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Physical Hydrogels via Charge Driven Self-Organization of a Triblock Polyampholyte – Rheological and Structural Investigations

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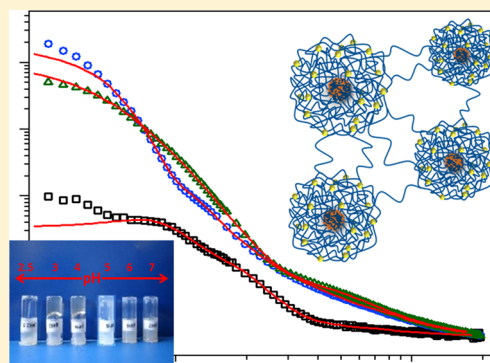
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ABSTRACT: We investigate the conformational properties of stimuli-responsive hydrogels from triblock polyelectrolytes PtBA-*b*-P2VP-*b*-PtBA (PtBA and P2VP are poly(*tert*-butyl acrylate) and poly(2-vinylpyridine)) and the corresponding polyampholytes PAA-*b*-P2VP-*b*-PAA (PAA is poly(acrylic acid)), the latter with nonquaternized or quaternized P2VP blocks. The block lengths are the same in all three polymers with relatively short end blocks and long middle blocks. The mechanical properties of the hydrogels have previously been found to depend strongly on the pH value and on the nature of the blocks (*Polymer* 2008, 49, 1249). Here, we present results from rheological studies and small-angle neutron scattering revealing the underlying hydrogel structures. The hydrogel structure of the polyampholyte depends on the charge asymmetry, controlled by the pH value, and reveals several transitions with increasing charge ratio. A low charge asymmetry causes the collapse of the chains into large globular structures due to the fluctuation-induced attractions between oppositely charged moieties. In contrast, at higher charge asymmetry, a network is formed. The latter is also found for the polyelectrolyte system. These results demonstrate the origin of the strong changes in mechanical properties upon change of pH.



INTRODUCTION

Significant progress has been made in the past decade in the field of reversible hydrogels, due to macromolecular engineering that permits design of segmented macromolecules with tunable molecular characteristics (i.e., chain length of low polydispersity, block topology, hydrophobic/hydrophilic balance, and specific functionality). These block copolymers and/or terpolymers can self-assemble in specific environments, forming hydrogels with tunable properties, such as injectability and responsiveness (i.e., precise sol-to-gel transitions triggered by one or more stimuli); mesh size and mechanical strength.^{1–15} The driving force of the self-organization of the macromolecular building blocks toward a 3D transient network are the various intermolecular interactions, namely hydrophobic and H-bonding as well as electrostatic interactions that can be developed among the specific functional groups carried by the macromolecular chains. We should notice here that the electrostatic interactions involve two contributions: Coulombic attraction and entropy gain through counterion release, which is an entropy driven process.

Most of the studies have been devoted to copolymers, carrying short hydrophobic blocks (stickers) either as pendant chains along a central hydrophilic long chain (graft type)^{16–26}

or as end-capped blocks (telechelic type)^{27,28} which accordingly self-associate through hydrophobic interactions in aqueous media. In recent years, charge-driven association of triblock copolymers that leads to the formation of transient networks has also been developed.^{29,30} In such systems, electrostatic attractions between oppositely charged moieties, located in the macromolecules, form the so-called interpolyelectrolyte complexes (IPEC)^{31,32} that constitute the temporary cross-links of the network. As the resulting complexes are electroneutral and thus precipitate out of aqueous solution, the strategy toward hydrogel formation (also adopted here) was to use asymmetric double hydrophilic ABA triblock copolymers so as to prevent phase separation. Two different systems have appeared so far which are based on self-organization^{29,33–36} or on co-organization.^{37–40} In the latter case, two macromolecules different in nature are needed to participate in the system.

In the first report, dealing with a hydrogel resulting from charge-driven association, a highly asymmetric block polyampholyte of the type PAA-*b*-P2VP-*b*-PAA was used (PAA

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Table 1. Molecular Characteristics of PAA-*b*-P2VP-*b*-PAA

polymer	M_w^a g/mol	M_w/M_n^b	P2VP ^c (wt %)	P2VP DP _w	PtBA/PAA (wt %)	PtBA/PAA DP _w
P2VP	147000	1.29		1397		
PtBA- <i>b</i> -P2VP- <i>b</i> -PtBA	192000	1.31	76.6	1397	23.4	175
PAA- <i>b</i> -P2VP- <i>b</i> -PAA	173000		85.0	1397	15.0 ^d	175 ^d

^aBy SLS. ^bBy SEC. ^cBy ¹H NMR. ^dA few PtBA units remained after the hydrolysis reaction. DP_w: degree of polymerization.

stands for poly(acrylic acid) and P2VP for poly(2-vinylpyridine)).²⁹ This polymer exhibits pH-responsive self-organization behavior due to protonation–deprotonation equilibrium of both PAA and P2VP blocks. In the isoelectric point (iep) region $4 < \text{pH} < 7$, phase separation occurred due to strong electrostatic interactions between the protonated 2VP repeating units and the deprotonated AA units, as well as the increasing hydrophobicity of the P2VP major component above pH 5. Beyond this region, at $\text{pH} < 4$ and $\text{pH} > 7$, homogeneous solutions were obtained. In the low pH region, the triblock copolymer behaved as a hydrophilic polyampholyte, forming a stiff hydrogel in the vicinity of the two-phase boundary (pH 3.4). At this particular pH, the formed network was mainly attributed to ionic intermolecular interactions among oppositely charged moieties.^{33–36}

In the case of the hydrogels formed by co-organization, two polymer partners are needed to form a network. Two different types of systems were explored so far. The first consisted of a mixture of double hydrophilic ABA triblock copolymer, having a hydrophilic, neutral and long central B block and two charged A blocks, with an oppositely charged homopolymer C (ABA/C).^{30,37,38} The second one comprises two similar double hydrophilic triblock copolymers with the same central block but oppositely charged (anionic and cationic) end-blocks (ABA/CBC).^{39,40}

In the ABA/C system, the oppositely charged chains, A and C, interact electrostatically and associate into flower like micelles with an IPEC core, stabilized by looped hydrophilic B chains of the triblock copolymer. In the case where the polyelectrolyte complex core was liquid-like, a complex coacervate micellar core was formed.³⁸ At polymer concentrations above the gel concentration, C_{gel} , bridging of micelles occurs, leading to a reversible 3D network. The polyelectrolyte complex micelles which constituted the building elements of the network, were strongly dependent on the charge ratio between the oppositely charged polyelectrolyte blocks.

The other strategy for the formation of charge-driven coacervate hydrogels suggested mixing of ABA with CBC triblock copolymers with oppositely charged anionic A and cationic B blocks in stoichiometric ratio. A common triblock copolymer precursor was designed comprising PEG as central block and identical outer blocks which could be transformed to the oppositely charged partners by a postpolymerization “click” reaction.^{39,40,40} This strategy eliminated any uncertainty in the stoichiometry of the charged end-blocks and the effect that charge asymmetry might have on the resulting properties of the hydrogel.

In the present work, the pH-dependent gelation ability of a triblock copolymer having PAA end blocks and a fully quaternized P2VP middle block, designated as PAA-*b*-QP2VP-*b*-PAA is explored. This polymer differs from its PAA-*b*-P2VP-*b*-PAA precursor, studied previously,³⁵ in that the central block has been modified from a weak to a strong cationic polyelectrolyte, which also prevents the P2VP hydrophobicity above pH 5. Therefore, only the PAA end-

blocks exhibit pH dependent ionization which may facilitate the understanding. Moreover, the corresponding triblock polyelectrolyte precursor PtBA-*b*-P2VP-*b*-PtBA (PtBA stands for poly(*tert*-butyl acrylate)), featuring uncharged, hydrophobic PtBA end-blocks, was investigated. In order to gain deeper insights on the aqueous solution behavior of the quaternized version in comparison to the nonquaternized one, rheological and structural studies with small-angle neutron scattering (SANS) were carried out at various pH conditions.

■ EXPERIMENTAL SECTION

Synthesis. The PAA-*b*-P2VP-*b*-PAA triblock copolymer was synthesized by “living” anionic polymerization using a difunctional initiator and sequential addition of the monomers, 2VP and the protective *tert*-butyl acrylate monomer. The final polymer resulted after deprotection by acidic hydrolysis. Details of the synthetic procedure are reported elsewhere.^{29,35} Quaternization of the central P2VP block was carried out according to the established procedure.⁴¹ Briefly, in a 1 wt % solution of the polymer in dimethylformamide (DMF), methyl iodide was added (10-fold excess MeI with respect to the number of 2VP units). The reaction mixture was kept at 35 °C for 7 days under argon atmosphere. After the reaction termination, the reaction medium was condensed, and the polymer was precipitated in cold ethyl ether. The polymer was redissolved easily in water, and the solution was transferred into a dialysis tube (Visking MWCO 12000), followed by dialysis against water, and was recovered by freeze-drying. The molar fraction of quaternized 2VP units was calculated to 99.5% from the iodine content, determined by titration with silver nitrate, AgNO₃, (Aldrich, 99.9%) (0.1 M) using potassium chromate, K₂CrO₄ (5 wt %) as indicator. The molecular characteristics of the copolymers under investigation are summarized in Table 1.

Size Exclusion Chromatography (SEC). Size exclusion chromatography was performed using PL gel columns of different pore size and an RI detector in order to determine the molecular weight distribution of the precursor P2VP and the PtBA-*b*-P2VP-*b*-PtBA triblock copolymer. The mobile phase was a 1% triethylamine solution in tetrahydrofuran and the flow rate 0.5 mL/min.

Nuclear Magnetic Resonance (NMR). ¹H NMR spectra were measured on a Bruker AC-400 spectrometer using CDCl₃ and the mixture methanol-*d*₆/CDCl₃, as deuterated solvent for the precursor PtBA-*b*-P2VP-*b*-PtBA and the hydrolyzed copolymer PAA-*b*-P2VP-*b*-PAA, respectively. ¹H NMR measurements were carried out in order to determine the percentage of the different species that constitute the copolymer as well as the degree of hydrolysis of the final product and the exact molar mass of both samples. The M_w of the P2VP central block (precursor) was determined by static light scattering.

Sample preparation. Dissolution was performed at room temperature (20–25 °C). Gel homogenization was achieved mechanically by rigorous stirring and centrifugation. For all samples tested, the pH was adjusted by adding 0.1 M HCl or 0.1 M NaOH. Afterward, the samples were stirred and centrifuged once more.

Rheometry. The linear and nonlinear rheological experiments were performed using a stress-controlled Rheometrics Scientific SR200 rheometer, equipped with either a cone-and-plate geometry (diameter 25 mm, cone angle 5.7°, truncation 56 μm), or a Couette geometry (gap 1.1 mm) for the less viscous solutions. All steady state viscosities were determined as limits of the transient viscosities following the criterion that the time evolution of the transient viscosity is lower than 1% during 1 min. After each sample loading, the normal force was monitored, and measurements were only carried out after complete

relaxation of the sample. All rheological experiments were performed at 25 °C.

z-Potential. z-Potential measurements were carried out at 25 °C, using a Zetasizer 5000 (Malvern Instruments Ltd.) equipped with a cell type ZET 5104 (cross beam mode).

Turbidity. Turbidity measurements were carried out at 490 nm, using a UV-2001 Hitachi spectrophotometer, at 25 °C.

Potentiometric Titration. Potentiometric titration was performed using a digital pH-meter 751 GPD Titrino (Metrohm), at 25 °C.

SANS. The polymers were dissolved in D₂O at 4 wt % at room temperature. Dissolution of the quaternized polyampholyte system results in pH 3.4. Appropriate amounts of 0.01 M NaOH solutions in D₂O were added to install pH values of 7.0 and 5.0. The nonquaternized polyampholyte and the triblock polyelectrolyte gels were prepared at pH 3.0. Gel homogenization was achieved by rigorous stirring and centrifugation. Room temperature measurements were carried out at the instrument KWS-2 at the JCNs outstation at MLZ in Garching, Germany. The scattering signal was collected by a 128 × 128 scintillation detector having a pixel size of 0.5 × 0.5 cm². The neutron wavelength was chosen at $\lambda = 0.45$ nm with a spread $\Delta\lambda/\lambda = 20\%$. Using the sample–detector distances (SDDs) of 3.64 and 19.64 m, a range of momentum transfers $q = 0.03$ to 2 nm^{-1} was covered. $q = 4\pi \sin(\theta/2)/\lambda$ and θ is the scattering angle. The samples were mounted in 0.5 mm quartz cuvettes (Hellma). The exposure times were 10 min at SDD = 3.64 and 15 min at SDD = 19.64 m. The scattering of boron carbide was used for correcting the intensities for the dark current. Poly(methyl methacrylate) was used to measure the detector sensitivity and for calibration of the intensity. The scattering of D₂O and the empty cell were subtracted from the sample scattering, taking the transmissions into account. The data were azimuthally averaged. All data reductions were performed with the software QtiKWS provided by JCNs.

Temperature series and room temperature measurements of the quaternized polyampholyte were performed at the instrument D22 at the Institut Laue-Langevin (ILL) in Grenoble, France. The neutron wavelength was chosen at $\lambda = 0.8$ nm with a spread $\Delta\lambda/\lambda = 10\%$. A 128 × 128 ³He tube detector (pixel size 0.8 × 0.8 cm²) was used at SDDs of 3.98 and 13.98 m in order to cover a q range from 0.028 to 2.0 nm^{-1} . The sample having pH 3.0 was mounted in a 0.5 mm quartz cuvette. After setting the temperature to 43 °C, 10 measurements of duration of 120 s were carried out immediately. The sample having pH 5.0 was mounted in a 1 mm quartz glass cuvette. The temperature was set to 37 °C and, subsequently 60 measurements of duration of 15 s were performed. The exposure times were 10 and 15 min at SDD = 3.98 and 13.98 m, respectively. H₂O was used to measure the detector sensitivity and for calibration of the intensity. The dark current was measured using boron carbide. The data were corrected for absorption and background scattering by subtraction of the scattering of D₂O and the empty cell from the sample scattering taking into account the respective transmissions. The two-dimensional images were azimuthally averaged. The software LAMP from ILL was used for the raw data treatment.

SANS Data Analysis. For the SANS curves obtained from PAA₁₆₃-*b*-QP2VP₁₃₉₇-*b*-PAA₁₆₃ at the three pH values, different models were used. At pH 7.0, the charge imbalance is finite, resulting in complexes of the oppositely charged QP2VP and PAA blocks, which were modeled by polydisperse spheres with their radius having a Gaussian distribution:

$$I(q) = \frac{I_0}{V} (\Delta\rho)^2 \langle F^2(q) \rangle + S_{\text{OZ}}(q) + I_{\text{bkg}} \quad (1)$$

Here, I_0 is the scaling factor, V is the averaged particle volume, $\Delta\rho^2 = (\rho_{\text{sph}} - \rho_s)^2$ is the contrast factor and I_{bkg} is the incoherent background intensity. ρ_{sph} and ρ_s stand for the mean scattering length densities (SLD) of the sphere and the solvent, respectively. We used the literature value for the scattering length density of D₂O, $\rho_s = 6.36 \times 10^{-4} \text{ nm}^{-2}$. Using the mass densities 1.2 g/cm³ and 1.0 g/cm³ for PAA and QP2VP, respectively, the SLDs of PAA and QP2VP were calculated at $1.66 \times 10^{-4} \text{ nm}^{-2}$ and $1.26 \times 10^{-4} \text{ nm}^{-2}$.

The scattering amplitude of a sphere, $F(q)$, reads:

$$F(q) = \frac{3[\sin(qR) - qR \cos(qR)]}{(qR)^3} \quad (2)$$

Polydispersity of the radius R is taken into account using a Gaussian distribution:

$$f(R) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2\sigma^2}(R - R_{\text{avg}})^2\right] \quad (3)$$

where R_{avg} is the average radius and $p = \sigma/R_{\text{avg}}$ the polydispersity. The Ornstein–Zernike function, $S_{\text{OZ}}(q)$ in eq 1, describes the concentration fluctuations of polymers in solution:⁴²

$$S_{\text{OZ}}(q) = \frac{I_{\text{OZ}}}{1 + (\xi q)^2} \quad (4)$$

with ξ being the correlation length of the fluctuations, which is related to the mesh size in the transient network inside the globule, and I_{OZ} the intensity of this contribution.

At pH 5.0, the net charge imbalance is higher than at pH 7.0 because the PAA blocks are less deprotonated, thus contributing less to the core formation. The SANS curve was modeled using the form factor of spherical core–shell particles, a structure factor of small fractal aggregates and the incoherent background:

$$I(q) = P_{\text{mic}}(q)S_{\text{FR}}(q) + I_{\text{bkg}} \quad (5)$$

The form factor of a spherical particle having core–shell structure is given by⁴³

$$P_{\text{mic}}(q) = \frac{1}{V_m} \left[\frac{3V_c(\rho_c - \rho_{\text{shell}})j(qR_c)}{qR_c} + \frac{3V_m(\rho_{\text{shell}} - \rho_s)j(qR_m)}{qR_m} \right]^2 \quad (6)$$

where R_m and V_m are the radius and the volume of the entire particle and R_c and V_c the radius and the volume of the particle core, respectively. ρ_c , ρ_{shell} and ρ_s stand for the mean scattering length densities of the core, the shell and the solvent, respectively. $j(x)$ denotes the first-order Bessel function:

$$j(x) = \frac{\sin x - x \cos x}{x^2} \quad (7)$$

The polydispersity of the core radius was taken into account using eq 3. P2VP blocks, which are not complexed to the core, construct the shell. Attempts to use in a fitting procedure the form factor of homogeneous spheres were not successful. For the structure factor, describing the correlation between these particles, a structure factor for small mass-fractal aggregates was used:⁴⁴

$$S_{\text{FR}}(q) = 1 + \frac{1}{(qR_m)^{d_f}} \frac{d_f \Gamma(d_f - 1)}{\left[1 + \frac{1}{(qR_d)^2}\right]^{(d_f-1)/2}} \times \sin[(d_f - 1) \tan^{-1}(qR_d)] \quad (8)$$

R_m is again the radius of the entire spherical core–shell particles, R_d the cluster radius and d_f the fractal dimension of the cluster. The latter is expected to take values between 2 and 3; the higher the value, the more compact is the cluster.

At pH 3.0, the scattering curve shows an additional pronounced peak at $q \sim 0.1 \text{ nm}^{-1}$, which was ascribed to an interaction between the particles. Thus, the following expression was fitted to the curve:

$$I(q) = P_{\text{mic}}(q)S_{\text{HS}}(q) + S_{\text{OZ}}(q) + I_{\text{bkg}} \quad (9)$$

where $P_{\text{mic}}(q)$ is again the form factor of spherical core–shell particles (eq 6). The values of the SLDs were calculated at $5.5 \times 10^{-5} \text{ nm}^{-2}$ and $1.7 \times 10^{-4} \text{ nm}^{-2}$ for PtBA and P2VP, respectively. $S_{\text{HS}}(q)$ is the interparticle structure factor; here, the Percus–Yevick hard-sphere structure factor was used:⁴⁵

$$S_{\text{HS}}(q) = \frac{1}{1 + 24\eta G(2R_{\text{HS}}q)/(2R_{\text{HS}}q)} \quad (10)$$

where

$$G(x) = \gamma \frac{\sin x - x \cos x}{x^2} + \delta \frac{2x \sin x + (2 - x^2) \cos x - 2}{x^3} + \varepsilon \frac{-x^4 \cos x + 4(3x^2 - 6 \cos x + (x^3 - 6x) \sin x + 6)}{x^5} \quad (11)$$

with the functions

$$\gamma = \frac{(1 + 2\eta)^2}{(1 - \eta)^4}, \quad \delta = \frac{-6\eta(1 + \eta/2)^2}{(1 - \eta)^4}, \quad \varepsilon = \frac{\gamma\eta}{2} \quad (12)$$

R_{HS} is the hard-sphere radius, i.e., half the center-to-center distance between the particles. η is the hard-sphere volume fraction, i.e. the fraction of micelles which contribute to the formation of the micellar network. An attempt to use a Hayter-Penfold structure factor for a system of charged objects instead was not successful. At high q -values, the polymer network structure formed by the bridges between the micelles contributes significantly to the scattered intensity. This contribution was again described by an Ornstein–Zernike function (eq 4).

The scattering curve of PAA_{163} - b - $P2VP_{1397}$ - b - PAA_{163} at pH 3 features noticeable forward scattering which was assigned to large aggregates or other large-scale inhomogeneities due to the restricted mobility in the network. This contribution was modeled by⁴⁶

$$P_{agg}(q) = \frac{I_{agg}}{q^d} \quad (13)$$

Here, I_{agg} is the scaling factor and d the scaling dimension. The latter is expected to take values between 3 and 4; the higher the value; the smoother the aggregate surface.⁴⁷ Thus, the following expression was fitted to the scattering curve:

$$I(q) = P_{mic}(q)S_{HS}(q) + S_{OZ}(q) + P_{agg}(q) + I_{bkg} \quad (14)$$

For the modeling of all scattering curves, the NCNR SANS and USANS Data Reduction and Analysis package within the Igor Pro environment was used.⁴⁸ The resolution was in all cases taken into account using standard procedures.⁴⁸ The incoherent background was calculated for each case from the incoherent scattering cross sections of the components and was consistent with the experimental data.

RESULTS

This section includes the optical, electrical, rheological and structural characterization of three different triblock copolymers, the quaternized PAA_{163} - b - $QP2VP_{1397}$ - b - PAA_{163} and the nonquaternized PAA_{163} - b - $P2VP_{1397}$ - b - PAA_{163} as well as the triblock polyelectrolyte $PtBA_{163}$ - b - $P2VP_{1397}$ - b - $PtBA_{163}$, all being derived from the sequential hydrolysis and quaternization of the latter precursor, thus having the same block lengths. After a discussion of the charge conditions at different pH values, the pH dependent structures of PAA_{163} - b - $QP2VP_{1397}$ - b - PAA_{163} are described. Second, the comparison between PAA_{163} - b - $QP2VP_{1397}$ - b - PAA_{163} and PAA_{163} - b - $P2VP_{1397}$ - b - PAA_{163} demonstrates the influence of the net system charge on the micellar dimensions and the nature of the physical network. Finally, the comparison of PAA_{163} - b - $QP2VP_{1397}$ - b - PAA_{163} and $PtBA_{163}$ - b - $P2VP_{1397}$ - b - $PtBA_{163}$ is presented.

Optical Density. The solubility behavior of the PAA_{163} - b - $QP2VP_{1397}$ - b - PAA_{163} in aqueous media as a function of pH has been substantially changed with respect to the nonquaternized precursor, as can be seen by optical density measurements in Figure 1. The precipitation region observed in the vicinity of the isoelectric point of PAA_{163} - b - $P2VP_{1397}$ - b - PAA_{163} ²⁹ has vanished in the quaternized polyampholyte, rendering it water-soluble in the entire pH region. Moreover, no significant

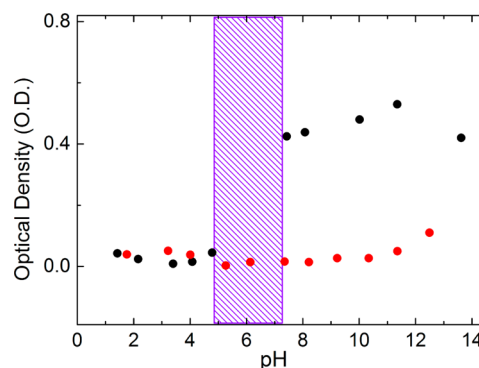


Figure 1. pH dependence of the optical density for PAA_{163} - b - $P2VP_{1397}$ - b - PAA_{163} (black circles) and for PAA_{163} - b - $QP2VP_{1397}$ - b - PAA_{163} (red circles) at $c = 0.2$ wt %. The purple region represents the isoelectric point region ($4.8 < \text{pH} < 6.8$) for PAA_{163} - b - $P2VP_{1397}$ - b - PAA_{163} .

sign of intermolecular association that could lead to aggregates of detectable size can be observed at the high pH region, at least at the concentration investigated ($c = 0.2$ wt %), in contrast to the micellization behavior observed in PAA_{163} - b - $P2VP_{1397}$ - b - PAA_{163} arising from the hydrophobic association of the deprotonated P2VP blocks.²⁹ The above results are attributed to the high asymmetry of the block lengths of the triblock in which the permanent ionized P2VP block predominates even at high pH where electrostatic interactions among oppositely charged blocks (deprotonated PAA) are expected to occur.

Charge Conditions. In order to better understand the association behavior, driven via the electrostatic interactions, potentiometric titration and z -potential were measured as a function of pH. The degree of ionization, α , of the PAA blocks in PAA_{163} - b - $QP2VP_{1397}$ - b - PAA_{163} , in salt-free solutions, is shown in Figure 2a. The apparent pK_a of the PAA blocks is shifted to lower values with respect to that of PAA homopolymer at low degrees of ionization, e.g. $pK_a = 3.5$ at pH 3, ($pK_a = 4.2$, ref.⁴⁹) due to the presence of the quaternized P2VP, a strong polybase, in accordance with theoretical predictions.⁵⁰ Thus, the degree of ionization of PAA blocks is about 0.25 even at pH 3.

The central QP2VP block is a strong polybase and thus positively charged, independently of pH, whereas P2VP in the nonquaternized counterpart exhibits pH-dependent protonation (ionization) below pH ca. 5. In the presence of the short negative PAA blocks, the degree of ionization of which increases with pH, the net charge of the polymers should be altered differently with pH (Figure 2b). Indeed, in the nonquaternized polyampholyte the z -potential changes sign, from positive at low pH (ionized P2VP predominates) to negative at high pH, (deprotonated PAA segments prevail since P2VP has been transformed to hydrophobic), whereas in the quaternized sample, the z -potential remains positive, decreasing slightly only above pH 9.

From the above, it follows that all polymers have a positive net charge in the low pH region of interest (formation of hydrogels) (Figure 2b).

Rheological Properties. In order to explore the ability of the PAA_{163} - b - $QP2VP_{1397}$ - b - PAA_{163} triblock polyampholyte to form hydrogels, aqueous solutions of 4 wt % polymer concentration were prepared at pH values between 2.5 and 7. Steady state shear viscosity measurements were carried out, and

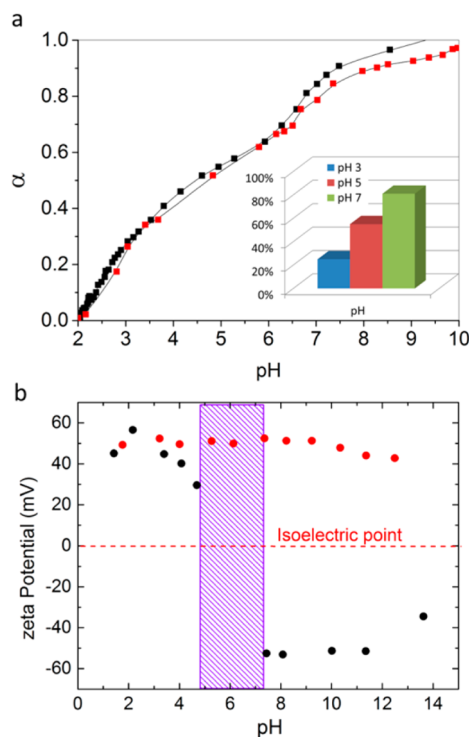


Figure 2. (a) pH dependence of degree of ionization of the PAA blocks in salt free solutions of $\text{PAA}_{163}\text{-}b\text{-QP2VP}_{1397}\text{-}b\text{-PAA}_{163}$; increasing pH by titration with NaOH (red symbols), decreasing pH by titration with HCl (black symbols) and degree of ionization of PAA blocks at the chosen pH values (inset); (b) pH dependence of z-potential for $\text{PAA}_{163}\text{-}b\text{-P2VP}_{1397}\text{-}b\text{-PAA}_{163}$ (black circles) and for $\text{PAA}_{163}\text{-}b\text{-QP2VP}_{1397}\text{-}b\text{-PAA}_{163}$ (red circles). The blue region represents the isoelectric point region ($4.8 < \text{pH} < 6.8$) for $\text{PAA}_{163}\text{-}b\text{-P2VP}_{1397}\text{-}b\text{-PAA}_{163}$.

the viscosity versus shear stress profiles are depicted in Figure 3. As observed by tilting the vials (Figure 3b), transparent free-standing gels were obtained in the low pH region and particularly at pH 3 and 4.

In Figure 4, the zero shear viscosity obtained at the Newtonian plateaus of Figure 3 is plotted versus pH. In the inset, the zero shear viscosity for the $\text{PAA}_{163}\text{-}b\text{-P2VP}_{1397}\text{-}b\text{-PAA}_{163}$ precursor has been included for the sake of comparison. Note that the polymer concentration in the nonquaternized counterpart is 1.2 wt %. Both systems exhibit gelation in the

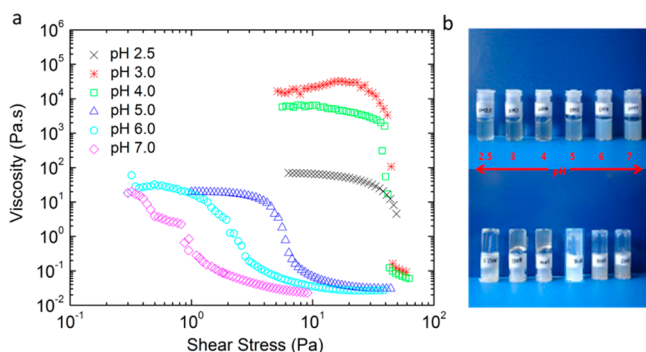


Figure 3. (a) Apparent viscosity as a function of shear stress for salt-free aqueous solutions of $\text{PAA}_{163}\text{-}b\text{-PQ2VP}_{1397}\text{-}b\text{-PAA}_{163}$ at $c = 4$ wt % and various pH conditions; (b) photos showing free-standing gels at pH 3 and 4, whereas solution behavior is observed at other pH values.

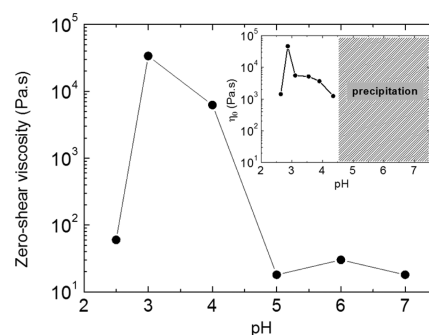


Figure 4. pH dependence of zero-shear viscosity, η_0 , in salt free aqueous solutions for $\text{PAA}_{163}\text{-}b\text{-QP2VP}_{1397}\text{-}b\text{-PAA}_{163}$ at $c = 4$ wt % and its precursor $\text{PAA}_{163}\text{-}b\text{-P2VP}_{1397}\text{-}b\text{-PAA}_{163}$ at $c = 1.2$ wt % (inset).

same pH region and, more importantly, they display a maximum close to pH 3. This result suggests that the driving force for the formation of an “open” 3D network, underpinning gelation, is of electrostatic nature since, in the quaternized version, all 2VP moieties of the central block are permanently charged, excluding therefore hydrophobic interactions that may act in the nonquaternized precursor.

More importantly, the fact that the viscosity drops remarkably at pH 5 and/or 2.5 suggests also that the charge ratio between the oppositely charged moieties is critical, provided that this ratio is varied with pH due to the weak polyelectrolyte nature of the PAA end-blocks.

Oscillatory measurements were accordingly accomplished on $\text{PAA}_{163}\text{-}b\text{-P2VP}_{1397}\text{-}b\text{-PAA}_{163}$ in the linear viscoelastic regime at different pH. In Figure 5, the storage, G' , and loss, G'' , modulus

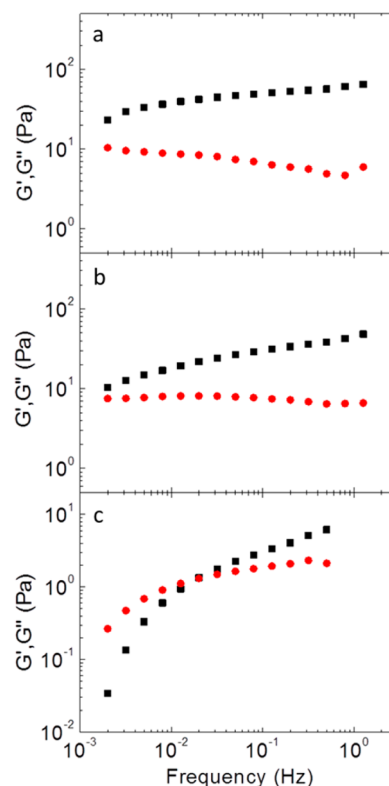


Figure 5. Dynamic moduli, G' (black symbols) and G'' (red symbols) versus frequency at different pH values for $\text{PAA}_{163}\text{-}b\text{-QP2VP}_{1397}\text{-}b\text{-PAA}_{163}$ at $c = 4$ wt %: at pH 3 (a), pH 4 (b), and pH 5 (c).

are plotted versus frequency. Two different viscoelastic responses can be observed depending on pH. At pH 3 and 4, G' is higher than G'' in the whole frequency range, being 1 order of magnitude higher at high frequencies. Yet, the terminal zone (G' , G'' crossover) is not visible, implying long relaxation times—at least higher than 500 s. This behavior is in accordance with the appearance of free-supporting hydrogels visually observed (Figure 3b). At pH 5, the viscoelastic behavior changes from gel-like to viscoelastic. The G' , G'' crossover occurs at $f = 0.02$ Hz, implying that the terminal relaxation time is decreased substantially to 50 s, which is more than 1 order of magnitude lower than that observed at pH 4. Evidently, pH affects significantly the nanostructure underpinning the viscoelastic response, since the degree of ionization of PAA end blocks increases with pH which, in turn, gives rise to electrostatic interactions. The same viscoelastic behavior is observed (plot not shown) with the nonquaternized counterpart. However, in the latter case, the viscoelastic behavior appears at lower pH, i.e., at pH 4.35, the terminal relaxation time is already decreased to 13 s. This differentiation should be attributed to the parallel increase of the hydrophobicity of the P2VP block that is deprotonated upon pH increase.

Focusing on pH ~ 3 , where maximum viscosity and gel-like behavior are observed, the concentration dependence of the zero-shear viscosity was explored for both systems. Figure 6

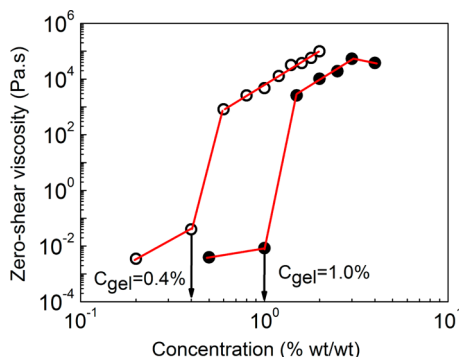


Figure 6. Concentration dependence of the zero shear viscosity at the pH of maximum viscosity for PAA₁₆₃-*b*-QP2VP₁₃₉₇-*b*-PAA₁₆₃ (pH 3.0) (closed symbols) and PAA₁₆₃-*b*-P2VP₁₃₉₇-*b*-PAA₁₆₃ (pH 2.9) (open symbols). Lines along the data guide the eyes and arrows indicate the gelation concentration.

shows that the zero shear viscosity of the aqueous solutions of PAA₁₆₃-*b*-QP2VP₁₃₉₇-*b*-PAA₁₆₃ increases sharply, from 1 to 1.5 wt % polymer concentration about 6 orders of magnitude which may be ascribed to the formation of a transient network above a percolation threshold, named C_{gel} . The same concentration dependence is observed for the nonquaternized sample. However, C_{gel} occurs at remarkably lower concentration, namely ca. 0.4 wt %, than in the quaternized copolymer. Moreover, the C_{gel} observed herein was considerably lower than the one of a similar polyampholyte with different degrees of polymerization of the blocks (PAA₁₃₅-*b*-P2VP₆₂₈-*b*-PAA₁₃₅), reported previously.³³ Therefore, the percolation threshold seems to depend remarkably on the molecular characteristics of the gelator, i.e., relative lengths of the different blocks, as well as the degree of ionization of the oppositely charged moieties. We should mention here that C_{gel} was found to be even lower for the telechelic polyelectrolyte precursor with respect to the nonquaternized polyampholyte counterpart.³⁵

Finally, the nonlinear behavior of the quaternized copolymer hydrogel was explored in a steady state shear experiment. Figure 7 demonstrates an increasing/decreasing stress sweep

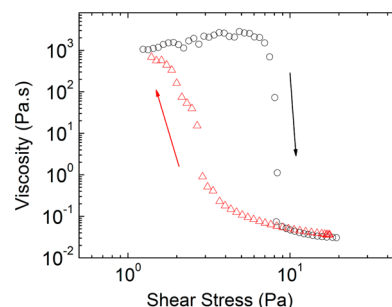


Figure 7. Apparent viscosity versus shear stress of 1.6 wt % aqueous PAA₁₆₃-*b*-QP2VP₁₃₉₇-*b*-PAA₁₆₃ solution at pH 3: increasing stress (black circles) and decreasing stress (red triangles).

test at a polymer concentration of 1.6 wt %, just above the gel formation. The Newtonian plateau was hardly observed at low shear stresses, followed by a shear thickening effect prior a dramatic shear thinning, marked by a drop of the viscosity of 5 orders of magnitude. The latter effect occurred at a relatively low stress of about 8 Pa, implying easy disruption of the network structure. Upon decreasing stress, the viscosity increases again, approaching the initial value at low stress but the flow curve follows a different pathway, exhibiting remarkable hysteresis. This phenomenon may be attributed to the slow structure recovery which is in agreement with the long relaxation time observed by oscillatory measurements (Figure 5).

Thus, rheological characterization marked a different viscoelastic behavior of the presented systems. Particularly, it was established that electrostatic interactions between QP2VP/P2VP and PAA units are a crucial parameter for the formation of a 3D network. In case of PAA₁₆₃-*b*-P2VP₁₃₉₇-*b*-PAA₁₆₃, hydrophobic associations between nonionized P2VP units contribute additionally to the stiffening of the network. Moreover, altering pH, the change in the net charge of polymers (due to the varying degree of ionization of the oppositely charged moieties) influences the nanostructure with a following impact on viscoelastic response. We derived the correlation between percolation threshold and nature of intermolecular associations. In order to gain a deeper understanding of the origin of network formation and properties of formed structures, we continued with small-angle neutron scattering measurements.

Structural Investigation via SANS. The structures of the samples were investigated at a concentration of 4 wt % in D₂O, which is above the percolation threshold (Figure 6) and at which a pronounced effect of the pH value on the mechanical properties was observed (Figure 5).

Quaternized System—Influence of pH. In Figure 8, SANS curves from the quaternized polyampholyte PAA₁₆₃-*b*-QP2VP₁₃₉₇-*b*-PAA₁₆₃ at pH 7.0, 5.0, and 3.0 are compiled. Their shapes differ significantly from each other; thus, with increasing charge imbalance, three different morphologies are detected. Whereas the curve at pH 7.0 features a decay with a shallow minimum at $q \cong 0.1 \text{ nm}^{-1}$, the curve at pH 5.0 shows a shallow minimum at higher q ($\sim 0.2 \text{ nm}^{-1}$). The curve at pH 3.0 has a completely different shape with a maximum at $q \cong$

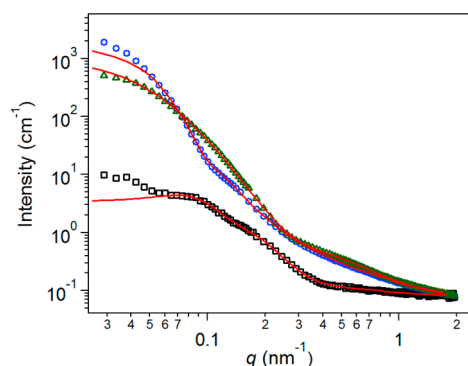


Figure 8. Scattered intensity, $I(q)$, as a function of the momentum transfer, q , for solutions of PAA₁₆₃-*b*-QP2VP₁₃₉₇-*b*-PAA₁₆₃ at a concentration of 4 wt % in D₂O at 26 °C at pH 7.0 (blue circles), pH 5.0 (green triangles) and pH 3.0 (black squares). The solid red lines are the model fits, see text.

0.08 nm⁻¹ and a shoulder at $q \cong 0.2$ nm⁻¹ together with a broad decay at $q > 0.4$ nm⁻¹.

In a previous work on similar systems, it was shown that the chain conformation of a diblock polyampholyte depends on the charge imbalance in the polymer chain. Chains with high charge imbalance are elongated similarly to polyelectrolyte chains and can form network connections. On the contrary, if the diblock polyampholyte is nearly charge-symmetric, it collapses into a globule. The equilibrium density of the globule is determined by the balance between fluctuation-induced attraction and repulsion between excess charges.⁵¹ Thus, we expected structural reorganizations with increasing charge asymmetry. In the following, we will extract structural parameters from all three curves and deduce the pH-dependent morphologies by model fitting.

The scattering curve of PAA₁₆₃-*b*-QP2VP₁₃₉₇-*b*-PAA₁₆₃ at pH 7.0, where the charge imbalance is minimum and extended attractive electrostatic interactions take place, is fitted using eq 1, describing the scattering from large spherical particles together with concentration fluctuations. Figure 9a displays the contributions to the model fit. The spheres are uncorrelated, as seen from the absence of a structure factor. The model fits the scattering curve well. Thus, the observed spherical objects resemble microgels, i.e. finite size networks, stabilized by the excess P2VPCH₃⁺ positively charged moieties, which stay apart from each other in accordance with the rheological results (low viscosity). The average microgel radius was found at $R_{\text{avg}} = 37.1 \pm 1.9$ nm with a polydispersity $p = 0.27 \pm 0.08$. These spherical microgels are composed of complexed negatively charged groups of the PAA end blocks and positively charged groups of the long QP2VP middle block. By fitting, the value of SLD for the core was found at 2.0×10^{-4} nm⁻². This value is higher than the literature values of either blocks (see the Experimental Section); thus, the microgel contains D₂O (about 14 wt % as deduced from the difference between calculated SLD value for a 1:1 mixture of PAA and QP2VP and experimental value of SLD of the core) which, in turn, leads to a swelling of the chains. The correlation length which was found to be $\xi = 2.6 \pm 0.6$ nm was therefore attributed to an average correlation length between complexed PAA and QP2VP chains (hydrophobic domains) inside the microgel. The ratio of positively and negatively charged chains may be imbalanced within the microgel due to a fast aggregation process. We note that other models may fit the scattering curves as well; however, the

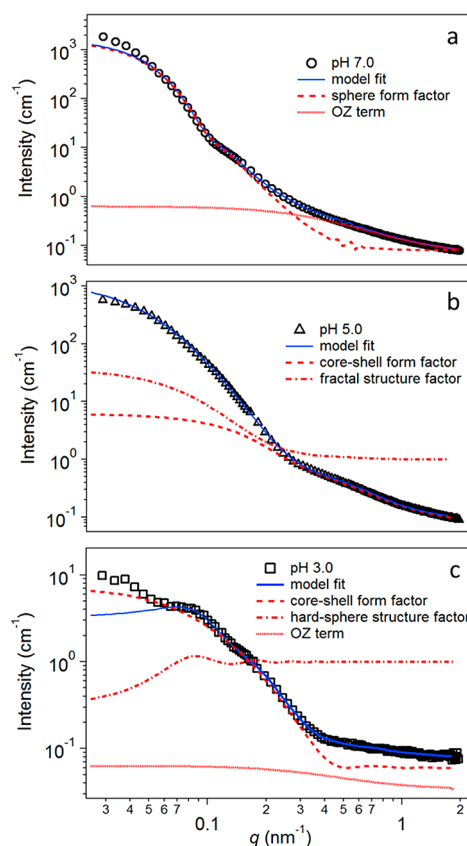


Figure 9. SANS curves from Figure 8, PAA₁₆₃-*b*-QP2VP₁₃₉₇-*b*-PAA₁₆₃ at pH 7.0 (a), 5.0 (b), and 3.0 (c). The symbols are the experimental data and the solid lines the overall model fits. The noncontinuous lines are the contributions to the models as described in the respective figures.

model presented here is the simplest one and reproduces the curves over a wide range.

Decreasing the pH of the solution to 5.0, the charge imbalance on the chain increases due to the smaller fraction of negatively charged PAA units. In Figure 8, the SANS curve of a solution of PAA₁₆₃-*b*-QP2VP₁₃₉₇-*b*-PAA₁₆₃ at pH 5.0 is presented. At q -values below 0.2 nm⁻¹, the curve is bent and reaches a shallow minimum at $q \cong 0.2$ nm⁻¹. At $q \cong 0.6$ nm⁻¹, another broad and flat maximum is encountered. The curve could successfully be modeled using eq 5 (Figure 9b) which assumes that fractal aggregates of finite size are formed by spherical core-shell particles. (It was not possible to fit the curves with eq 1 but a shell was needed.) These aggregates contain voids, i.e., they are not densely packed. The lower degree of ionization of the PAA blocks implies that less electrostatic attractive interactions take place leading to smaller hydrophobic cores. Indeed, the radius of the particle core is found at $R_c = 3.4 \pm 1.1$ nm with a polydispersity of 0.35 ± 0.06 . The micellar radius is found at $R_m = 4.7 \pm 1.1$ nm, and the shell thickness is 1.3 ± 0.8 nm. Formation of such small aggregates, consisting of 1–2 polymer chains, happens because now the degree of ionization is lower than at pH 7.0. The average distance between charges is thus larger which results in more compact chain conformations. The fractal dimension amounts to $d_f = 2.8 \pm 0.2$ which is only slightly lower than 3 and thus corresponds to a relatively compact aggregate. The aggregate radius was found to be $R_{cl} = 17.8 \pm 1.3$ nm. An aggregate thus consists of ~ 50 micelles. The findings corroborate the

viscoelastic behavior described above: The sample consists of aggregates which are only loosely connected. At long times (>50 s), they may be disrupted by shear forces. Within the aggregate, hydrophobic domains exist which are formed by the ionized PAA groups ($\sim 50\%$ of the PAA monomers, i.e., ca. 160 per molecule) which are complexed with the corresponding number of QP2VP groups. The remaining QP2VP groups form a denser shell around these complexes and the more loosely packed matrix of the aggregate. They may form loops or may bridge different complexes. Thus, a comparatively small aggregate radius is consistent with the low optical density (Figure 1).

At pH 3.0, with maximum charge imbalance, the attractive electrostatic interactions are still present since the degree of ionization of PAA is about 25% as shown in Figure 2a. Thus, the oppositely charged units in the triblock copolymer were expected to associate intermolecularly, though to a lesser extent, and to form micelles with even smaller hydrophobic cores with respect to those at pH 5. At higher concentration, the nonassociated excess P2VPCH_3^+ sequences of the middle block (which now are longer) are able to bridge the micelles, leading to a transient network of interconnected particles.

The SANS curve of this system is given in Figure 8. It shows a maximum at $q \cong 0.1 \text{ nm}^{-1}$ and a shoulder at $q \cong 0.2 \text{ nm}^{-1}$ together with a broad decay at $q > 0.4 \text{ nm}^{-1}$, thus more features than at the higher pH values discussed above. It was fitted using eq 9 which includes again the form factor of polydisperse spherical core-shell particles and an Ornstein-Zernike term accounting for concentration fluctuations of the network, but now the correlation between the core-shell micelles is described by a hard-sphere structure factor, i.e., the simplest possible expression. In Figure 9c, the contributions from different components of the fitting functions are presented. From the form factor, we deduce a mean core radius $R_c = 2.7 \pm 0.9 \text{ nm}$ with a polydispersity of 0.4 ± 0.2 and a shell thickness of $12.2 \pm 1.6 \text{ nm}$. Modeling with a form factor of polydisperse, homogeneous spheres instead of polydisperse core-shell spheres did not succeed, i.e. there seems to be a denser shell around the cores. We attribute this finding to the localization of counterions which reduces the chain stretching. The structure factor results in a hard-sphere radius $R_{HS} = 30.8 \pm 2.1 \text{ nm}$ (half distance between bridged hydrophobic cores) and a volume fraction $\eta = 0.21 \pm 0.08$. R_{HS} is larger than the sum of R_c and the shell thickness, i.e., around the "visible" inner part of the shell, there is a highly diluted matrix of P2VP chains linking the cores to each other. The contribution at $q > 0.4 \text{ nm}^{-1}$ was attributed to the scattering from fluctuations of the network of interconnected QP2VP chains with a mesh size $\xi = 1.3 \pm 0.5 \text{ nm}$ (Figure 9c). Without this contribution, the fit was not successful. The sample thus forms a three-dimensional micellar network where hydrophobic interpolyelectrolyte complexes formed between the oppositely charged moieties are bridged by the excess free QP2VP sequences in accordance with the observed gel like behavior.

Effect of temperature. Previous rheological investigations of a similar nonquaternized polyampholyte at pH 3.0 have indicated a strong influence of temperature on the steady-state shear viscosity: The viscosity increased significantly when the temperature rose from 25 to 55 $^{\circ}\text{C}$.³⁵ This was attributed to temperature-induced changes of the molecular conformation of the PAA end-block. Below the upper critical solution temperature (UCST) point of 14 $^{\circ}\text{C}$, the PAA blocks contribution to the network formation is minimal. Above this

temperature, intermolecular interactions with the positively charged P2VP middle blocks develop and cause an increased connectivity of the network which is at the origin of the elevated viscosity. Moreover, increasing temperature weakens existing intramolecular H-bonds between the acrylic units which enhances the tendency to form additional links between the P2VP and PAA blocks, hence enhancing the viscosity even further. To gain information on the associated structural changes, the quaternized polyampholyte was investigated at pH 3.0 using temperature-resolved SANS between 26 and 43 $^{\circ}\text{C}$ (Figure 10). Contrary to expectations, the curves do not show

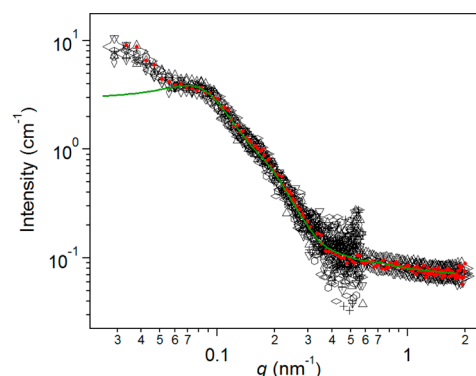


Figure 10. SANS curves for $\text{PAA}_{163}\text{-}b\text{-QP2VP}_{1397}\text{-}b\text{-PAA}_{163}$ at a concentration of 4 wt % in D_2O at 26 $^{\circ}\text{C}$ (open stars) and at 43 $^{\circ}\text{C}$ (red squares) at pH 3.0. Scattering curves with temperatures in-between are shown with different symbols. The solid green line is a fit to the curve at 26 $^{\circ}\text{C}$.

any changes with temperature. This is due to the fact that in the quaternized polyampholyte, 25% of the AA groups are still ionized which is enough to keep the PAA end blocks in a noncompact conformation (far above UCST) as probably occurred in the nonquaternized sample. This might explain why we do not see structural changes in Figure 10. Thus, the reason provided for the thermo-sensitivity observed in the non-quaternized polyampholyte does not hold for the quaternized polyampholyte.

Effect of Quaternization. In Figure 11, the SANS curves of the quaternized and the nonquaternized polyampholyte solutions at pH 3.0 and 26 $^{\circ}\text{C}$ are compiled. The general shape of the curve for nonquaternized polyampholyte is similar to the one of the quaternized polyampholyte, although the features are stronger; thus, the structure is more pronounced in the

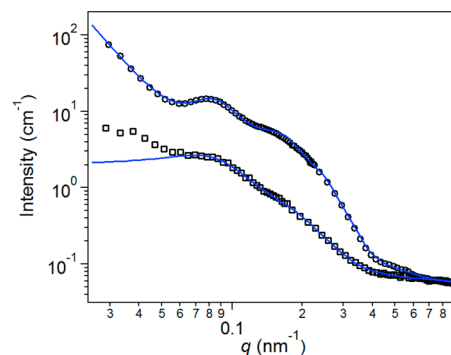


Figure 11. SANS curves of solutions of the quaternized (squares) and the nonquaternized polyampholyte (circles) at concentration 4 wt % at pH 3.0 and 26 $^{\circ}\text{C}$. The solid lines are the models fits; see text.

nonquaternized polyampholyte. The observed differences may be ascribed to the different features of the involved macromolecules on the molecular level. The nonquaternized polyampholyte exhibits a lower degree of ionization of the P2VP central block (protonation less than 40% at pH 3)⁵² and thus contains a significant hydrophobic P2VP content which does not participate in electrostatic interactions. Yet, the degree of ionization of the PAA end blocks should be lower since their pK_a should not shift as much as in the quaternized polyampholyte (presence of strong base). Therefore, we anticipate a lower extent of P2VPH⁺/PAA⁻ electrostatic complexation. In addition, from the rheological data, the plateau modulus at the same polymer concentration (e.g., 2 wt %) was found to be about four times higher for the nonquaternized polyampholyte (data not shown), implying a higher degree of bridging for the latter. We should also recall that the percolation threshold observed by viscometry (Figure 6) occurs at a lower concentration for the nonquaternized sample, which suggests a less compact structure for the less ionized sample.

In view of the almost identical network morphology, the influence of molecular features is remarkable. The peak of the structure factor is shifted from $q = 0.1 \text{ nm}^{-1}$ in the quaternized polyampholyte to $q = 0.08 \text{ nm}^{-1}$ in the nonquaternized polyampholyte gel, thus, the hard-sphere radius is higher in the latter ($36.1 \pm 2.2 \text{ nm}$ in comparison with $30.8 \pm 2.1 \text{ nm}$ in the quaternized polyampholyte gel). The distance between cross-links is given by twice the length of the hard-sphere radius. This distance is slightly higher for nonquaternized polyampholyte, which could be correlated with its lower percolation threshold. Thus, in the latter case the effective bridging chains are longer which suggests a higher ability to interconnect the physical cross-links at lower concentrations. Moreover, neutral neighboring segments in the P2VP chain in the nonquaternized polyampholyte are able to fold together with a formation of additional small hydrophobic blobs along the chain and influence the strength of the network. The volume fraction of correlated micelles was calculated from the structure factor at 0.25 ± 0.06 . The second maximum is shifted in a similar way. By fitting the model given in eq 14, we find that the micellar radius is $R_m = 10.4 \pm 1.5 \text{ nm}$ in the nonquaternized polyampholyte, thus lower than in the quaternized polyampholyte ($R_m = 14.9 \pm 1.6 \text{ nm}$). From the forward scattering, the scaling exponent is found at 3.7 ± 0.2 , which means that the aggregate surface is rather rough, presumably due to local inhomogeneities. In case of the nonquaternized polyampholyte, the amount of uncharged and hence water-insoluble P2VP units is higher than in the quaternized polyampholyte. These contribute accordingly to the formation of hydrophobic cores. Thus, a smaller fraction of P2VPH⁺ is connected to the shell. The fact that the core size is bigger in the nonquaternized system tells us also about the higher number of chains contributing to the core formation. Therefore, the cross-link functionality is higher, and as a result, a stronger network could be formed, which is in accordance with a remarkably higher relaxation time (about twice) and hence higher Newtonian viscosity observed in the nonquaternized hydrogel. Thus, the core, incorporating a higher number of chains as in case of PAA₁₆₃-*b*-P2VP₁₃₉₇-*b*-PAA₁₆₃, is more resistant to applied stress, preserving the connectivity in hydrogel up to a higher load. The SANS results thus explain the different rheological properties and why the nonquaternized polyampholytes form a gel already

at a lower concentration (above 0.4 wt %) than the quaternized polyampholytes (above 1 wt %).

Triblock Polyelectrolyte. Finally, we were interested in comparing the structural features of the quaternized polyampholyte network with those of the PtBA-*b*-P2VP-*b*-PtBA telechelic polyelectrolyte precursor, for which it is well-known that it adopts a flower-like micellar network.^{15,35} Figure 12

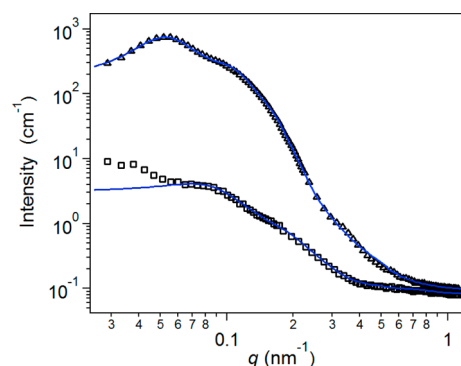


Figure 12. SANS curves of solutions of the telechelic polyelectrolyte (triangles) and the quaternized polyampholyte (squares) at 4 wt %, pH 3.0 and 26 °C. The solid lines are model fits; see text.

shows the SANS curves of the quaternized polyampholyte and the telechelic polyelectrolyte solutions at pH 3.0. Both curves show a correlation peak at low q (at 0.1 nm^{-1} for the quaternized polyampholyte and at 0.06 nm^{-1} for the telechelic polyelectrolyte) which is due to the structure factor and thus reflects the distance between micelles as well as the strength of the correlation. The peak is more pronounced for the telechelic polyelectrolyte. Also the shoulder at $q \sim 0.13 \text{ nm}^{-1}$ is more pronounced in the curve of the telechelic polyelectrolyte. The curve of the telechelic polyelectrolyte was analyzed using eq 9 in the same way as the one from the quaternized polyampholyte presented above.

From the structure factor, it is found that, in the telechelic polyelectrolyte, the hard-sphere radius is $R_{HS} = 55.5 \pm 1.9 \text{ nm}$, thus much higher than in the quaternized polyampholyte ($30.8 \pm 2.1 \text{ nm}$). This increase of micellar distance may be due to a change of the molecular conformation of the P2VP middle block: In the polyampholyte, the negatively charged PAA groups interact with the protonated P2VPH⁺ groups. This is expected to neutralize a certain amount of charges in the P2VP middle blocks. They are less extended but, at the same time, the length of the potentially bridging chains (from the remaining uncomplexed moieties) becomes lower, thus the distance between the hydrophobic particles is lower for the quaternized polyampholyte than for the telechelic polyelectrolyte where the end blocks are neutral. An alternative explanation could be the one given previously which was based on rheological experiments:³⁵ Active chains of charged PAA blocks form random electrostatic connections with the central part of P2VPR⁺ middle block, thus decreasing effectively the length of the bridges by about a factor of 2.

In spite of the structural similarities, it is striking that the quaternized polyampholyte forms a much softer gel at pH 3.0 than the telechelic polyelectrolyte, which has been ascribed to different association mechanisms depending on the nature of the end blocks.³⁵ The network structure in the quaternized polyampholyte system is predefined to some extent by the protonated PQ2VP middle blocks which tend to form

hydrophobic complexes with the negatively charged PAA units. These complexes are connected by the remaining PQ2VP blocks to a gel network. In case of the telechelic polyelectrolyte, the hydrophobic PtBA end blocks agglomerate and form spherical particles, which are screened against unfavorable contacts with water by the PQ2VP shell (flower-like micellar structure). The volume fraction of correlated micelles is determined at 0.19 ± 0.06 . The size of the PtBA spheres results mainly from the balance between the surface tension of the hydrophobic core and the electrostatic repulsion with the charged corona. At higher concentrations, the micelles become connected to each other by the bridging middle blocks, leading to a physical network.

Because the cores of the telechelic polyelectrolyte are composed from PtBA, that entirely contributes to the core formation, they are considerably larger ($R_c = 10.8 \pm 1.5$ nm) than those in the quaternized polyampholyte ($R_c = 2.7 \pm 0.9$ nm, see above), where electrostatic interactions between the oppositely charged moieties are minimum (low hydrophobic content).

Summary and Conclusion. We have studied the gelation efficiency of a quaternized PAA-QP2VP-PAA polyampholyte in aqueous solutions as a function of pH, which determines the ratio of the oppositely charged moieties (charge imbalance). To gain better insights to the behavior and structure of this kind of systems, we also investigated the nonquaternized precursor, as well as the telechelic polyelectrolyte, from which the nonquaternized polyampholyte arises. It was found that the maximum viscosity is attained at the same pH 3 for all polyampholyte hydrogels which implies that the driving force for gelation mainly is the electrostatic attractions among the oppositely charged moieties of the different blocks. The 3D network is formed at a minimum charge molar ratio, $[AA^-]/[2VPR^+]$, of ca. 6% (derived from 25% charged AA units at pH 3, mentioned above) for the quaternized polyampholyte which should be about the same for the nonquaternized counterpart.

Accordingly, the influence of charge asymmetry on the self-organized structure in the quaternized polyampholyte system was explored at different pH values by SANS. The scattering studies were performed on quasi-dilute solutions. A progressive transformation of the structure was observed upon decreasing pH from 7 to 3 (Figure 13). At pH 7, extended complexation of the opposite charges led to the formation of uncorrelated dense

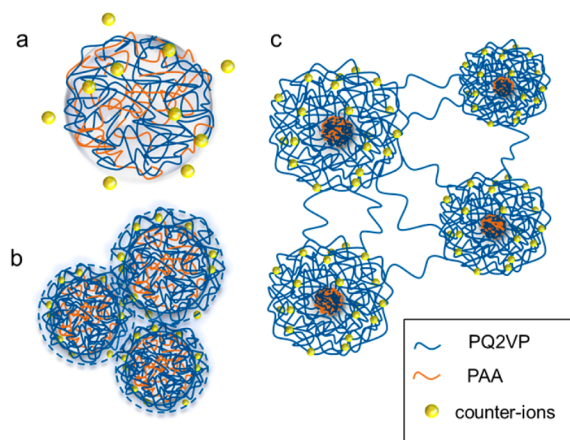


Figure 13. Schematic representation of different nanostructures in PAA₁₆₃-*b*-QP2VP₁₃₉₇-*b*-PAA₁₆₃ system: dense microgel at pH 7.0 (a), micellar clusters at pH 5.0 (b), and 3D network at pH 3.0 (c).

microgels. Moving to a higher charge asymmetry at pH 5, micelles form with part of chains being localized in the hydrophobic core, while an excess of positive charges are pushed out to the micellar corona. The resulting core-shell particles aggregate into fractal clusters, which are weakly connected.

Finally at pH 3, where the charge asymmetry is high, a 3D network is formed. Each micellar shell contains noncompensated positive charges on the QP2VP units which preferably stay stretched in aqueous solution in order to minimize contacts with each other. The gel at pH 3 contains a high amount of I^- counterions due to the higher ionization degree of QP2VP units, and thus ion condensation is expected to occur, which keeps the corona less stretched. But nevertheless, each micelle carries a positive surface charge, which could cause long-ranged electrostatic repulsion with coronas from neighboring micelles and hence influences the distance between the particles in the gel.

The comparison of quaternized and nonquaternized polyampholytes prove once more the observations obtained from rheological measurements. The latter ones are stiffer and have a lower limit for gelation which is due to higher stability of the P2VP chains, acting as bridges between the micelles, which give an additional impact to the connectivity being “frozen” or hydrophobic in a higher extent than in its quaternized version where the number of charges is fixed during synthesis.

In the telechelic polyelectrolyte, a gel is formed by flower-like micelles, where the core is formed by the hydrophobic outer PtBA blocks, surrounded by a shell of P2VPH⁺. As in the previous case, the presence of uncompensated charges plays a role in the formation of the micellar gel. For the same reason, the shell blocks are not completely stretched and smaller in size compared to the quaternized polyampholyte.

Moreover, we were able to compare the gel and network properties in the three different systems, with the same triblock architecture and block lengths but with different degree of ionization and end-block nature (telechelic polyelectrolyte case) (Table 2). The main aim was to determine the structural differences underpinning the obtained hydrogels and to correlate them with the rheology response.

Table 2. Parameters from Fitting the SANS Curves of Three Different Hydrogels at pH 3

	PAA-QP2VP-PAA	PAA-P2VP-PAA	PtBA-P2VP-PtBA
R_c (nm)	2.7 ± 0.9	4.4 ± 1.1	10.8 ± 1.5
R_m (nm)	14.9 ± 1.6	10.4 ± 1.5	17.8 ± 1.5
R_{HS} (nm)	30.8 ± 2.1	36.1 ± 2.2	55.5 ± 1.9
η	0.21 ± 0.08	0.25 ± 0.06	0.19 ± 0.06
ξ (nm)	1.3 ± 0.5	1.9 ± 0.9	3.7 ± 1.0

The results showed that the mean distance (R_{HS}) between the hydrophobic cores (physical cross-links) in the three different networks, follows the order (Table 2) telechelic polyelectrolyte > nonquaternized polyampholyte > quaternized polyampholyte, which could be correlated with the opposite trend in C_{gel} (percolation threshold), i.e., telechelic polyelectrolyte < nonquaternized polyampholyte < quaternized polyampholyte. Therefore, it could be deduced that the higher the effective length of the bridging chain, the lower is the percolation threshold.

Because of the shift of C_{gel} and the physical cross-linking, the rheological properties of the three hydrogels differ remarkably

at a given pH and concentration. At pH 3, the gel is softer; i.e., the viscosity and the elastic modulus are lower, for the quaternized polyampholyte, followed by the nonquaternized counterpart and finally by the telechelic polyelectrolyte that form kinetically “frozen” networks with very high viscosity and elasticity.^{53,54}

The lower viscosity and softer gel in the case of the quaternized polyampholyte in comparison with the free-standing gels from the nonquaternized polyampholyte and the telechelic polyelectrolyte are partially due to the high number of equally charged units in the polymer, which are not completely screened by the presence of counterions. Hence these QP2VP units prefer to remain stretched or more mobile, which restricts their ability to bridge the micelles. The second reason is the quite high hard-sphere radius, which exceeds the micellar radius by a factor of 2, being an additional obstacle preventing or weakening the network connectivity.

Thus, the combination of optical, electrical, rheological and structural measurements revealed several morphological transitions depending on the charge ratio of the oppositely charged moieties along the different blocks.

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