Supporting Information

Stimuli-responsive Amphiphilic Polyelectrolyte Heptablock Copolymer Physical Hydrogels: An Unusual pH-response

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Since the present heptablock copolymer system exhibits a yield stress above 3 wt%, the modified Cox-Merz model, combining elastic, viscous and yielding phenomena was used to correlate the steady shear and the complex viscosities. Figure S1 shows that above 0.002 rad s^{-1}, the $\eta^*(\omega)$ and $\eta(\gamma)$ curves nearly superimpose, satisfying the modified Cox-Merz rule. [1,2] In the region below 0.002 rad s^{-1}, a strong deviation from the model is observed which could be ascribed to artifacts of the flow measurement at this shear rate region. Thus, data below this shear rate are not reliable. Note that in time sweep flow experiments at stresses below that corresponding to 0.002 s^{-1} (yield stress) cannot generate any flow.

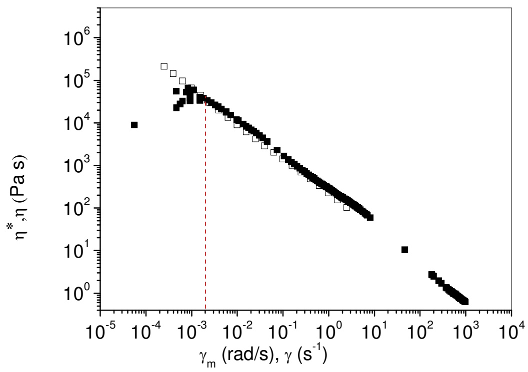

Figure S1. Dynamic and steady-state viscosities, $\eta^*(\omega)$ (□) and $\eta(\gamma)$ (■), as a function of γ_m and γ, respectively. Copolymer concentration was 3.5wt% and pH 6.

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In Figure S2, the dynamic viscosity is plotted as a function of frequency for various heptablock copolymer concentrations above 3 wt%. Since at this high concentration range

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there is no Newtonian plateau, η^* values were obtained at the lowest frequency (0.01 Hz) and plotted as a function of concentration in a double-logarithmic scale (Inset). The dynamic viscosity shows an increase until 4 wt%, followed by stabilization at higher polymer concentrations.

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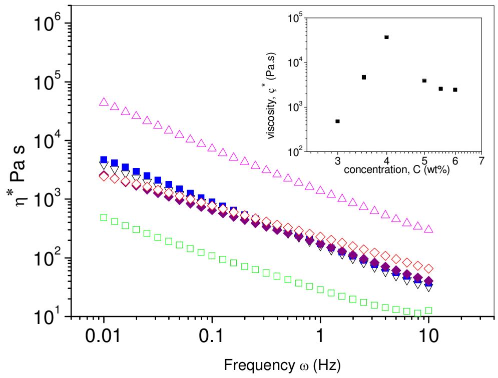

Figure S2. Dynamic viscosity η^* as a function of frequency for various polymer concentrations: 3 wt% (□), 3.5 wt% (■), 4 wt% (△), 5wt% (▽), 5.5 wt% (◆), 6 wt% (◇). Inset: Double-logarithmic plot of η^* (at 0.01 Hz) as a function of polymer concentration.

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Effect of pH on the rheological properties

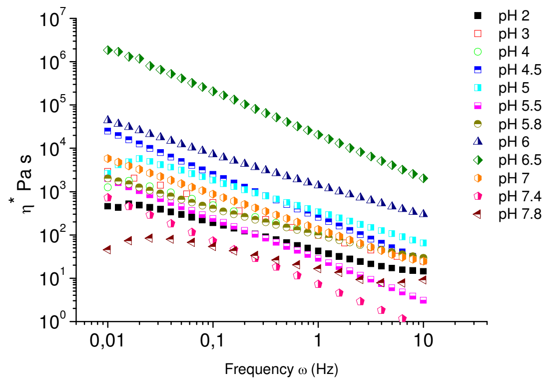

Figure S3. Dynamic viscosity η^* as a function of frequency (ω) for a 4 wt% heptablock copolymer concentration at different pH values.

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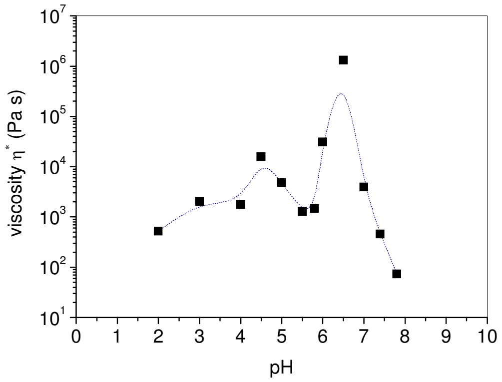

Figure S4. Dynamic viscosity $\eta^*(\omega)$ determined at the same lowest frequency of 0.01 Hz (from Figure S3) as a function of pH for a 4 wt% heptablock copolymer concentration.

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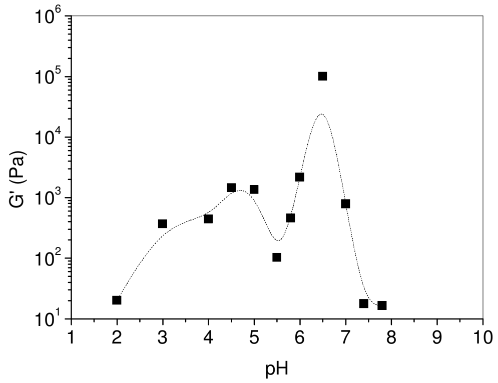

Figure S5. Elastic modulus (G', Pa) from strain sweep experiments in the linear viscoelastic regime, as a function of pH for a 4 wt% heptablock copolymer aqueous solution.

(1) Doraiswamy, D.; Mujumdar, A. N.; Tsao, I.; Beris, A. N.; Danforth, S. C.; Metzner, A. B. *J. Rheol.* **1991**, *35*, 647.

(2) Cox, W. P.; Merz, E. H. *J. Polym. Sci.* **1958**, *28*, 619.