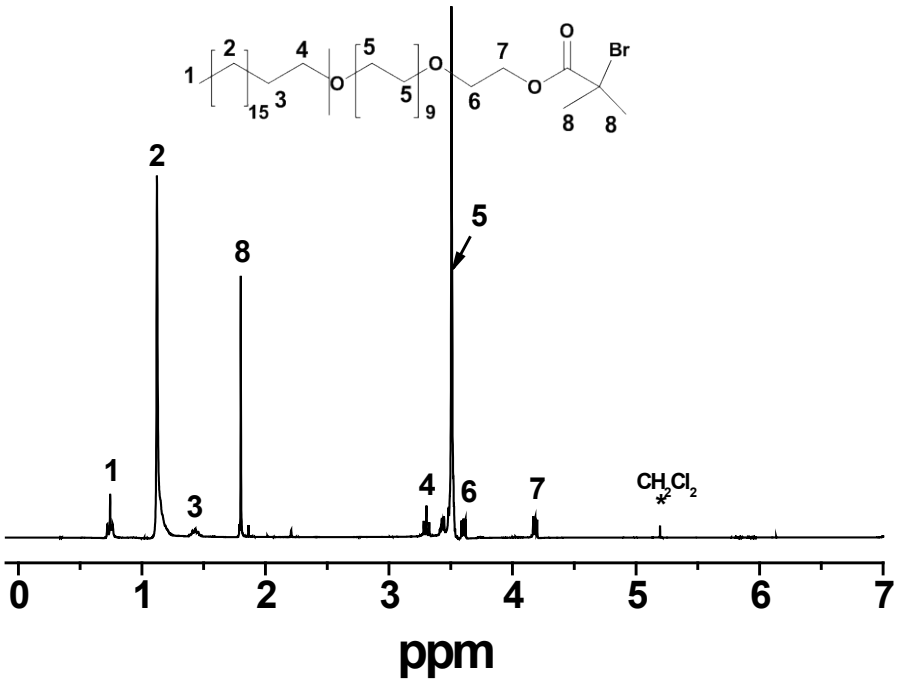

Figure S4 ^{1}H NMR spectrum of C_{18}-PEG_{10}-Br in $CDCl_3$

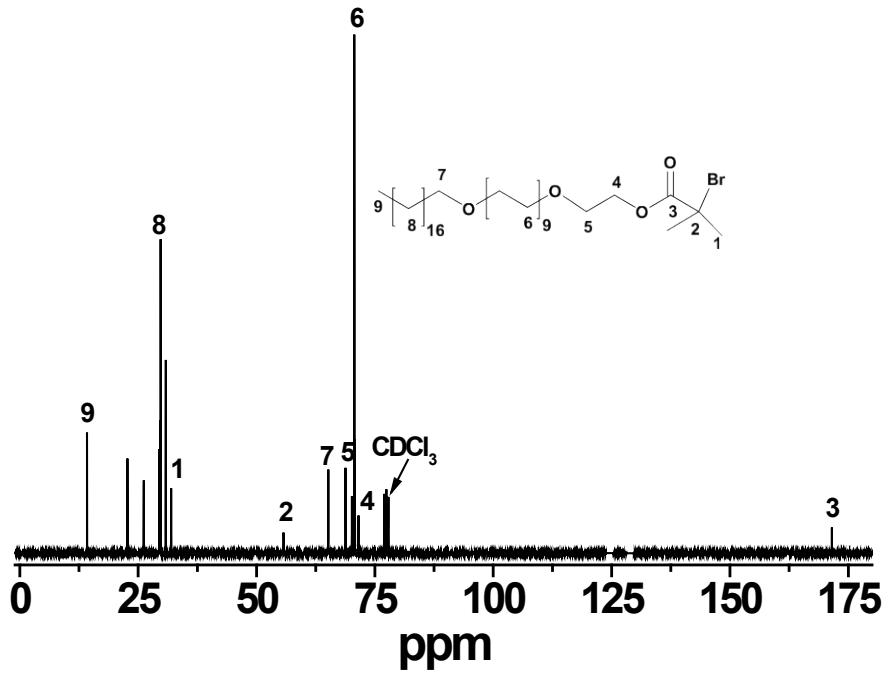

Figure S5 ^{13}C NMR spectrum of C_{18}-PEG_{10}-Br in $CDCl_3$

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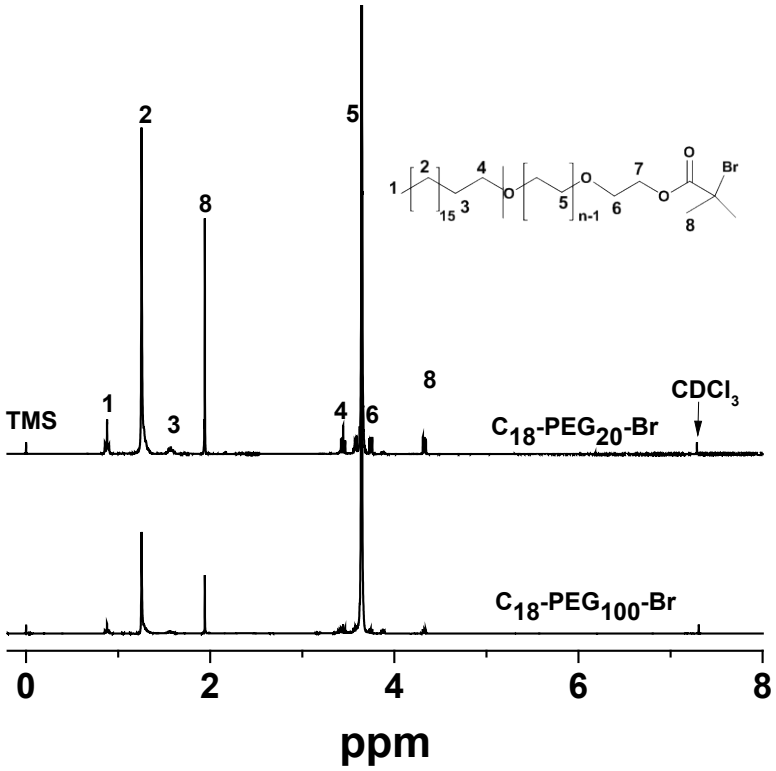

Figure S6 ^{1}H NMR spectrum of C_{18}-PEG_{20}-Br and C_{18}-PEG_{100}-Br in $CDCl_3$

Poly(ethylene glycol) methyl ether 2-bromoisobutyrate (C_{18}-PEG_{10}-Br)

^{1}H NMR (300MHz, $CDCl_3$): δ = 0.72 (t, 3H, C***H***$_3$-CH_2-), 1.12 (m, 30H, -(C***H***$_2$)$_{15}$-), 1.43 (m, 2H, $CH_3(CH_2)_{15}C$***H***$_2CH_2O$-), 1.8 (s, -COC(C***H***$_3$)$_2$ Br), 3.3 (m, 2H, $CH_3(CH_2)_{16}C$***H***$_2O$-), 3.50 (m, 36H, -O-(C***H***$_2$C***H***$_2$)$_9$-O-CH_2CH_2O-), 3.58 (m, 2H, -O-$(CH_2CH_2)_9$-O-C***H***$_2CH_2O$-, 4.16 (m, 2H, -O-$(CH_2CH_2)_9$-O-CH_2C***H***$_2O$-);

^{13}C NMR (75MHz, $CDCl_3$): δ = 171 (***C***=O), 71-66 (-O-(***C***H_2***C***$H_2)_n$-O), 65(-O***C***$H_2(CH_2)_{16}CH_3$), 56(-***C***$(CH_3)_2$ Br), 32(-C(***C***$H_3)_2$Br), 22-30(-OCH_2(***C***$H_2)_{16}CH_3$), 14 (-$O(CH_2)_{17}$***C***H_3).

Poly(ethylene glycol) methyl ether 2-bromoisobutyrate (C_{18}-PEG_{20}-Br):

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^{1}H NMR (300MHz, $CDCl_3$): δ = 0.88 (t, 3H, C***H***$_3$-CH_2-), 1.26 (m, 30H, -(C***H***$_2$)$_{15}$-), 1.57 (m, 2H, $CH_3(CH_2)_{15}C$***H***$_2CH_2O$-), 1.94(s, -COC(C***H***$_3$)$_2$ Br), 3.42 (m, 2H, $CH_3(CH_2)_{16}C$***H***$_2$O-), 3.57 (m, 76H, -O-(C***H***$_2$C***H***$_2$)$_{19}$-O-CH_2CH_2O-), 3.72 (m, 2H, -O-$(CH_2CH_2)_{19}$-O-C***H***$_2CH_2$O-, 4.34 (m, 2H, -O-$(CH_2CH_2)_{19}$-O-CH_2C***H***$_2$O-);

^{13}C NMR (75MHz, $CDCl_3$): δ = 172 (***C***=O), 72-69 (-O-(***C***H_2***C***H_2)$_n$-O), 65(-O***C***$H_2(CH_2)_{16}CH_3$), 56(-***C***$(CH_3)_2$Br), 32(-C(***C***$H_3)_2$Br), 23-31(-OCH_2(***C***$H_2)_{16}CH_3$), 14 (-$O(CH_2)_{17}$***C***H_3).

Poly(ethylene glycol) methyl ether 2-bromoisobutyrate (C$_{18}$-PEG$_{100}$-Br):

^{1}H NMR (300MHz, $CDCl_3$): δ = 0.88 (t, 3H, C***H***$_3$-CH_2-), 1.27 (m, 30H, -(C***H***$_2$)$_{15}$-), 1.58 (m, 2H, $CH_3(CH_2)_{15}C$***H***$_2CH_2$O-), 1.95 (s, -COC(C***H***$_3$)$_2$ Br), 3.44 (m, 2H, $CH_3(CH_2)_{16}C$***H***$_2$O-), 3.58 (m, 396H, -O-(C***H***$_2$C***H***$_2$)$_{99}$-O-CH_2CH_2O-), 3.73 (m, 2H, -O-$(CH_2CH_2)_{99}$-O-C***H***$_2CH_2$O-, 4.34 (m, 2H, -O-$(CH_2CH_2)_{99}$-O-CH_2C***H***$_2$O-);

^{13}C NMR (75MHz, $CDCl_3$): δ = 172 (***C***=O), 71-66 (-O-(***C***H_2***C***H_2)$_n$-O), 65(-O***C***$H_2(CH_2)_{16}CH_3$), 56 (-***C***$(CH_3)_2$Br), 32(-C(***C***$H_3)_2$Br), 22-30(-OCH_2(***C***$H_2)_{16}CH_3$), 14 (-$O(CH_2)_{17}$***C***H_3).

The numbers of repeating units of the ethylene glycol (EG) in the PEG polymers were recalculated according to their proton NMR spectra of the fully esterification products, based on a simple formula: n = ($3I_a/2I_b$), where I_a is the corresponding integral area of the methenyl group of EG (-O-C***H***$_2$C***H***$_2$-) at 3.7 ppm and I_b is the integral area of the end-capped methyl group (-C(C***H***$_3)_2$Br, 6H) at 1.9 ppm. The number of repeating units of EG were estimated to be 10 for Brij®S10, 20 for Brij®S20 and 100 for Brij®S100, and they are designated C_{18}-PEG_{10}, C_{18}-PEG_{20} and C_{18}-PEG_{100}, respectively. [2,3]

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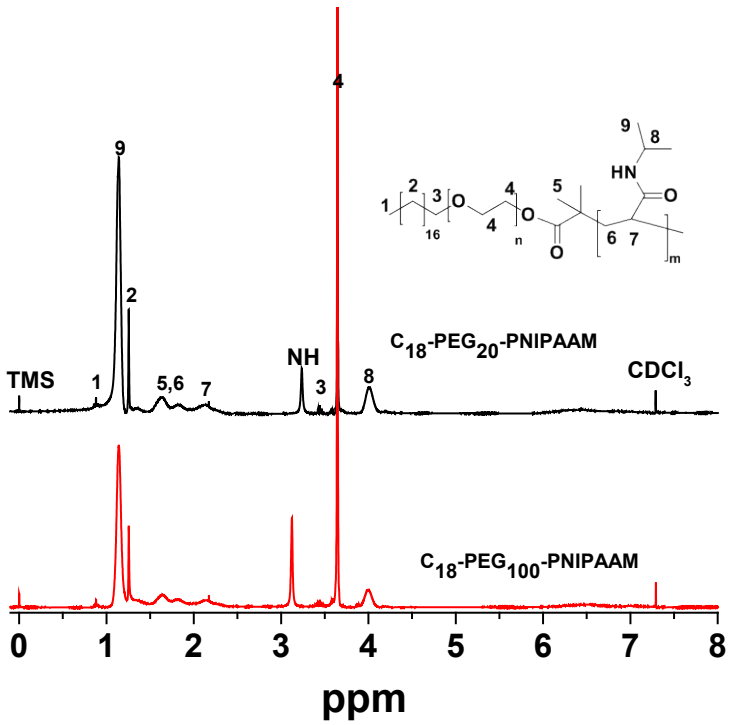

Figure S7 ^{1}H NMR spectrum of C_{18}-PEG_{20}-PNIPAAM and C_{18}-PEG_{100}-PNIPAAM in $CDCl_3$

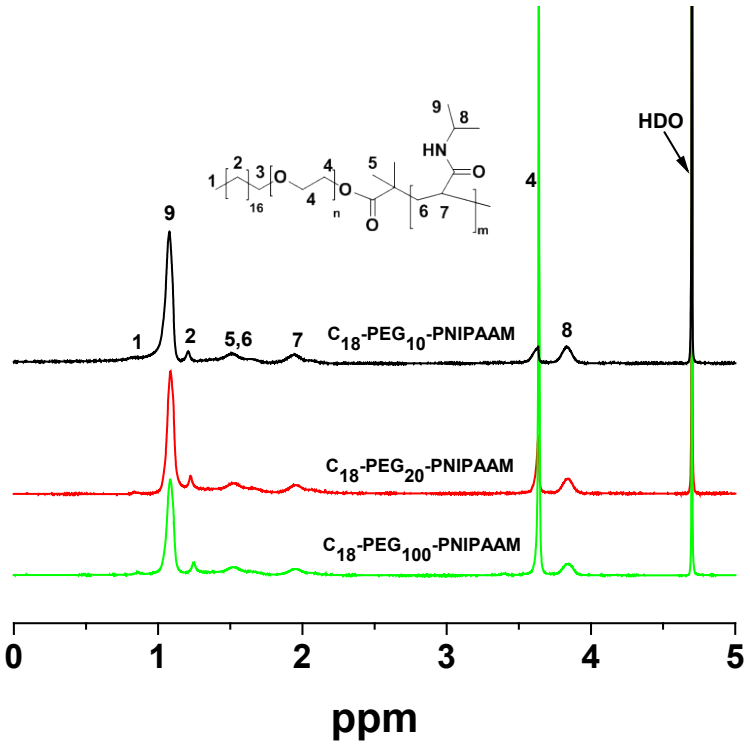

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Figure S8 ^{1}H NMR spectra of C_{18}-PEG_{10}-PNIPAAM, C_{18}-PEG_{20}-PNIPAAM and C_{18}-PEG_{100}-PNIPAAM in D_2O (25^{o}C)

References:

1 S. Liu and S. P. Armes, *J. Am. Chem. Soc.,* 2001, **123**, 9910.

2 N. Beheshti, K. Zhu, A.-L. Kjøniksen, K. D. Knudsen, and B. Nyström, *Soft Matter,* 2011, **7**, 8111.

3 W. Wang, H. Mauroy, K. Zhu, K. D. Knudsen, A.-L. Kjøniksen, B. Nyström and S. A. Sande, *Soft Matter,* 2012, **8**, 11514