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SUPPORTING INFORMATION

Electrospinning Polyelectrolytes Complex: pH Responsive Fibers

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Methods

Rheology

Discovery DHR-2 rotational rheometer (TA Instruments, USA) was used for investigation of rheological properties of the solutions under steady-state shear deformation. Cone-plate geometry with diameter of 40 mm and the angle at cone tip of 1° was applied. All tests have been carried out at 23 °C.

HRSEM and cryo-HRSEM

A single fiber was collected onto a specially designed SEM sample holder comprising a conducting trench and was adhered to the sides of the trench. In order to compare between the dry and the swollen state of the fibers, we performed RT HR-SEM imaging prior to cryo HR-SEM imaging. For cryo-SEM specimen preparation, as spun fibers were immersed into water at pre-determined pH. After 3 min of swelling, the water excess was removed with a filter paper, and the sample was quenched into liquid ethane at its freezing temperature. After vitrification the sample holder was mounted onto a sample-table for cryo-HR-SEM imaging (Leica AG. Liechtenstein), and was transferred in a pre-cooled BalTec VCT-l00 shuttle to a BAF060 system (Leica AG. Liechtenstein), pumped to 5x10-7 mBar, and cooled with liquid nitrogen to -170 °C. To expose the fiber surface we etched the cryo-specimen inside BAF060 by warming the specimen stage to -80 °C for 30 minutes, following cooling back to -170 °C. The cryo-specimen was transferred into a Zeiss Ultra Plus HR-SEM by pumped and pre-cooled BalTec VCT-l00 shuttle. The microscope is equipped with a cold-stage (part of the Leica VCT-100 system) maintained at -145 °C. After imaging, the sample was left to reheat to room temperature to further analysis.

Rheological measurements

Figure S1 presents flow curves of PAA/PAH, a polycation PAH and polyanion PAA solutions, all in the same concentration in 40:60 ethanol/water. The PAA solution demonstrates a pseudoplastic behavior. Transition from Newtonian flow with constant viscosity, to pronounced shear thinning occurred at moderately high shear stresses, τ>20Pa, which is typical for semidiluted entangled and concentrated polymer solutions. In contrast, the viscosity of PAH solution was almost constant throughout the entire range of shear stresses applied. Only a very mild decrease in viscosity was detected at high τ, implying that the solution can be considered unentangled. In addition, orientational effects may lie at the basis of the weak shear thinning. PAH solution viscosity was nearly 60 times lower than that of the PAA solution of the same concentration.

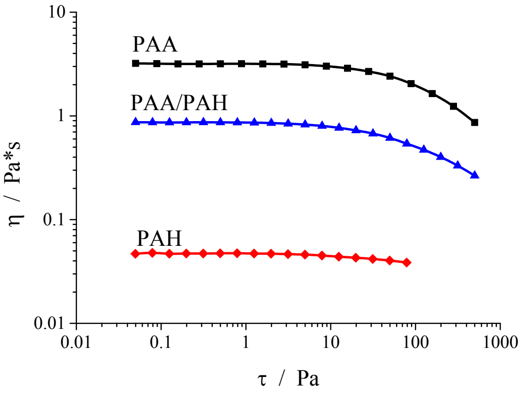

Figure S1: Flow curves of 10.3% PAA, PAH and PAA/PAH solutions at 23° C.

The PEC solution (PAA/ PAH) demonstrated a pseudoplastic behavior with a viscosity between the viscosities measured for the individual solutions. The solution became more resistant to high shear stresses leading to reduced shear thinning. The slope of the PEC flow curve at high shear stresses ($\tau > 50$ Pa) was 0.42 s, a decrease from the 0.56 s measured for PAA. According to the log-additivity rule[1] the viscosity of the PEC solution is ~0.3 Pa·s. However, the measured viscosity of the PEC solution was 0.86 Pa·s, namely, 2.7 times higher than expected. Thus, the solution behavior is determined not only by the presence of the entanglement network formed by PAA macromolecules. Specific interactions between polyanions and polycations enable formation of supplementary networks composed of PEC sites resulting in a non-additive increase in the viscosity of the system.[2]

Electrospinning of a 1:1 (by repeating unit) PAA/PAH solution proved successful upon addition of ethanol to the water solvent. In order to evaluate the optimal water/ethanol ratio, 10.3% PEC solutions in water/ethanol mixtures, with component ratios ranging from 100:0 (pure water) up to 40:60, were investigated (see Figure S2).

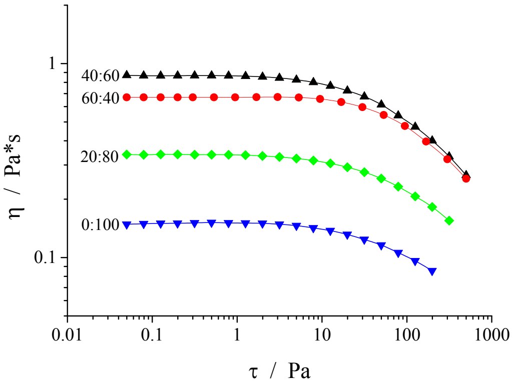

Figure S2: Flow curves of 10.3% PAA/PAH solutions in an ethanol/water solvent prepared at different ratios, at 23º C.

All solutions exhibited pseudoplastic behavior. Shear viscosity was constant at low stresses and shear thinning was observed at high stresses, behavior which is typical for most semidiluted and concentrated polymer solutions. Viscosity increased with ethanol content up to 40% and then decreased for solutions containing 60% alcohol. A solution of 40% ethanol demonstrated an approximate 6-fold increase in viscosity versus the ethanol-free solution. It should be mentioned that shear thinning began at similar shear stresses ($\tau \approx 5$ Pa) for solutions with ethanol content up to 40%. This value was slightly higher ($\tau \sim 10$ Pa) for solution with 60% alcohol implying a minor enhancement of the strength of the entanglement network formed in this solution.

The water/ethanol mixture is a well characterized system. Specifically, it was established that viscosity and activation energy of viscous flow are extreme functions of alcohol content and reach their maximum at 60:40 water/ethanol composition.[3,4] Relative viscosity $\eta_r = \eta_0/\eta_s$ (where η_0 is zero-shear rate viscosity of solution and η_s is the viscosity of pure solvent) is a useful measure to evaluate the contribution of the structure formed by polymer chains to the total viscosity of the solutions. Figure S3 shows the relative viscosity of the PAA/PAH solutions at different ethanol/water ratios. Viscosities of solvents were obtained by recalculation of data previously reported.[3]

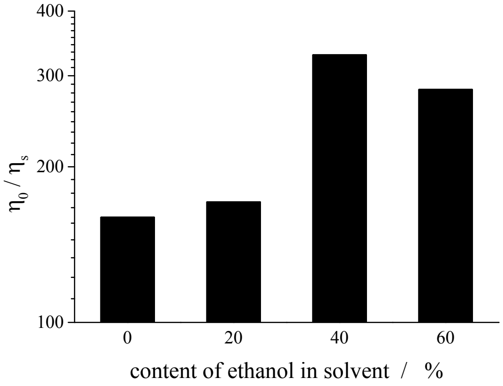

Figure S3: Relative viscosity of PAA/PAH solutions at 23° C.

As shown, the relative viscosity increased with increasing ethanol content up to 40%, but decreased with a 60% ethanol content. For 40% ethanol, relative viscosity was two-fold higher than that measured for PAA/PAH in pure water and roughly 20% higher than the η_r value for solutions containing 60% of ethanol.

1. L. A. Utracki and M. R. Kamal, "Ch. 7 The Rheology of Polymer Alloys and Blends," in *Polymer Blend Handbook, Vol 1-2*, Dordrecht, Netherlands, Kluwer Academic Publishers, 2002, pp. 449-546.
2. Dreval', V. E.; Vasil'ev, G. B.; Litmanovich, E. A.; Kulichikhin, V. G. *Polym. Sci. Ser. A* **2008,** 50, (7), 751-756.
3. Wroth, B. B.; Reid, E. E. *Journal of the American Chemical Society* **1916,** 38, (11), 2316-2325.
4. *Handbook of Chemistry and Physics (Ed.* Weast, R. C.). Chemical Rubber Corporation: Cleveland, OH, 1977.