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Synthesis and Characterization of Amphiphilic Polyelectrolyte Brush Copolymers Based on Poly(2,7-carbazole)

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ABSTRACT: Amphiphilic polyelectrolyte brush polymers with a rigid, hydrophobic backbone formed by poly(2,7-carbazole) and flexible pH-sensitive side chains of poly(L-lysine) (PLL) are presented and their aggregation is studied. The hydrophilic polyelectrolyte side chains of PLL are attached to the 9-position of every second carbazole unit, alternatingly to hydrophobic alkyl side groups, substituting the residual moieties. The PLL side chains can be switched between different conformations by varying the pH. At lower pH the free amino groups in PLL become protonated and the side chains have a rodlike conformation, while at higher pH values the PLL chains form in their unprotonated form coil structures. This process is proven by circular dichroism and ^{13}C NMR experiments. Fluorescence emission spectra, dynamic light scattering, and atomic force microscopy (AFM) experiments demonstrate that the aggregation behavior of the synthesized polyelectrolyte brush polymers can be controlled by the pH as well. In the charged form the polymers are observed as single molecules due to the electrostatic repulsion; in its unprotonated form, however, large aggregates are formed. The water-soluble brush polymers can be considered due to the stiffness of the backbone and the switchable PLL side chains either as a rod-*g*-coil or a rod-*g*-rod polymer.

Introduction

Conjugated polymers are active components of electronic devices,[1] as for example in plastic solar cells,[2] light-emitting diodes,[3] and field-effect transistors.[4] Their electronic and optical properties such as charge carrier mobility, light absorption, and emission strongly depend upon the molecular structure but also upon the morphology obtained in bulk or at interfaces after processing.[5] Amphiphilic block polymers with π-conjugated rigid backbones became of special interest since they enable the control of the aggregation and packing behavior in solution, in bulk, or at interfaces.[6−9] As a result, they gave rise to cylindrical, shape-persistent micelles and show microphase separation.[8,10−12] In the case that the amphiphilicity was caused by charges as for example for polyphenylene sulfonates,[13] the aggregation properties and the packing behavior were additionally influenced by the pH as the amphiphilicity of the polymers was adjustable by the degree of protonation.[14,15] Remarkably, the conformation of the conjugated polyelectrolytes and therefore the effective conjugation length have not been affected by the ionic strength of the applied system.[16−19] To further increase the amphiphilicity, attempts were made to use instead of the charged groups, which are directly attached to the backbone, polyelectrolyte side chains and to obtain amphiphilic conjugated brush polymers. It was expected that the side chains allow for a better control of the morphology by self-assembly and additionally show a stimulus-responsive behavior e.g. by varying the pH.[9] In particular, polyphenylenes with polystyrenesulfonate side chains were proposed.[20] This concept included the synthesis of macromonomers from polystyrenesulfonate ethyl esters carrying polymerizable phenylene end groups. However, the polymerization failed which was attributed to the steric hindrance caused by the long side chains on the reactive units of the phenylene moieties. Herein, we present the synthesis of a conjugated polyelectrolyte brush polymer with a poly(2,7-carbazole) backbone and alternating side chains of poly(L-lysine) (PLL) and hydrophobic 2-ethylhexyl groups (**1**) (Figure 1).

We selected polycarbazole for the backbone as it is one of the most applied materials for photovoltaics and as especially for the application in solar cells a control of the aggregation during device formation is required.[21] Synthetically this polymer is attractive as for a carbazole building block functionalized with PLL grafts the steric hindrance should be lower in a polycondensation process in comparison to the smaller phenylene units. Additionally, carbazole allows for a specific monofunctionalization in the 9-position, the exclusion of defect structures caused by side reactions such as oxidation,[22] and a better conjugation due to a reduced torsion along the backbone as a result of the nitrogen-bridged biphenyls.[23] PLL homopeptide was chosen due to its pH-responsive properties similar to polyelectrolytes and also due to the formation of the typical secondary structures of peptides.[24,25] PLL exhibits a random coil structure below pH 12, changing spontaneously into a helical conformation with rising pH.[26] The obtained polyelectrolyte brush polymers are characterized, and their aggregation behavior depending on pH is described.

Results and Discussion

Polymer Synthesis. To obtain the amphiphilic polymer **1**, the synthesis via a macromonomer approach,[27] in a related fashion used for PPP graft polymers,[7,12,28,29] was adopted. The polymerization employed dibromide **4** and diboronic ester **5** of two carbazole derivatives that were subsequently reacted via Suzuki polycondensation (Scheme 1). PLL-containing macromonomers were synthesized starting from 2,7-dibromocarbazole with the 9-position functionalized with phthalimide (**2**).[30] Compound **2** was converted into amine **3** in a reaction with hydrazine monohydrate.[31] Monodisperse poly(ε-Z-L-lysine(Z))−OH was synthesized by means of solid phase chemistry[32] and coupled to the carbazole

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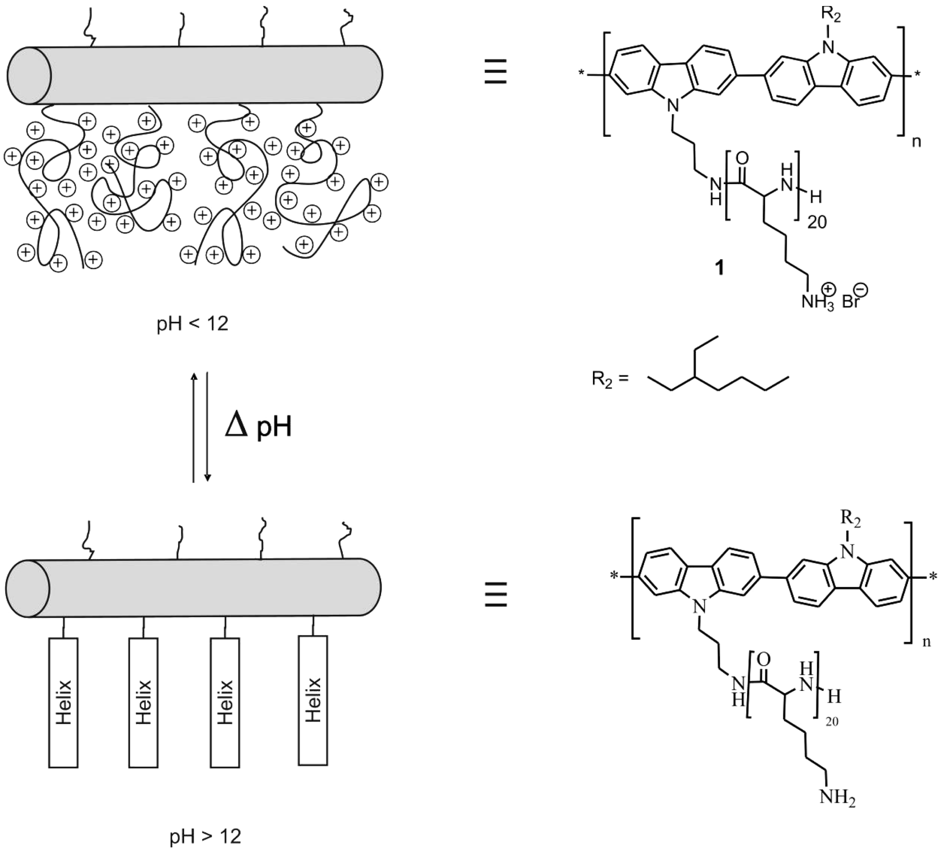
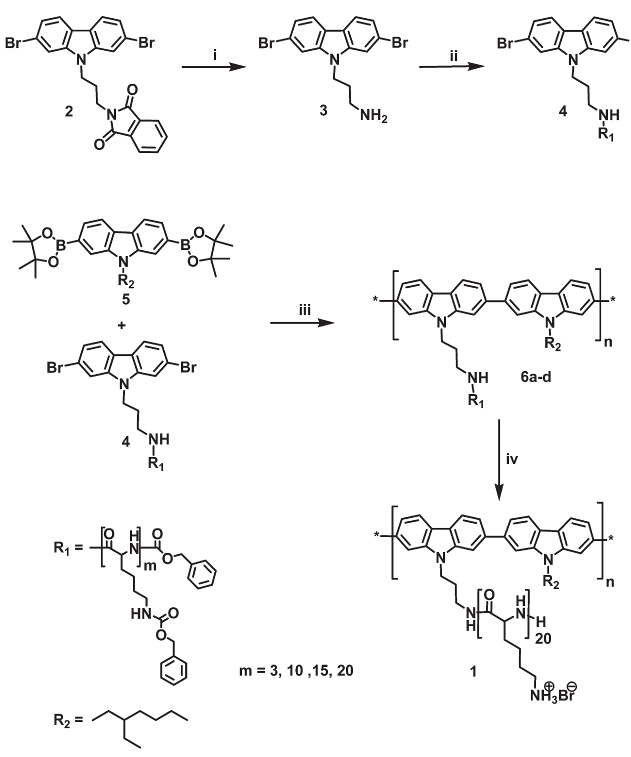


Figure 1. Polyelectrolyte comb-type polymer **1** with a conjugated backbone and polyelectrolyte side chains.

Scheme 1. Synthesis of the Conjugated Polyelectrolyte 1[a]



[a] Conditions: (i) hydrazine monohydrate, MeOH, reflux, 2 days, 97%; (ii) oligo(ε-Z-L-lysine(Z))−OH, HOBt, HBTU, DIPEA, NMP, argon, rt, 3 days, light-exclusion, 94%; (iii) Pd(PPh$_3$)$_4$, DMF, 2 M K_2CO_3, 75 °C, 5 days, 40−80%; (iv) HBr/acetic acid (5.7 M), TFA, rt, 1 h, 95%.

derivative **3** via HOBt-activated ester synthesis to yield macromonomer **4**. The diboronate ester with branched alkyl chain **5** was synthesized according to the literature.[33] Monomers **4** and **5** were polymerized in a Pd-mediated Suzuki-type polycondensation to generate the uncharged precursor **6**. Polymer **6** was then converted into the conjugated polyelectrolyte brush copolymer **1** by removal of the Z-protecting group with HBr/acetic acid (5.7 M) in trifluoroacetic acid.[34] The complete disappearance of the Z-group signals in the ^{1}H and ^{13}C NMR spectra proved the quantitative cleavage of the Z-protection group. Under these strongly acidic conditions, the amino functionalities of PLL were transformed into ammonium groups increasing the hydrophilicity. Since it is known from other PLL systems that a dried sample is difficult to be redissolved,[26] our polymer was kept in aqueous solution until further investigation.

As PLL was synthesized by the solid phase technique, it was monodisperse to give structurally defined macromonomers and could thus facilitate further characterization. The degree of polymerization (DP) of the PLL side chain was chosen to be 20 to adopt a pH-responsive secondary structure.[35] During polymerization, the amino groups of the lysine monomers were protected by the benzoyloxycarbonyl (Z-) group as free amines have been reported to lower the yield in Suzuki-polycondensation reactions.[36] This Z-group is stable to most basic and acidic conditions and therefore suitable for all reaction conditions used. The introduction of a branched alkyl chain at the N-position in compound **5** became necessary to enhance the solubility of the resulting polymer in common organic solvents such as DMF. During Suzuki polymerization the temperature was decreased to 75 °C in comparison to standard conditions (T > 80 °C)[37] to avoid denaturation of the PLL.

Table 1. GPC Data of Suzuki Polymerizations with Variation in Side-Chain Length of Poly(L-lysine(Z)), Determined against PS Standards in DMF

	$\overline{\mathrm{DP}}$ (PLL) macromer	$\overline{M}_n$/g mol^{-1}	$\overline{M}_w$/g mol^{-1}	$\overline{M}_n/\overline{M}_w$	$\overline{\mathrm{DP}}$	monomer conversion	yield/%
6a	3	1.5×10^3	3.9×10^3	3.1	2		40
6b	10	19.0×10^3	29.5×10^3	1.5	12	0.83	75
6c	15	15.4×10^3	26.8×10^3	1.8	9	0.75	78
6d	20	58.3×10^3	103.7×10^3	1.8	20	0.90	65

Polymer aggregation is a known phenomenon of polyelectrolytes with hydrophobic groups even in very dilute solutions.[18] This effect is seen as the major drawback with regard to precise structural characterization, such as GPC and light scattering.[38,39] Therefore, the molecular weights were measured of the neutral precursor **6**. GPC analysis (DMF, poly(styrene) (PS) standard) revealed in the best case **6d** a number-average molecular weight ($\overline{M}_n$) of 58.3×10^3 g mol^{-1}, a weight-average molecular weight ($\overline{M}_w$) of 103.7×10^3 g mol^{-1}, and a polydispersity of 1.82 (Table 1). The obtained $\overline{M}_n$ corresponded to a degree of polymerization ($\overline{\mathrm{DP}}$) of 20. The results of GPC analysis, as a relative method, were compared to static light scattering (SLS) for absolute M_w determination to evaluate the obtained molar mass since no molecules were available to serve as a standard for compound **6**. SLS analysis detected for **6d** a $\overline{M}_w$ of $106 \times 10^3 \pm 5.5 \times 10^3$ g mol^{-1}. As GPC gave results comparable to SLS, only this very fast method GPC was used as a standard method for the determination of the molecular weights.

The low DP of the precursor polymer **6a**−**6c** was attributed to various reasons. First, there was a significant difference in molecular weight of the monomers used, which caused difficulties in meeting the 1:1 stoichiometry essential for achieving high $\overline{M}_n$ in a polycondensation process. Therefore, in a series of experiments the monomer amounts were increased from 546 to 2.208 mg to ensure stoichiometric control. This optimization resulted for **6d** in a higher molar mass, with an increase from 21.2×10^3 to 58.3×10^3 g mol^{-1}. Second, the steric hindrance of the polymerizable functionalities by the bulky poly(L-lysine(Z)) side chain in macromonomer **4** was proposed to limit the obtained molar mass. Consequently, shorter PLL side chains were used. Contrary to our expectations, substitution with shorter PLL resulted in lower $\overline{\mathrm{DP}}$ (Table 1, **6a, 6b, 6c** vs **6d**). This effect on $\overline{\mathrm{DP}}$ was probably caused by a precipitation[40] of the formed oligomers **6a**−**6c** during polymerization, resulting from a lower solubility due to the decrease in the length of the PLL side chain. The reduced reaction temperature during polymerization in comparison to standard conditions is proposed as a further reason for the lower $\overline{\mathrm{DP}}$s.

Monomer conversions were calculated for the obtained $\overline{\mathrm{DP}}$ and the values are reported in Table 1. They were found to be higher than the yield of the polymerization reaction. The differences between the yields and monomer conversions were attributed to fractionation during the precipitation process, which caused $\overline{\mathrm{DP}}$s lower than 2.

Conformational Characterization. *Conformational Investigation of the PLL Side Chain.* Further investigation on the pH sensitivity was performed only on polymer **1** obtained after cleavage of the protecting group from **6d** as only poly(L-lysine(Z)) with a DP higher than 15 can adopt a pH-responsive secondary structure.[14] Circular dichroism experiments were performed in order to obtain information on the secondary structure of the PLL side chains within our comb-type polymer **1** in dependence on the pH in solution. The molar ellipticities θ of compound **1** for different pH are displayed in Figure 2. The neutral precursor **6d** could not be investigated as it was only soluble in DMF, which shows an overlapping absorption at $\lambda < 260$ nm. For compound **1** under acidic and neutral conditions, minima at 195 nm and maxima at 215 nm were found, which indicated unordered structures. Further increasing of the pH resulted in two minima at 205 and 222 nm. These are characteristic for helical structures.[41−43]

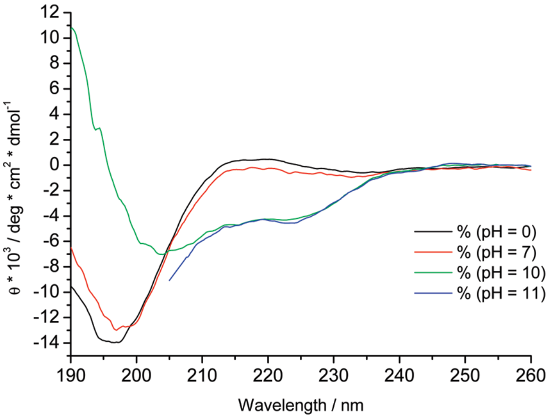


Figure 2. Circular dichroism spectra of compound **1** in dependence on the pH with $c_{\mathrm{polymer}} = 0.19$ mg mL^{-1}.

The results demonstrated a conformational change for the PLL side chains in polymer **1** from random coil to helix with increasing pH. This effect corresponded to the deprotonation of ammonium species in the ε-position of the lysine. The disappearance of the repulsive force finally led to ordered helical structures. Thus, it was proven that, beside the ionic strength of the system, PLL side-chain conformation of polymer **1** is also responsive to the pH in solution. This comb-type polymer, therefore, can be considered as the first structure not only with a rigid backbone and a polyelectrolyte side chain but also with a rod-*g*-coil structure which can be switched to a rod-*g*-rod structure (Figure 1).

For confirmation of the conformational changes, the PLL side chains were further investigated by solid-state NMR experiments performed on the polymers **1** and **6d**. ^{13}C cross-polarization magic-angle spinning (CPMAS) NMR spectroscopy was used to elucidate the conformational features from the conformation-dependent ^{13}C chemical shifts.[44] The conformation was determined by the chemical shift of the PLL amid peak at $\delta \sim 170-180$ ppm.[45] Conformational analysis of the PLL amide peak of the solid precursor polymer **6d** gave a ratio of 82% α-helix to 18% β-sheet. This ratio was consistent with the values obtained for unsubstituted poly(L-lysine(Z)) homopeptides.[44,45] In contrast, compound **1** exclusively exhibited a coil conformation. In analogy to the liquid phase, these unordered structures were explained by the electrostatic repulsive forces between adjacent charged ammonium groups along the PLL side chains as a consequence of the cleaving procedure of the Z-group.

To investigate the influence of the degree of protonation on the conformation of PLL side chains in solid state, sample **1** was treated with aqueous solutions of different pH values. After lyophilization, CPMAS-NMR analysis showed a random coil conformation for samples obtained from the aqueous solution with a pH of 2.5 (a) and 10 (b). Increasing the

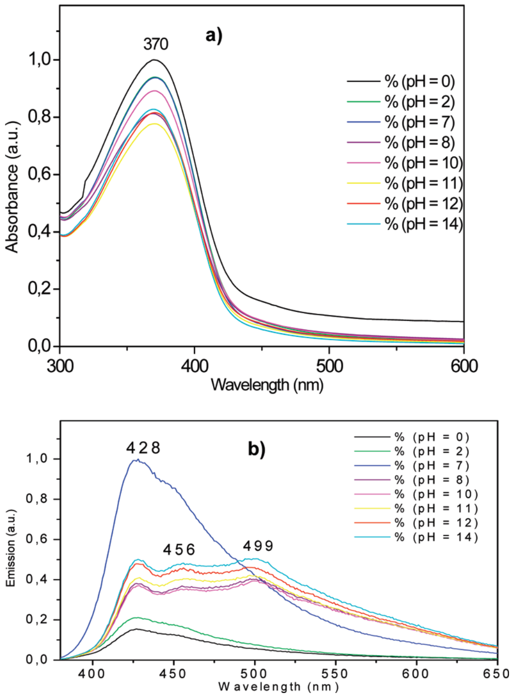


Figure 3. Optical properties of compound **1** as a function of pH: (a) absorption spectra; (b) emission spectra (λ_{exc} = 370 nm) in water.

pH to 14 gave a 45% α-helix and a 55% β-sheet. This behavior was consistent with PLL adopting helical and β-sheet secondary structures for pH > 12.[26] The occurrence of a β-sheet conformation can be explained by the sample preparation.[35,46] After freeze-drying, a change to a more predominant β-sheet structure is known for PLL homopeptides in the solid state, which is energetically more favorable in a dried solid.[47] To prove the reversibility of the conformational changes, the sample **1** obtained at pH = 14 was redispersed in a strongly acidic solution (pH = 0), and a switch-over from α-helix/β-sheet to random coil was found. By contrast, the transition from acidic to basic conditions resulted in a change from random coil to a mixture of 40% α-helix and 60% β-sheet. Hence, the conformational change between random coil and α-helix/β-sheet was proven to be reversible. The appearance of β-sheet conformation described the existence of strong hydrogen bonds between the PLL side chains.

Analysis of the Conformation of the Poly(2,7-carbazole) Backbone. Furthermore, the effect of the conformational changes of the stimulus-responsive side chains on the conformation of the poly(2,7-carbazole) backbone was investigated. It was expected that any conformational changes of the poly(2,7-carbazole) would affect its conjugation length and could thus be monitored by absorption and fluorescence characteristics of the polyelectrolyte brush polymer **1**.

pH-dependent UV−vis and PL spectra of compound **1** were recorded in an aqueous solution at different pH values ranging from 0 to 14 (Figure 3), normalized to the most concentrated sample. The pH of the sample was adjusted with HCl and NaOH. Polymer **1** showed a strong absorption band at a wavelength of 370 nm, which arose from the π, π* transition. Remarkably, no shift of the absorption maximum was observed in dependence on the pH. This behavior indicated that drastic changes of the conformation as described for flexible polyelectrolytes in the case of a polymer **1** cannot be assumed. In contrast to the absorption, the fluorescence was strongly pH-dependent. At low pH the fluorescence showed one maximum at 425 nm and a shoulder at 460 nm. With increasing pH the fluorescence broadened significantly and further maxima arose at 497 and 459 nm. No isosbestic point was monitored, which would indicate a change between two different chromophoric species. The changes in fluorescence of compound **1** as a function of pH suggested that the polymer was aggregated in basic media and less aggregated or unaggregated under acidic and neutral conditions. The broad fluorescence of the uncharged polymer at high pH was attributed to emission from an "excimer-like" state arising from interchain $\pi-\pi$ stacking.[14] This broad emission is characteristic for conjugated polymers in the solid state when interchain aggregation is occurring.[13] Since lysine has a pK_a = 10.5, the side chain was partially neutralized at pH between 10 and 11. Thus, electrostatic repulsion was decreased for increased pH and interchain aggregation occurred.

Table 2. Hydrodynamic Radii of Compound 1 ($c_{polymer}$ = 1.13 mg mL^{-1}) for Different pH

pH	R_h/nm
0	85 ± 6
2	85 ± 5
7	94 ± 6
10	135 ± 9
11	128 ± 8
12	179 ± 15
14	111 ± 9

In anticipation of these changes, the formation of aggregates of compound **1** was investigated by dynamic light scattering at different pH (Table 2). At pH ≤ 7, the hydrodynamic radius (R_h) was in the range of 85−94 nm. For higher pH, an increase of the particle size was found. These data clearly indicated that an aggregation of chains occurred upon deprotonation of the ammonium groups in the polylysine side chains as the electrostatic repulsion became minimized.

UV−vis and PL characteristics of the brush polymer **1** in dependence on the ionic strength in solution are displayed in Figure 4. The ionic strength was adjusted by different concentrations of guanidine hydrochloride. Similar to the pH-dependent measurements, no shift of the absorption maxima at a wavelength of 370 nm and the emission band at 425 nm and its shoulder at 453 nm with increasing the ionic strength was found. While the intensity of the absorption band was slightly reduced, the fluorescence band decreased and broadened significantly. Again, the broadening of fluorescence was attributed to the formation of aggregates which were also found in DLS. It was assumed that, typical for polyelectrolytes,[20] the addition of salt shields the electrostatic repulsive forces causing the interchain aggregation.

No shift of λ_{max} and thus no conformational changes were found in the results of UV−vis and PL characteristics of polymer **1**. This behavior confirmed that the conformation of the π-conjugated poly(2,7-carbazole) backbone was independent of the pH and ionic strength and that conformational changes within the brush polymer were restricted to the flexible polyelectrolyte PLL side chain.

Morphological Investigations. Initial studies on the surface morphology of the polyelectrolyte brush polymer **1** were performed by AFM measurements to obtain structural information at the molecular level. Mica was chosen for polymer adsorption because its negatively charged surface becomes a multivalent counterion for the cationic PLL brushes.[48,49] Measurements displayed untextured wormlike particles which had a uniform height and width but a bimodal length distribution. While they possessed a width of around 3−5 nm and a height between 1 and 2 nm, the

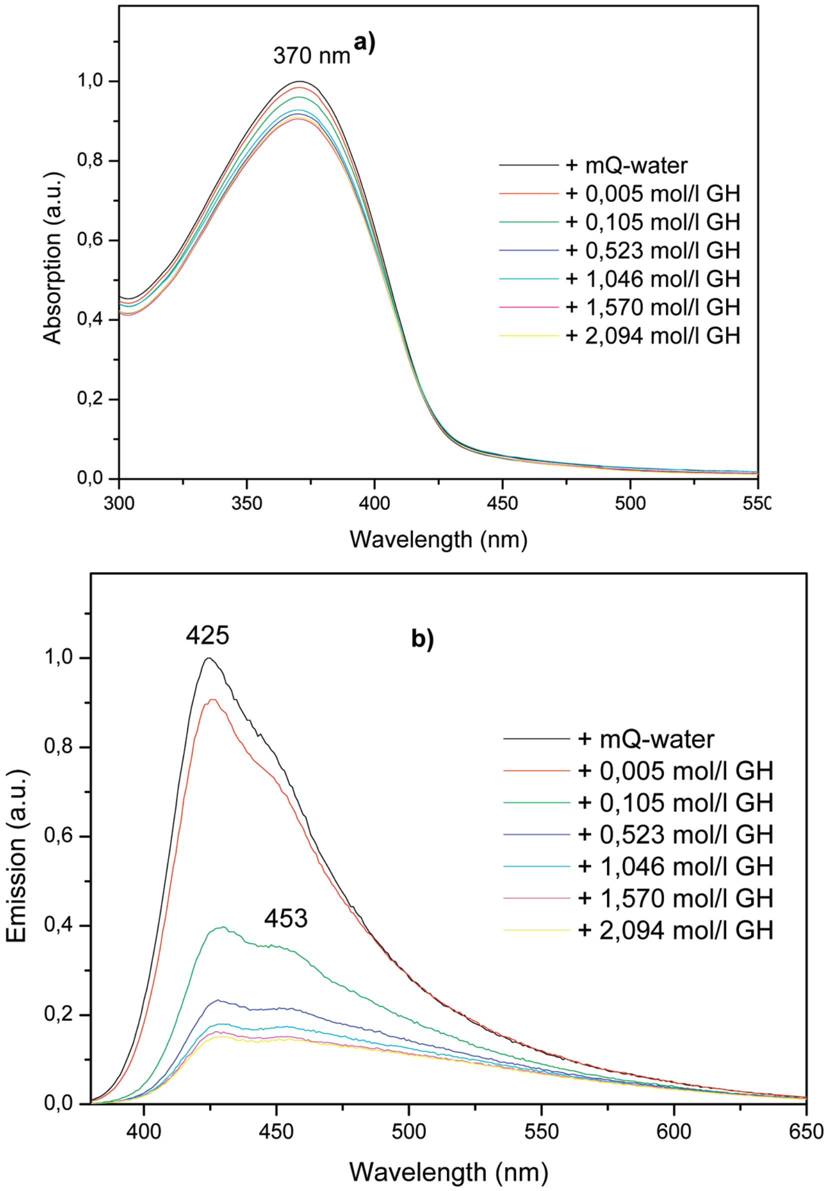


Figure 4. Optical properties of polymer **1** as a function of the ionic strength: (a) UV−vis spectra; (b) PL spectra (λ_{exc} = 370 nm) in water.

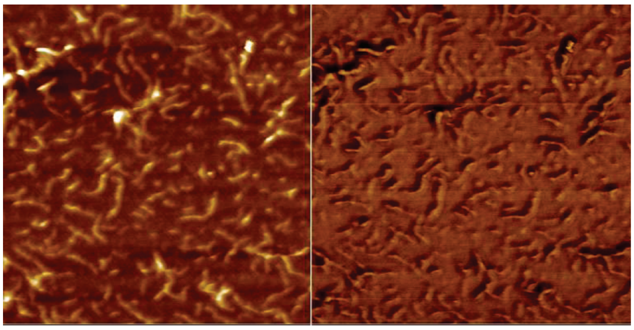


Figure 5. Tapping-mode AFM height (a) and phase (b) images (scan size 500 nm × 500 nm) of spin-coated (U = 2000 rpm, t = 2 min) polymer **1** on mica from mQ-water as solvent; $c_{polymer}$ = 0.5 mg/mL. Vertical scale is 8 nm.

larger particles had a length of about 50−100 nm and the smaller ones of ~20−30 nm (Figure 5).

The absence of textured aggregates proposed that no long-range organization[50−52] took place. Such behavior is also known for amphiphilic block copolymers where the thermodynamically controlled formation of micelles was kinetically locked by very polar solvents.[53] Thus, the observed result was attributed to the amphiphilicity of the polyelectrolyte brush polymer in context with the unsolubility of the hydrophobic compounds in water which immediately led to the formation of kinetically frozen aggregates.

Conclusion

A new type of amphipilic brush polymer which combines the properties of a conjugated polymer, a brush polymer, and a polyelectrolyte is presented. The structural design comprises a π-conjugated rigid 2,7-polycarbazole backbone substituted with pH-responsive flexible PLL and branched alkyl side chains. Typical polyelectrolyte behavior of the PLL side chain within the polyelectrolyte brush polymer was demonstrated by DLS. Circular dichroism in liquid and solid-state NMR proved the pH-dependent secondary structure of the PLL side chains. In liquid, the secondary structure only consisted of α-helix, while for measurements in solid state a mixture of α-helix/β-sheet was found. UV−vis and PL experiments clearly showed that conformational changes were restricted to the flexible PLL side chains while the polymeric backbone remained unaffected. Preliminary morphology studies demonstrated wormlike structures of the brush polymer. As these novel amphiphilic brush polymers are responsive to the ionic strength and pH in solution, they offer the opportunity to control the self-assembly just by an external stimulus. While at lower pH the brush polymers are completely dissolved, they can be aggregated and precipitated by altering the pH. The polymers will also be of interest as model compounds for studying the mechanical properties. While typically stiff polymers have high mechanical strength in the direction of the main chain, perpendicularly the properties are rather weak. It is expected that by the change from rod-*g*-coil to rod-*g*-rod polymers the interaction due to an interdigitation of the rigid combs will be enhanced, and a polymer material with improved mechanical properties, for example a higher Young modulus, can be expected.

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