ELECTRONIC SUPPLEMENTARY INFORMATION FOR THE MANUSCRIPT

Reappearance of Slow Mode in Mixtures of Polyethylene Glycol and Poly(sodium methacrylate)

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The normalized intensity correlation functions, $G_2(t)$, measured at an angle of 90° for a 2.5 g/L NaPMA solution in 0.2 M NaCl clearly show the biexponential character when the concentration of PEG1500 increases (Figure S1).

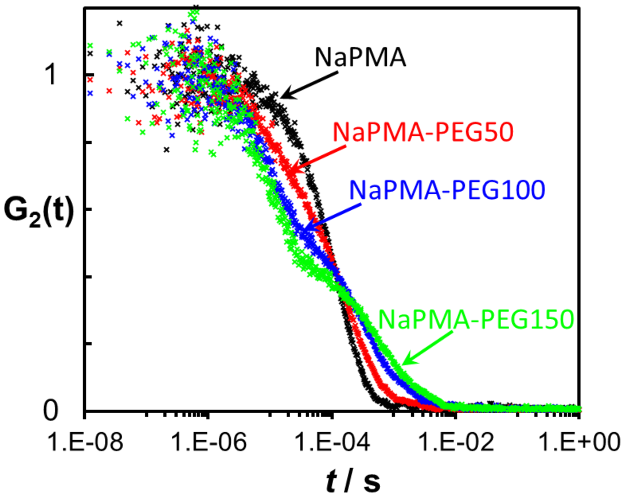

Figure S1. The normalized correlation functions of the scattered light intensity, $G_2(t)$, measured at θ = 90° for pure NaPMA solutions (black) and for NaPMA-PEG1500 solutions with increasing concentration of PEG, c_{PEG} (= 50, 100, and 150 g/L; sample designation: NaPMA-PEG50 (red), NaPMA-PEG100 (blue), and NaPMA-PEG150 (green), respectively); solvent: 0.2 M NaCl; T = 25°C.

Figure S2 shows the angular dependency of the hydrodynamic radii, $R_{\mathrm{h,PMA}}$, and the decay rates, Γ_{f}, of single NaPMA coils in NaPMA-0.2 M NaCl-PEG solutions without added PEG and for the lowest concentration of PEG (c_{PEG} = 50 g/L) for both PEG samples (M_{w} = 1500 and 3000 g/mol). This is so called fast decay mode (see manuscript). The Γ_{f} vs. q^2 curves are linear. Some deviation from linearity is detected only in PEG3000 solutions. This observation is related to rather monodisperse character of NaPMA coils and is expected because NaPMA sample with a low PDI was used for measurements.

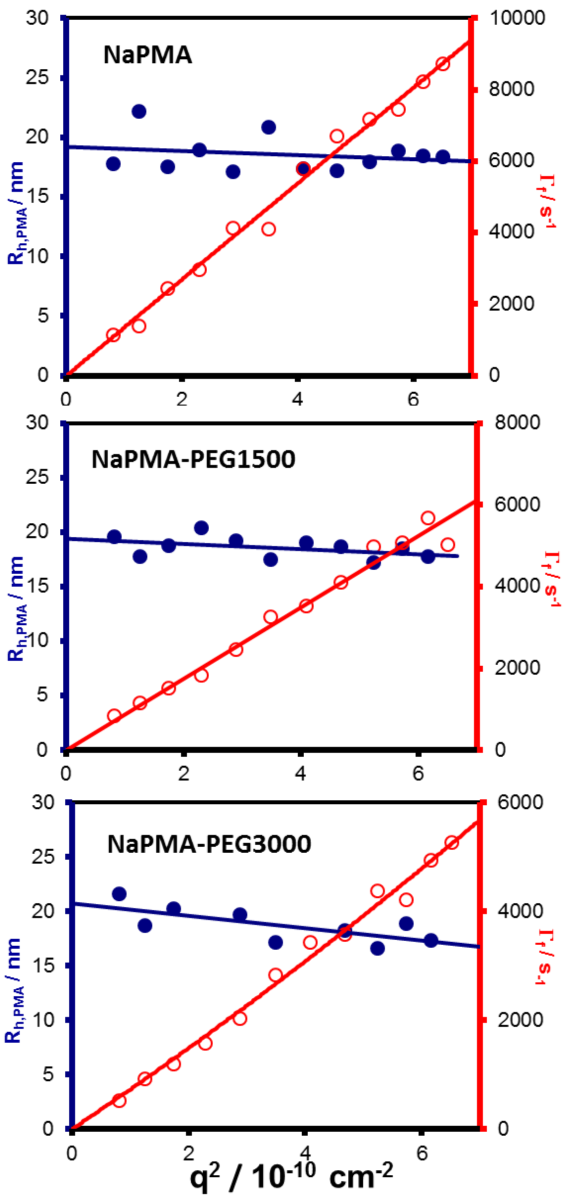

Figure S2. Hydrodynamic radius, $R_{h,PMA}$, and the fast decay rate, Γ_f ($= \tau^{-1}$), as a function of the square of the scattering vector, q^2, for NaPMA coils in NaPMA solutions without and with added PEG: c_{NaCl} = 0.2 M, c_{PEG} = 50 g/L, T = 25°C. These data apply to peak 2 in the τ-distributions (for details see manuscript).

Figure S3 shows the angular dependency of similar data as in Figure S2, but obtained for the polyelectrolyte slow mode: the apparent hydrodynamic radius, R_h^{app}, and the slow mode decay rates, Γ_s, in NaPMAPEG solutions with added PEG. Pure NaPMA in 0.2 M NaCl (no PEG!) is not shown because in the polyelectrolyte slow mode was not detected in this case. The Γ_s curves in PEG solutions clearly do not start from the center of coordinates and exhibit rather irregular dependence on q^2. For a purely diffusive process these curves should start from $\Gamma_s = 0$ and follow a relationship $\Gamma \propto q^2$.

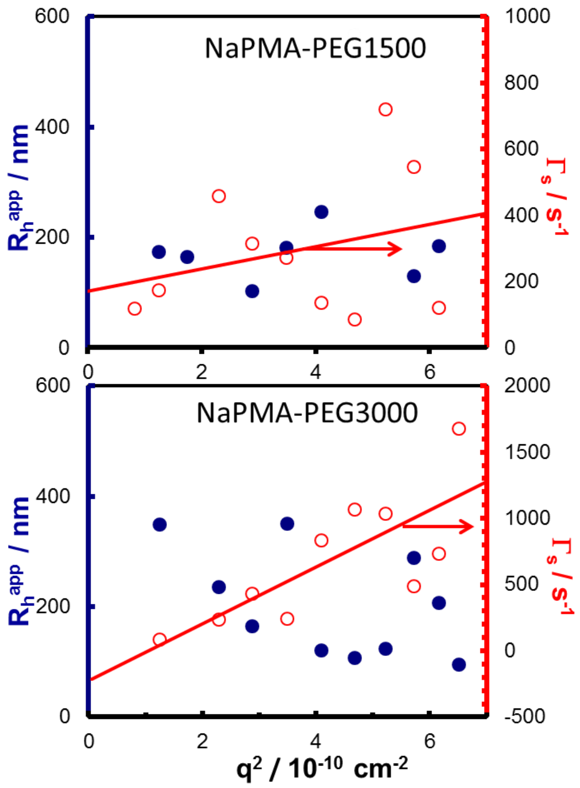

Figure S3. Apparent hydrodynamic radius, R_h^{app}, and the polyelectrolyte slow decay rate, Γ_s (= τ^{-1}), as a function of the square of the scattering vector, q^2, in NaPMA solutions with added PEG: c_{NaCl} = 0.2 M, c_{PEG} = 50 g/L, T = 25°C. These data apply to peak 3 in the τ-distributions that was observed only in the presence of PEG (for details see manuscript).

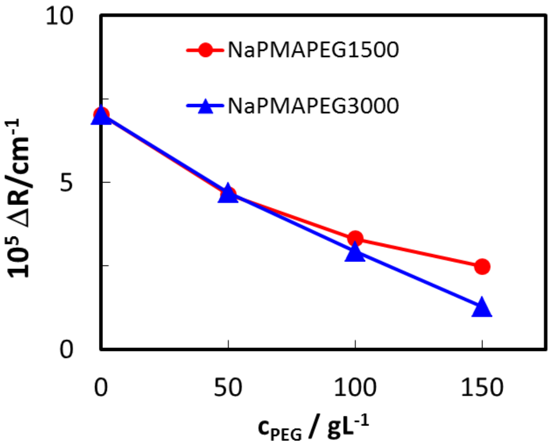

Figure S4. The absolute scattering intensity, ΔR, for NaPMA coils in aqueous NaPMA-PEG-0.2 M NaCl solutions as a function of c_{PEG}: c_p = 2.5 g/L, T = 25°C, θ = 90°; M_w(PEG) = 1500 (PEG1500) and 3000 (PEG3000) g/mol.

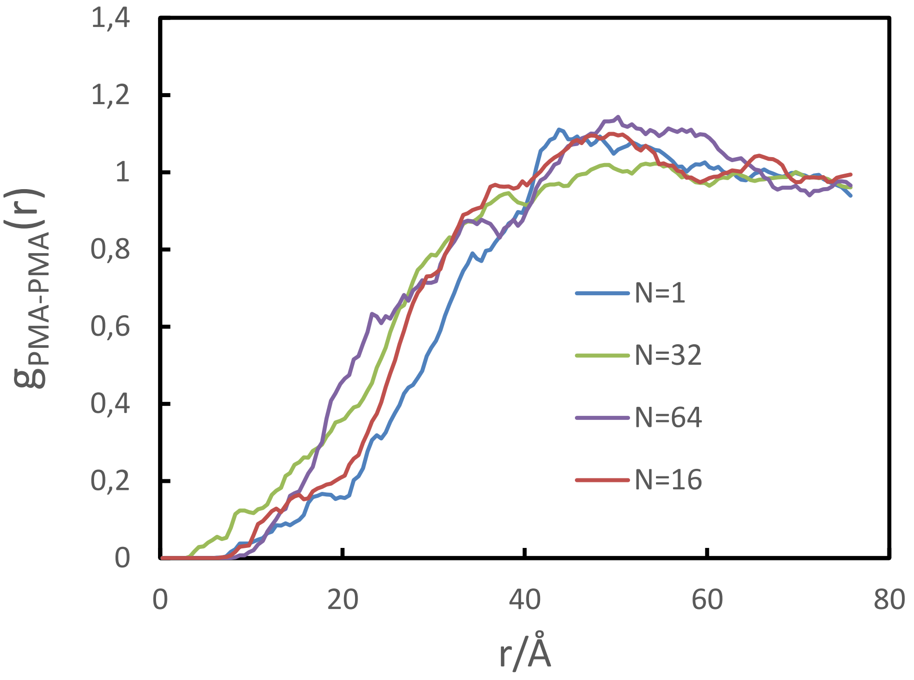

Figure S5. PMA-PMA radial distribution functions at volume fraction of PEG 0.25 for different PEG chain length. N=1 represent free PEG monomers.

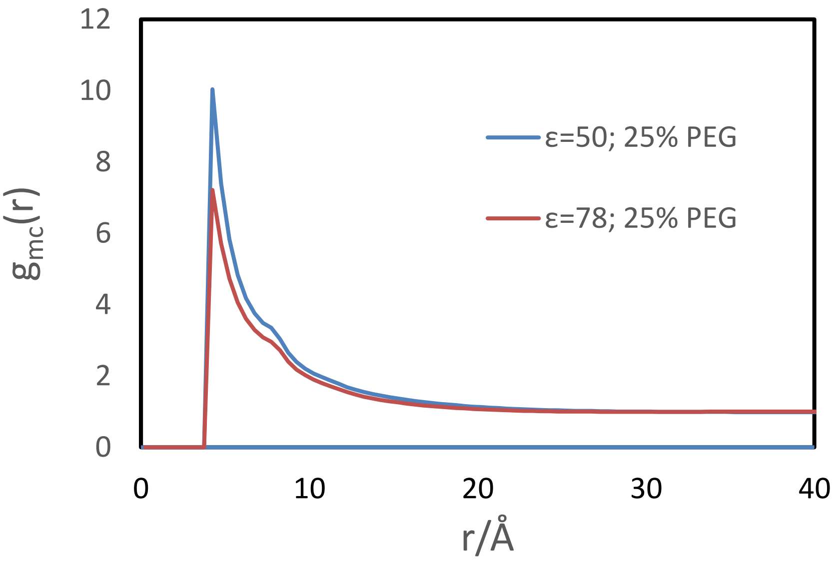

Figure S6. PMA monomer unit - counterion radial distribution functions at volume fraction of PEG 0.25 for two different values of dielectric constant of the solution.

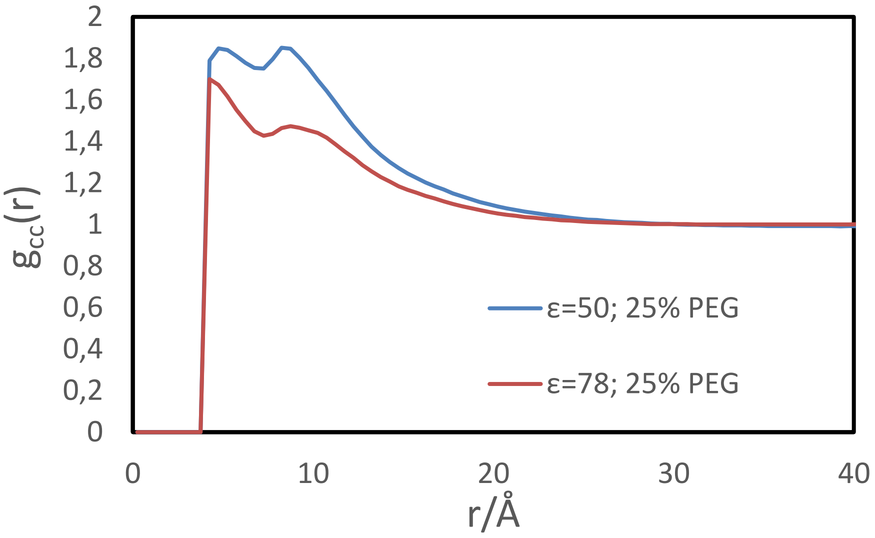

Figure S7. Counterion - counterion radial distribution functions at volume fraction of PEG 0.25 for two different values of dielectric constant of the solution. Smaller dielectric constant enhances ion-ion correlations.