<u>Supporting Information</u>

The formation of colloidally-stable phase separated poly(N-vinylcaprolactam) in water: a study by dynamic light scattering, microcalorimetry, and pressure perturbation calorimetry.

Antti Laukkanen,[a] Lauri Valtola,[a] Françoise M. Winnik,[b] and Heikki Tenhu[a]*

[a] Laboratory of Polymer Chemistry, PB 55 University of Helsinki, Helsinki FIN-00014 HY Finland;
[b]Department de Chemistry and Faculty of Pharmacy, University of Montreal, CP 6128 succursale Centre-Ville Montreal QC Canada H3C 3J7
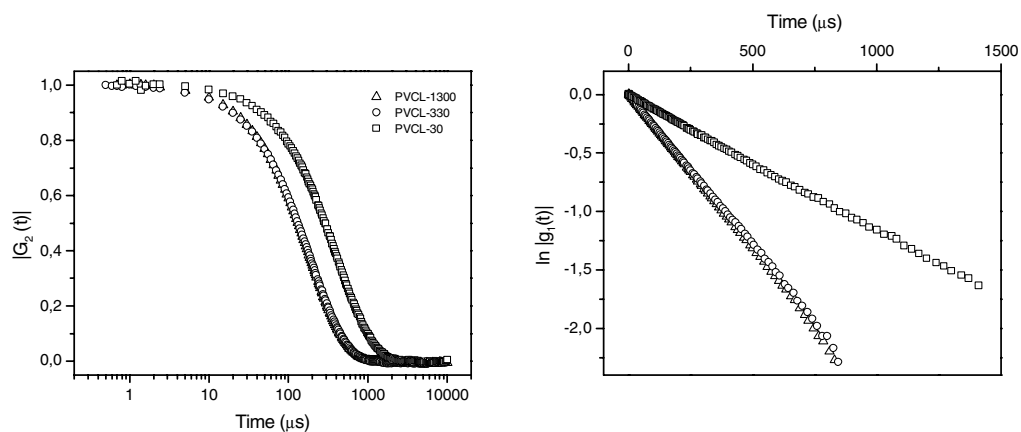
Figure S-1. (Left) Normalised time autocorrelation functions, $|G_2(t)|$, of the scattered light intensity for different PVCL aggregates. (Right) Corresponding correlation functions of the scattered electric field, $\ln |g_1(t)|$ *vs.* t. Nearly single exponential behavior is an indication of low polydispersity.
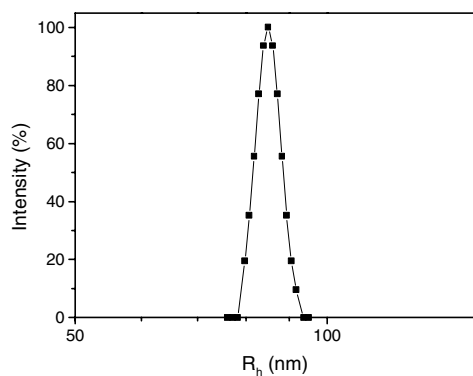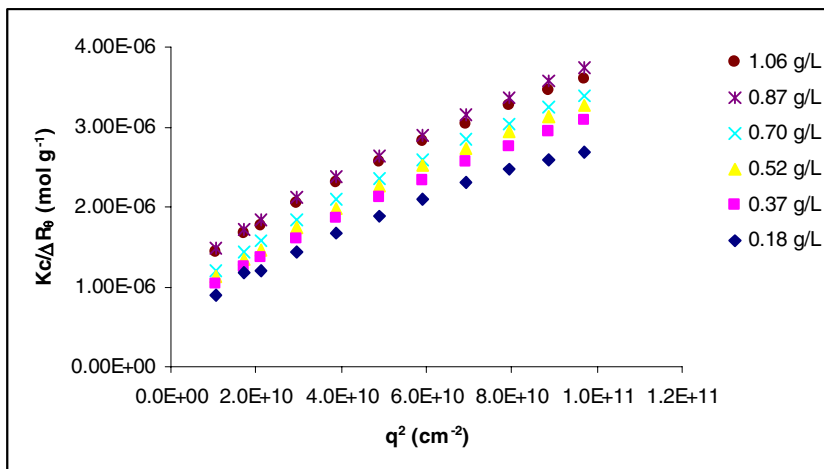

Figure S-2. Typical size distribution an aggregate particle calculated by the Inverse Laplace Transformation program CONTIN. The sample is 0.1 g/L aqueous solution of PVCL-1300 at 50 °C. The distribution is measured at the scattering angle of 90 °.
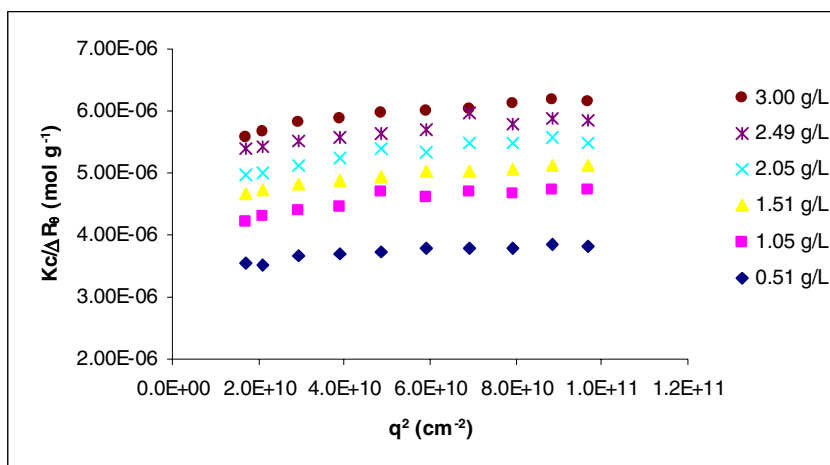
Molecular Weight for conc. → 0: 1.53e+06 g/mol ± 10.1 %
Molecular Weight for angle. → 0: 1.53e+06 g/mol ± 8.7 %
Relative difference of Molecular Weights = 1.63e-05 %
Radius of Gyration = 98.4 ± 6.3
Second Virial Coefficient = 3.01e-04 ± 4.78e-05 cm^3 mol/g^2

Figure S-3. Kc/ΔR_Θ for PVCL-1500 in THF.
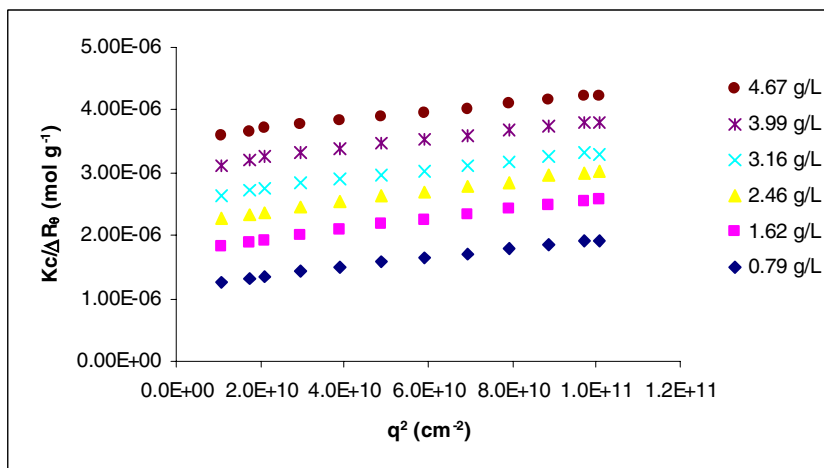
Molecular Weight for conc. → 0: 1.31e+06 g/mol ± 4.2 %
Molecular Weight for angle. → 0: 1.31e+06 g/mol ± 1.1 %
Relative difference of Molecular Weights = 1.81e-04 %
Radius of Gyration = 56.0 ± 6.3
Second Virial Coefficient = 2.94e-04 ± 5.20e-06 cm^3 mol/g^2

Figure S-4. Kc/ΔR_Θ for PVCL-1300 in THF.

Molecular Weight for conc. $\rightarrow$ 0: 3.30e+05 g/mol ± 4.6 %
Molecular Weight for angle. $\rightarrow$ 0: 3.31e+05 g/mol ± 3.5 %
Relative difference of Molecular Weights = 0.1 %
Radius of Gyration = 27.6 ± 3.8
Second Virial Coefficient = 4.00e-04 ± 3.53e-05 cm^3 mol/g^2

Figure S-5. Kc/ΔR_Θ for PVCL-330 in THF.