Optically Active Spherical Polyelectrolyte Brushes with a Nanocrystalline Magnetic Core**

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The unique properties of magnetic nanocrystals have triggered intensive research towards their effective functionalization and application in many technological fields. Although synthesis of magnetic colloids is being thoroughly studied, there is limited knowledge on the synthesis, characterization, and properties of magnetic polyelectrolyte spherical brushes. In the present work, the preparation of such hybrids and the subsequent formation of stable aqueous colloids are described. The core of the spherical brush consists of a magnetic \( \gamma-\text{Fe}_2\text{O}_3 \) nanocrystallite (faceted but mostly spherical-like) with a mean diameter of 17 nm. The bioadhesive polyelectrolyte poly(sodium 4-styrene sulfonate), forming the surrounding brush layer, was proven to be an effective covalently modifying macromolecule for the iron oxide surface, as Fourier transform IR spectroscopy revealed. Several observations on colloidal aspects are discussed and are successfully explained by models and experiments describing polyelectrolyte brushes with a soft polymeric core. Finally, the hybrids exhibit their multifunctional character and their technological importance by combining in a single and soluble product with magnetic and nonlinear optical properties.

1. Introduction

Iron and its oxides are among the materials that mankind discovered and used for practical and cultural reasons thousands of years ago. On the other hand, nature itself has preceded us by millions of years, since well-defined iron oxide magnetic nanoparticles are biogenically formed in organisms such as magnetotactic bacteria, algae, bees, and pigeons. Despite the “age” of iron-based compounds they still provoke intensive research activity, especially in the context of expanding the functionalities of condensed matter. This has been achieved by confinement of their dimensions to the nanoscale regime and, subsequently, by modifying their surfaces with various molecular entities, thus imparting new functionalities and physicochemical properties.

As such, nanoparticulate iron oxides, and more specifically the ferrimagnetic \( \gamma-\text{Fe}_2\text{O}_3 \) (magnemite) and its close relative \( \text{Fe}_2\text{O}_4 \) (magnetite), pertaining to the present work, have been successfully synthesized and modified with a variety of synthetic routes and surface-capping agents. The latter ascribe to the nanoparticles solubility and (bio)chemical activity (binding properties, fluorescence, while size confinement effects dramatic changes in magnetic properties (onset of superparamagnetism and single magnetic domain particle behavior). Owing to the above properties, several applications have emerged in the fields of chemistry, materials science, biochemistry, and environmental remediation. For example, they are widely used in catalysis, in pigment and ink technologies, as gas and bio-sensors, in magnetoelectronics, lithium storage, magnetic storage media, and furthermore in hyperthermia or in magnetic targeting and...
separation processes in biological systems. In addition, iron-based nanoparticles (NPs) are very effective decontamination agents decontamination of water from toxic metals and organic pollutants. Particularly interesting are the non-linear optical properties of iron oxides and their application as magnetically controlled non-linear optical materials.

In the present work, the preparation of a multifunctional nanohybrid material is reported, based on polyelectrolyte spherical polymer brushes with a nanocrystalline magnetic core. The strong polyelectrolyte poly(sodium 4-styrene sulfonate) (hereafter abbreviated as NaPSS) was found to be an effective covalently modifying macromolecule for the iron oxide surface, resulting in stable magnetic hydrosols (aqueous ferrofluids). The multifunctional character of the present hybrid spherical brushes stems from the combination of the properties of the metal oxide core and with those of the polymeric organic sheath. NaPSS, carrying an abundance of sulfonate anionic sites, imparts high solubility to the inorganic magnetic nanoparticles, antagonizing successfully the van der Waals and dipole/exchange magnetic interactions of the colloidal particles by means of both electrostatic and steric repulsive forces. Because of the same sites, it displays specific and non specific binding properties, rendering it bio-adhesive, plus it is a nontoxic but antimicrobial agent. On the other hand, the inorganic core is a ferrimagnetic material, readily responding to any external magnetic stimuli and furthermore it displays high non-linear optical susceptibility.

Structural characterization of the nanohybrid is elaborated by means of a variety of techniques and its colloidal, magnetic, and optical properties are also investigated with the final goal of gaining further knowledge and perspective towards the fabrication of such or similar nanostructures and contributing to contemporary research of materials suitable for applications such as those described previously. A central point of this work concerns the first experimental substantiation of these hybrids’ structural identity. It is shown that their behavior is successfully described by models and experimental results describing polyelectrolyte spherical brushes with a soft polymeric core. Furthermore, electron energy loss spectroscopy (EELS) mapping of the product provides factual evidence of the spherical-like brush formation.

2. Results and Discussion

2.1. Comments and Results on the Synthesis

Considering the synthetic routes towards production of magnetic iron oxide colloids (ferrofluids), the aqueous alkaline precipitation is a convenient and widely used approach. It is simple, cost effective, and falls within the concepts of green chemistry. On the other hand, routes involving thermolysis of organic iron precursors in high-boiling-point organic solvents are superior as far as the polydispersity of the produced particles is concerned. Particularly regarding the aqueous co-precipitation method, the general chemical path for magnetite formation concerns mixing of stoichiometric quantities of ferrous and ferric salts in a basic medium according to the formula:

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$$ (1)

which takes place in inert atmosphere conditions in order to avoid ferrous ions oxidation of the ferrous ions. Nevertheless, as will be shown, the equally strong, from the magnetic properties point of view, and more stable upon oxidation maghemite can be also formed by wet oxidation of a single ferrous molecular precursor under environmental conditions. In the present work, maghemite formation takes place after the initial formation of green ferrous hydroxides (and o xo-hydroxides) through solution reconstructive transformation, dehydration, and condensation reactions. A simplified path could be possibly described as follows:

$$2\text{Fe}^{2+} + 2\text{OH}^- + x\text{H}_2\text{O} \rightarrow \text{Fe}^{2+}(\text{OH})_2 \cdot (\text{H}_2\text{O})_x$$ (2)

Subsequent peptization and surface modification of the nanoparticles (in the case of Reaction 1) usually takes place by a post-reaction treatment or by in situ growth of the magnetic particles in the solution of a suitable monomeric or polymeric capping agent. Of course, depending upon their hydrophilic or hydrophobic nature, hydrosols or organosols can be obtained. Of particular interest is the preparation of aqueous ferrofluids owing to their biomedical applications but also because of the environmentally friendly synthetic approaches. Polyelectrolyte molecules fall within the category of polymeric coatings that can induce high hydrophilicity to the surfaces they bind. Interesting paradigms have appeared in the literature regarding magnetic–polyelectrolyte hybrid colloids. Nevertheless, the structural characteristics of the solvated hybrids are not clear, regarding, for example, whether it is a brush-type arrangement or a polymer wrapped around the core (Fig. 1).

Specifically concerning the preparation of polyelectrolyte brushes with a soft polymeric core and their properties the work by Haryharan et al. and Ballauf et al. should be

Figure 1. Two different types of polymer stabilized particles: a) polymer brush type and b) wrapped polymer type arrangements.
referenced, where macromolecules are adsorbed or grown in situ (“grafting to” and “grafting-from” technique\[28\]) on polystyrene latex nanoparticles of 100 nm diameter. On the other hand, work on hybrid organic–inorganic polyelectrolyte brushes is limited\[29\] or refer to non-aqueous and non-polyelectrolyte systems.\[30\]

In the present case, the polyelectrolyte of NaPSS was selected and the reaction progress was initially monitored with dynamic light scattering (DLS). The starting NaPSS salt-free solution shows a z-average hydrodynamic diameter $D_H = 7.4$ nm (Fig. 2a) ascribed to the blobs of the macromolecules\[31\] with a polydispersity index $P_dI = 0.21$. This value agrees well with other measurements of $D_H = 10$ nm for salt-free solutions of the same $M_w$ polyelectrolyte.\[32\] After the end of the reaction, nanoparticle formation, isolation, and re-suspension of the magnetic hybrids the $D_H$ increased to 113 nm\[33\] with a polydispersity index of 0.18, as estimated from the monomodal distribution shown in Figure 2b. Even after the final centrifugation of the product (see Experimental), only a minor quantity had sedimented. A diluted clear aqueous solution of the product (PSS-Mag) is shown in the right part of Figure 2, where the addition of concentrated HCl testifies the presence of iron-bearing particles by the decoloration of the dark brown solution to the characteristic yellow color of hydrated ferric complexes, released after acidic dissolution of the iron oxide crystallites. In addition, the X-ray diffraction (XRD) pattern of the dried material corresponds to the inverse cubic spinel structure of maghemite or magnetite. It is amply noted that the blank sample (FeO$_x$) displays no solubility in water and precipitates within minutes; post-reaction treatment of FeO$_x$ with NaPSS does not result in a stable colloid either. This observation indicates the importance of the polyelectrolyte co-presence during nanocrystallite growth and formation. That is, the successful synthesis of the present hybrid brushes is not based on a post-reaction adsorption step.

Another point that merits attention is that the procedure of acidic peptization and treatment with tetramethylammonium hydroxide for the preparation of stable sols of magnetite, after co-precipitation of Fe$^{+2}$/Fe$^{+3}$ upon NaOH addition (often noted as the Massart’s method\[19\]), is not successful in the case of Reaction 2. The co-precipitation path takes place in a subsecond time interval, while maghemite formation from a single ferrous precursor proceeds for several minutes (ca. 30 min, depending on temperature) through intermediate products of ferrous hydroxides. These observations underline the different mechanisms and nature of the two reaction paths and products respectively.

The UV-vis absorption spectrum of the soluble product (PSS-Mag) was recorded at various concentrations. A reference equation was obtained for facile concentration measurements of the ferrofluids, where the characteristic bands of NaPSS were evident. The broad band with a maximum at approximately 350 nm should be attributed to the iron oxide nanoparticles presence. The same band has been detected by other groups regarding thin films containing $\gamma$-Fe$_2$O$_3$ nanoparticles.\[34\] The colloids are optically clear as demonstrated in the inset of Figure 3b, where the scale numbers of the cylindrical vials lie on their back side.

2.2. Microscopy Results

Atomic force microscopy (AFM) measurements on a glass slide after evaporation of one drop of a dilute unsalted PSS-Mag suspension show the presence of spherical-like nanoparticles (Fig. 4a), in immediate antithesis to the practically featureless microscopy image of neat NaPSS (Fig. 4b). A mean value of ca. 36 nm is obtained from the height distribution function of the PSS-Mag image area, while the respective for the pure polymer is ca. 4.5 nm. The value of 36 nm could be possibly interpreted as a mean...
particle height, that is, the iron oxide core height plus the polyelectrolyte sheath thickness in the dehydrated conditions of the AFM measurement, under which the macromolecules are expected to contract closer to the oxide surface. On the other hand, the lateral particle size distribution histograms from two different regions of the sample display a mean diameter of 90 nm (see Supporting Information). Such large discrepancies in the vertical height vs. lateral diameter in the AFM micrographs could not be solely justified in terms of the tip surface convolution, although they are very commonly observed in the characterization of spherical polymer brushes.[27b,30b]

A very possible cause for the increased lateral diameter may be the polyelectrolyte molecules adsorption on the surface of the glass substrate during the drying process, which is schematically described in Figure 5a. Therefore, the macromolecules, instead of wrapping around the inorganic core during drying, attain a more or less flat orientation over the substrate surface. It is well known that, especially in the presence of attractive electrostatic forces, the flat adsorption of polyelectrolytes is greatly favored.[35] In the present case electrostatic forces may also be present because of triboelectric effects because, generally, glass surfaces easily get positively charged.

It is also worth commenting on the shape of the particles, which depends on whether or not they contact neighboring ones. In the inset of Figure 4a it is clearly observed that particles’ shape is modified when they assemble with neighboring ones, while free-standing particles attain a more spherical shape. The apparent change of the shape can be explained adopting the same model described above (polyelectrolyte adsorption on the glass substrate). In Figure 5b a graphical explanation for such arrangements is shown, corroborating the experimental results.

The characterization of the hybrid’s inorganic core was performed by transmission electron microscopy (TEM). The particles formed are relatively polydisperse in size (standard deviation $\sigma = 0.21$), with a mean value of 17 nm estimated from the log-normal distribution fitting, as shown in the inset of Figure 6a. High-resolution (HR-)TEM analysis, shown in Figure 6b, revealed that each particle constitutes a single nanocrystallite, evidenced by the consistent pattern of the lattice fringes and by the fast Fourier transform image produced from the latter. The $d$-spacing values of 2.53 Å and 2.96 Å are typical of the (311) and (022) lattice spacings for maghemite’s ($a = b = c = 8.3300$ Å, $\alpha = \beta = \gamma = 90^\circ$) or magnetite’s ($a = b = c = 8.3200$ Å, $\alpha = \beta = \gamma = 90^\circ$) unit cell. Although organic capping could not be visualized in TEM images, insight to this matter was provided by performing EELS mapping on the micrograph of Figure 6c. Using the $L_2,3$ edge and the three-window method,[36] the image of Figure 6d was obtained with the gray/white areas corresponding to sulfur that NaPSS contains. (see Supporting Information for an increased size of the image, where sulfur-containing areas are better resolved) The surrounding veil of sulfur,
expanding more than 20 nm away from the particles’ surface, is a direct proof for the polyelectrolyte brush formation and supports the adopted configuration of the dried nanobrushes described in the AFM part.

2.3. Thermal Analysis Results

In order to calculate a mean polyelectrolyte grafting density per particle of iron oxide, dried PSS-Mag and NaPSS were subjected to thermogravimetric analysis in normal air and humidity conditions. The thermogravimetric response of the hybrid (provided in the Supporting Information) reveals 2.5 wt % humidity presence, 12 wt % NaPSS, and 85.5 wt % iron oxide content in the hybrid polyelectrolyte brushes.

The thermal analysis results were verified by chemical analysis, from which a 6 wt % carbon content was found. In order to interpret carbon wt % content into polymer wt % content, a calculation of the carbon content of the NaPSS macromolecule was performed based on the monomer unit shown in Figure 7a (the sulfonation degree of the polyelectrolyte is 80%). The monomer’s molecular weight is 928.9 with elemental wt % contents: C: 51.7%, H: 3.9%, Na: 9.9%, and S: 13.8%. Therefore, the polymer mass that corresponds to 6 wt % carbon is calculated at 11.6%. That is, the results from thermal and chemical analysis are practically identical and can be safely used for further calculations.

From the data above, the number of grafted polyelectrolyte chains per inorganic particle can be estimated for a sample of 100 g, using the following formula:

\[ N = \frac{A_{PSS}}{A_{FeOx}} = \frac{m_{PSS}}{m_{FeOx}} = \frac{n_{NaPSS} \cdot M_{w}}{N_{A} \cdot d_{FeOx} \cdot 2^{\frac{3}{2}} \pi^{\frac{1}{2}}} \]

where \( N \) is the number of NaPSS chains per particle, \( A_{PSS} \) and \( A_{FeOx} \) are the numbers of NaPSS individual macromolecules and nanoparticles in the sample, \( m_{PSS} \) and \( m_{FeOx} \) are the total masses of the polymer and the inorganic phase corresponding to \( A_{PSS} \) and \( A_{FeOx} \) respectively, \( m_{NaPSS} \) and \( m_{FeOx} \) are the masses of one macromolecule of NaPSS and one particle of iron oxide, \( N_{A} \) is Avogadro’s number, \( d_{FeOx} = 5.2 \text{ g cm}^{-3} \) is the iron oxide density, and \( \pi \) is the mean particle radius as estimated from TEM results. The calculation result is 17.6 or by average 18 polyelectrolyte macromolecules are attached on every single inorganic particle.

According to Figure 7a, the contour length of the macromolecule is 90.5 nm, in agreement with molecular dynamic simulations, while the radius of gyration \( (R_g) \) from the same simulations was estimated at ca. 26 nm. Considering that \( R_g \) is an average measure of the size of the macromolecule, taking into account its conformation in the solution, then the full length in solution could be approximately 52 nm. These numbers agree well with the experimental mean hydrodynamic diameter of the present polyelectrolyte brushes of 113 nm, schematically described in Figure 7b. It is amply noted that this scheme does not aim to a pragmatic representation of the polymer’s configuration, but to a simple approximate visualization of the basic structural unit of the product. In the Supporting Information a dis-

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**Figure 5.** a) Schematic representation of the drying and deposition of PSS-Mag particles onto a glass substrate, and b) graphical explanation of the AFM patterns observed on adjacent particles.

**Figure 6.** a) TEM image of PSS-Mag. Inset: log-normal distribution function of the particle diameters as obtained from TEM results. b) HR-TEM of the darker nanocrystallite shown on the right part of the previous image and its fast Fourier transform image. c) TEM image of the area where EELS mapping was performed, and d) EELS mapping on the PSS-Mag sample, with the gray/white spots corresponding to sulfur.
discussion is available concerning the probability of existence of the proposed basic structural unit.

In addition, for the case of dense polyelectrolyte brushes, the energy penalty from the high osmotic pressure and the steric interactions inside the brush layer is counterbalanced by polymer chain expansion. Hence, the brush thickness would be normally expected to be somewhat higher than just the double of the $R_g$ of the unbound solvated polymer, unlike the present case. The calculated low grafting density of 0.02 chains nm$^{-2}$, which is significantly lower compared to the respective of 0.1 chains nm$^{-2}$ for NaPSS brushes grown from 100 nm latex particles$^{[27a]}$ provides an explanation on the above matter. Indeed, Hariharan et al.$^{[26]}$ have reported that brush layer thickness was substantially decreased upon lowering the grafting density of polymer chains.

### 2.4. Interactions between PSS and Inorganic Particles

It is well-known that iron oxide particles carry surface hydroxyl groups, imparting a pH-dependent surface charge density.$^{[15b,24]}$ In acidic mediums the charge is positive, evidenced by a positive zeta-potential value and turns negative at basic pH owing to deprotonation of the hydroxyl groups. That is, during particle growth, both polyelectrolyte macromolecules and iron oxide particles are negatively charged, leading to a mutual electrostatic repulsion.

Confronted with this problem, Fourier transform (FT-)IR measurements were carried out on the product. Sulfonate group (SO$_3^-$) stretching vibrations of the NaPSS give rise to characteristic absorption bands in the region of 1000–1300 cm$^{-1}$ which can be exploited for the detection of any changes of the sulfonate anion environment and, in this case, for any interactions with the iron oxide surface. Nevertheless, FT-IR spectra of NaPSS and PSS-Mag were identical in that region. It appears that the sulfonate groups of the NaPSS chains in the final product (or the vast majority of them) are in the same state as in neat NaPSS. This is sufficiently explained by considering the spherical brush model, where the polymer chain is partly attached to the solid surface of the particle and therefore only a very small fraction of the sulfonate groups interact with it, while the rest of the macromolecule extends towards the solvent. A hypothesis for successfully probing of the nature of the interactions was that the synthesis of PSS-Mag in a very low ratio of PSS/Fe$^{3+}$ would offer access to more sulfonate groups of the same macromolecule to the

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**Figure 7.** a) Monomer unit of poly(sodium 4-styrene sulfonate) ($M_w = 70000$) on the basis that the sulfonation degree is 80% ($M_w$ of the monomer $= 928.9$ g). b) An approximate graphical representation of the basic structural unit of PSS-Mag spherical hybrid brushes, displaying a central iron oxide nanoparticle with 18 grafted polyelectrolyte chains. The 121 nm diameter, based on the theoretical $R_g$ of 70000 NaPSS, is in reasonable accord with the experimental value of 113 nm.

**Figure 8.** A) FT-IR absorption spectra in the region of sulfonate group stretching vibrations of a) neat NaPSS macromolecules ($\nu_1$, $\nu_2$, $\nu_3$, $\nu_4$ are the sulfonate group bands and the asterisk (*) is the phenyl ring band), b) PSS-5Mag, c) PSS-7Mag, and d) PSS-10Mag hybrid materials. B) a) $\cdot$: experimental spectrum of neat NaPSS, $\cdot$: deconvoluted subspectra ascribed to sulfonates, $\cdot$: deconvoluted subspectra ascribed to H$_2$O, b) $\cdot$: experimental spectrum of PSS-10Mag, $\cdot$: deconvoluted subspectra ascribed to sulfonates, $\cdot$: deconvoluted subspectra ascribed to adsorbed sulfate (SO$_4^{2-}$) ions and $\cdot$: experimental spectrum of FeO$_x$. 

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particles' surface. Indeed, the above hypothesis was confirmed by the synthesis of three PSS-Mag products with increasing iron content. The interactions of the sulfonate groups with surface iron atoms are reflected by the progressive change of the $v_3$ and mainly $v_2$ vibration, shown in Figure 8A(a–d).

More specifically, in Figure 8A four spectra are presented starting with neat NaPSS. The sulfonate group vibration modes attached to the phenyl ring of the hydrophobic backbone of NaPSS give rise to mainly four absorption bands. Two broad antisymmetric stretching bands ($v_4 = 1236 \text{ cm}^{-1}$ and $v_3 = 1183 \text{ cm}^{-1}$) and two sharp symmetric ($v_2 = 1125 \text{ cm}^{-1}$ and $v_1 = 1038 \text{ cm}^{-1}$).[44] The band at 1009 cm$^{-1}$ is ascribed solely to the phenyl ring vibration. The differences observed in the spectra as the ratio of PSS/FeOx decreases are focused in the region of the antisymmetric bands and mainly in the band at 1236 cm$^{-1}$, which displays a considerable decrease in intensity and a red-shift to lower wavenumbers. These changes are better revealed after the deconvolution of the spectra shown in Figure 8B. On the bottom, the five bands of NaPSS (solid curves) are clearly resolved along with two bands (● dotted curves) from water presence.[44] In the upper spectrum, NaPSS bands are indicated by the solid Lorentzian curves as well. The $v_2$ band has now shifted from 1236 cm$^{-1}$ to 1215 cm$^{-1}$ and its relative intensity to the other sulfonate group bands has considerably decreased. In addition the $v_3$ band is also red-shifted by 10 cm$^{-1}$, which is clearly observed in Figure 8A as well. This observation is indicative of the S=O bond strength loss and partial electron density displacement due to the formation of another bond, most probably an S=O–Fe type bond. The rest Lorentzian (Δ) curves are attributed to sulfate groups adsorbed by the iron oxide nanoparticles due to the iron source precursor [(NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O], which can occupy external and internal surfaces of the inorganic nanoparticles.[45] This is further verified by the spectrum of the neat iron oxide (FeO$_x$, grey solid line) superimposed on the other spectra of Figure 8B(b). FT-IR results have been reported in the literature[46] regarding chemical bonding of a sulfonated dye to surface Ti$^{IV}$ atoms from TiO$_2$ nanoparticles, revealing similar band changes. Finally, hydrogen bonding is also expected to take place between the sulfonate group oxygen atoms and the hydroxyl groups of the nanoparticles because such interactions have been very well established between sulfonate-bearing anionic surfactants[44,47] and the hydroxyl groups of Al$_2$O$_3$ surfaces. In these cases, red-shift of the antisymmetric stretching vibrations is also observed to a lesser extent, but there is not such a pronounced decrease in their relative intensity. For these reasons, it is believed that chemical bonding participates in the grafting mechanism of NaPSS molecules onto the iron oxide surfaces.

### 2.5. Colloidal Behavior of the Hybrids

The effective surface charge of the hybrids (zeta potential), along with their $z$-average intensity-weighted hydrodynamic diameter, were measured in relation to pH and ionic strength (NaCl concentration) increase for a colloidal PSS-Mag sol. The zeta-potential ($\zeta$) value of $-40$ mV in salt-free distilled water indicates the high colloidal stability of the product (generally $\zeta$ values of $\geq 30$ mV denote adequate electrostatic repulsion to provide stability to the colloidal particles). The negative potential of the brushes and, more importantly, its stability upon pH changes, as shown in Figure 9a, is indicative of particles that carry permanent negatively charged chemical groups on their surface. Notably, unmodified iron oxide particles, display very different surface charge behavior,[138] as previously discussed. The small $\zeta$ absolute value increase upon further NaOH addition is mainly attributed to the ionic strength increase rather than to the pH of the solution, as will be following discussed.[48] The particles’ hydrodynamic diameter, after a certain amount of NaOH addition, starts growing up exponentially due to the eventual charge screening of the polyelectrolyte sulfonate groups and subsequent aggregation, which was also visually manifested by the increasing turbidity of the suspension and its final sedimentation.

Turning to the salt-concentration-dependent measurements in Figure 9b, some of the observations mentioned previously are repeated in a greater scale. The $\zeta$ absolute value increase could be justified by a stabilizing electrical double layer formed between the negatively charged brush layer and the surrounding sodium cations. This observation is rather in agreement with the main features of polyelectrolyte brushes. More specifically, the strong confinement of the polyelectrolyte’s counterions within the brush layer[49] gives rise to increased interlayer osmotic pressure. Thus, the initial added cations, not being able to enter the brush layer due to its high osmotic

![Figure 9. Colloidal behavior of the polyelectrolyte brushes a) upon pH, and b) upon salt (NaCl) concentration increase.](image-url)
pressure, result in an increased Na\textsuperscript{+} concentration at the borderline of the brush rim and, consequently, to the $z_p$ rise. It is noted that the $|z_p|$ rise upon ionic strength increase distinctively differs from “classical” colloidal particles, where $|z_p|$ decreases at higher ionic strengths.\cite{50} Not only until osmotic pressure difference is smeared out, (at $C_{NaCl} \approx 0.035 \text{M}$) the external sodium cations can enter into the brush layer, where the system crosses from that point forward the salted brush regime,\cite{51} and collapse of the brush layer takes place. The latter is well manifested by the abrupt rise in $D_H$, shown in Figure 9b, signaling aggregation because of the elimination of the steric and electrostatic stabilizing interactions formerly induced by the polyelectrolyte sheath.

The above described model of the hybrid’s behavior is in accordance with models describing spherical polyelectrolyte brushes, further substantiating the proposed structure of the present hybrids. In the work by Rühle et al.\cite{52} also described in Ref. [49], such a sudden collapse has also been observed. Matsuoaka et al.\cite{53} have also reported abrupt changes in the planar polyelectrolyte brush length observed by X-ray reflectivity, which could only be explained on the basis that added ions cannot enter the brush layer at salt concentrations below a critical value of 2 M. In the present study the critical concentration was found significantly lower (ca. 0.035 M), which is expected because of the lower polyelectrolyte grafting density of 0.02 chains nm\textsuperscript{-2} compared to the 0.23 chains nm\textsuperscript{-2} calculated for the planar NaPSS brushes.

2.6. Optical Properties

The nonlinear optical (NLO) properties of the PSS-Mag nanoparticles were investigated using the Z-scan technique. The experimental details of the technique and the procedure followed for the analysis of the Z-scan data have been presented in detail elsewhere.\cite{54,55}

Several “open” and “closed” aperture Z-scans, together with the corresponding “divided” Z-scans resulting from the division of the “closed” by the “open” aperture trace respectively, were obtained for each sample at different incident laser energies. Figure 10 shows as an example the Z-scan measurement of a 0.052 wt % PSS-Mag sample obtained at laser energy of 3.3 $\mu$J (i.e., $I_0 = 40 \text{ MW cm}^{-2}$). As can be seen in this figure, the “closed” (Fig. 10b) and “divided” (Fig. 10c) Z-scans were found to exhibit a transmission peak followed by a post-focal minimum (that is, a peak–valley configuration) indicative of the defocusing behavior of the sample, whereas the “open” aperture curve in Figure 10a was found to exhibit transmission peak near the focus, revealing saturable absorption behavior.

The same trend was found for all other samples studied. Under the same experimental conditions, measurements carried out for distilled water and neat polyelectrolyte NaPSS did not reveal any NLO response, indicating that the observed response was arising solely from the iron nanoparticles.

From the fitting of the divided Z-scan data with the following equation:\cite{54}

$$ T = 1 - \frac{4\Delta\Phi_0 x}{(x^2 + 9)(x^2 + 1)} $$

the on-axis nonlinear phase shift at the focus $\Delta\Phi_0$ was obtained, which is related with the nonlinear refractive index parameter ($\gamma'$) through the following relation:

$$ \Delta\Phi_0 = kI_0\gamma'/L_{\text{eff}} $$
The nonlinear refractive index parameter \( \gamma' \) (m\(^2\) W\(^{-1}\)) and the nonlinear refractive index \( n_2 \) (esu) (defined through equation: \( n = n_0 + \frac{n_2}{2} |E|^2 = n_0 + \gamma'I \)) are related through the following relation\(^{[54]}\):

\[
n_2(\text{esu}) = \left( \frac{c(m^{-1})n_0}{40\pi} \right) \gamma'(m^2 W^{-1})
\]

where \( c \) (m \( s^{-1} \)) is the speed of light in vacuum and \( n_0 \) is the linear index of refraction. The nonlinear absorption coefficient, \( \beta \) (m W\(^{-1}\)) was then deduced from the “open” aperture Z-scan data by fitting them according to the following equation:

\[
T = \sum_{n=0}^{\infty} \left( \frac{-\beta I_0 L_{\text{eff}} / (1 + c^2z^2/\omega_0^2) - \beta I_0 L_{\text{eff}}}{(m + 1)^{3/2}} \right)
\]

where \( T \) is the normalized transmittance, \( L_{\text{eff}} = (1 - \exp(-a_0 L))/a_0 \) is the effective thickness of the sample, \( a_0 \) is the linear absorption coefficient of the sample at the laser excitation wavelength, and \( I_0 \) is the on-axis irradiance at the focus.

Then, the real and imaginary parts of the third-order nonlinear optical susceptibility, \( \chi^{(3)} \), were obtained using the following relations:

\[
\text{Re}\chi^{(3)}(\text{esu}) = \frac{10^{-6}c^2n_0^2}{480 \pi^2} \gamma' \left( \text{cm}^2 \text{W}^{-1} \right)
\]

\[
\text{Im}\chi^{(3)}(\text{esu}) = \frac{10^{-2}c^2n_0^2}{96 \pi^2 \omega} \beta \left( \text{cm} \text{W}^{-1} \right)
\]

where \( c \) is the speed of light in cm \( s^{-1} \) and \( \omega \) is the fundamental frequency in cycles \( s^{-1} \).

The determined values of the third-order nonlinear optical susceptibility were found to be quite large and increasing linearly with the concentration, reaching a value of \((6.48 \pm 1.40) \times 10^{-12}\) esu for a 0.052 wt % concentration solution which was the largest concentration used in these experiments. Similarly, it was found that the \( \text{Re}\chi^{(3)} \) and \( \text{Im}\chi^{(3)} \) were increasing linearly with concentration both exhibiting negative sign (i.e., corresponding to defocusing and saturable absorption respectively). The values of the \( \text{Re}\chi^{(3)} \) and \( \text{Im}\chi^{(3)} \) were found to be \(-5.38 \pm 1.24) \times 10^{-12}\) esu and \(-3.60 \pm 0.66) \times 10^{-12}\) esu respectively for the 0.052 wt % concentration solution. The corresponding nonlinear refractive index \( n_2 \) and nonlinear absorption parameter \( \beta \) can then be calculated: \( n_2 = -1.51 \pm 0.35) \times 10^{-10}\) esu and \( \beta = -7.52 \pm 1.37) \times 10^{-10}\) m W\(^{-1}\).

Guo et al.\(^{[56]}\) have reported a \( \chi^{(3)} \) value of \( 10^{-13}\) esu for 4 nm diameter \( y\)-Fe\(_2\)O\(_3\) sols. In another study,\(^{[16]}\) the third-order susceptibility of 30 nm \( y\)-Fe\(_2\)O\(_3\) nanoparticles having been measured by means of the third-harmonic generation technique (THG), was found to be \( 2.1 \times 10^{-11}\) esu. That is, the \( \chi^{(3)} \) value of the present hybrid (ca. \( 6.5 \times 10^{-12}\) esu) with 17 nm mean \( y\)-Fe\(_2\)O\(_3\) diameter is found to be in between the previously reported values for 4 and 30 nm particle diameter. Such observations prompt for a more systematic investigation on the nonlinear properties in relation to the size of the iron oxide particles.

2.7. Magnetic Properties and Mössbauer Results

To get a deeper understanding of the structural, phase, and magnetic properties of the hybrid brushes, magnetic and Mössbauer measurements have been performed. The hysteresis loop, recorded at 2 K and shown in Figure 11, exhibits 300 Oe coercivity and 12.8 emu g\(^{-1}\) remnant magnetization, indicating that the magnetic moments of the individual complex particles behave cooperatively, which is outwardly manifested by an ordered state of the investigated system. The coercivity parameter is in the range reported for ferrimagnetic bulk maghemite and/or magnetite, as both phases exhibit similar values of the magnetocrystalline anisotropy constant due to the almost identical crystallographic structure they possess. However, the saturation magnetization \( M_s \) of the PSS-Mag sample (\( \approx 71\) emu g\(^{-1}\), after subtraction of the non-magnetic fraction) is somewhat lower that that of the bulk.
phases (≈ 80 emu g⁻¹ for maghemite and ≈ 90 emu g⁻¹ for magnetite). This reduction of the $M_s$ is utterly common in the nanosized systems and it is generally explained as a result of the small size of the particles and the presence of magnetically inactive surface, that is, the polymer’s functional groups bound to the surface of the magnetic cores. As the temperature increases, the area of the hysteresis loop progressively gets smaller (Fig. 11) and at 298 K the coercivity is approximately 68 Oe. The coercivity decrease at higher temperatures is attributed to the superparamagnetic behavior of the assembly of the hybrid brushes, when temperature gets sufficiently high. At this point, the thermal energy, associated with the fluctuation of the direction of the particle’s magnetic moment between orientations of the easy axes of material’s magnetization, becomes comparable or higher than its anisotropy energy, the latter holding the moment fixed (i.e., blocked) at one particular direction over the whole time scale of the measurement (i.e., $10^7$ s for magnetic measurement) [57]. Since the temperature, known as blocking temperature, above which particles start to be superparamagnetic depends on their size distribution, a blocking temperature distribution is also expected. The fact that the system is not totally superparamagnetic at 298 K can thus be connected with such a blocking temperature distribution, implying that the larger hybrid brushes fraction is still blocked at this temperature. The presence of interparticle magnetic interactions, which has not been unambiguously excluded, may also influence the blocking phenomenon, preserving it to higher temperatures. One should note that the saturation magnetization is reached at relatively low applied magnetic fields (at approximately 10 kOe). On further increase of the magnetic field, the magnetization remains constant as all magnetic moments within the magnetic carrier unit point to the direction of the applied magnetic field. This behavior together with the results of in-field Mössbauer analysis (vide infra) confirms that the synthesized particles do not possess any surface spin canting and disorder. Such characteristics, along with the negligible remnant magnetization (1 emu g⁻¹) and coercivity (68 Oe) at room temperature, impart to the products properties desirable for many practical applications, where strong magnetic signal at small applied magnetic fields is required (e.g., hyperthermia, magnetic separation techniques, drug targeting) [58].

The Mössbauer spectra, collected at room temperature in zero applied magnetic field and at 150 K under 5 T are depicted in Figure 12. The hyperfine parameters, derived from the fitting of the experimental data, are listed in Table 1. At room temperature, the Mössbauer spectrum consists of 4 components. The three sextets belong to the particles which are blocked at room temperature whereas the doublet component is characteristic of the superparamagnetic behavior of the smaller particles [59]. The coexistence of the sextets and the doublet is a common manifestation of systems possessing a size distribution, as in our case. The detailed analysis of the sextets’ hyperfine parameters reveals that the local Fe³⁺ environments differ. The isomer shift of the sextet with a value of 0.31 mm s⁻¹ is almost typical for the overlapped tetrahedral and octahedral positions of maghemite structure as well as near the value corresponding to Fe³⁺ ions in the tetrahedral positions of the magnetite structure. The values of the isomer shifts for the two other sextets (≈ 0.45 mm s⁻¹) are far from those of pure magnetite (≈ 0.67 mm s⁻¹) but somewhat higher than those mentioned for maghemite, indicating a small presence of divalent iron ions. Thus, we assigned those atoms as being Fe²⁺/Fe³⁺ ions in octahedral positions of the spinel structure. This conclusion is further supported by hyperfine magnetic fields of the tetrahedral and octahedral sextets that are lower for maghemite but closer to magnetite [60]. Regarding the hyperfine magnetic field of the third sextet, its lower value (≈ 39 T) than that for the other ones should be attributed to the significant portion of iron atoms located at the surfaces of the nanoparticles, for which reduced hyperfine fields are generally observed and to the fraction of the medium sized particles that are not relaxing fast enough in order to give rise to a typical superparamagnetic doublet [60].

In order to get a deeper insight into the structure of the magnetic cores, the Mössbauer spectrum at 150 K and under an
Table 1. Hyperfine parameters of Mössbauer spectra recorded at 298 and 150 K without and with an external magnetic field of 5 T, respectively [a].

<table>
<thead>
<tr>
<th>Temperature/External field</th>
<th>Component</th>
<th>δ [mm s⁻¹]</th>
<th>ΔE_Q [mm s⁻¹]</th>
<th>ε_Q [mm s⁻¹]</th>
<th>B [T]</th>
<th>RA [%]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 K/0 T</td>
<td>doublet</td>
<td>0.34</td>
<td>0.81</td>
<td>–</td>
<td>–</td>
<td>20</td>
<td>SP fraction</td>
</tr>
<tr>
<td></td>
<td>sextet 1</td>
<td>0.31</td>
<td>–</td>
<td>–0.01</td>
<td>48.3</td>
<td>25</td>
<td>tetrahedral Fe³⁺</td>
</tr>
<tr>
<td></td>
<td>sextet 2</td>
<td>0.47</td>
<td>–</td>
<td>0</td>
<td>45.0</td>
<td>38</td>
<td>octahedral Fe⁴⁺/²⁺</td>
</tr>
<tr>
<td></td>
<td>sextet 3</td>
<td>0.45</td>
<td>–</td>
<td>0.06</td>
<td>39.7</td>
<td>17</td>
<td>octahedral Fe⁴⁺/²⁺</td>
</tr>
<tr>
<td>150 K/5T</td>
<td>sextet 1</td>
<td>0.32</td>
<td>–</td>
<td>0</td>
<td>52.1</td>
<td>21</td>
<td>tetrahedral Fe³⁺</td>
</tr>
<tr>
<td></td>
<td>sextet 2</td>
<td>0.54</td>
<td>–</td>
<td>0.01</td>
<td>45.3</td>
<td>79</td>
<td>octahedral Fe⁴⁺/²⁺</td>
</tr>
</tbody>
</table>

[a] δ = isomer shift (with respect to α-Fe, δ±0.01), ΔE_Q = quadrupole splitting (±0.01), ε_Q = quadrupole shift (±0.01), B = hyperfine magnetic field (±0.3), RA = relative spectrum area (±1), SP = superparamagnetic.

The external magnetic field of 5 T has been measured. This temperature was selected in order to avoid the Verwey transition of magnetite,[61] where both isostructural systems are better distinguishable. The spectrum can be well fitted with two sextets with zero intensity of the 2⁴⁺ sextet being approximately 4:1 which is again far from the ideal values expected for stoichiometric maghemite (5:3) and magnetite (2:1) samples. Despite this fact, one should note that the magnetic moments of the magnetic cores are perfectly aligned in the external magnetic field of 5 T, since the 2⁴⁺ and the 5⁴⁺ line are not observed. This further proves that magnetic particles are easily magnetized and reach their magnetic saturation readily, with no surface or internal spin canting, which would have a negative impact on the net magnetic signal of the particles.

3. Conclusions and Perspectives: Practical and Fundamental Point of View

The present hybrid organic–inorganic polyelectrolyte brushes, endowed with pronounced colloid stability in low ionic strength aqueous solutions (<5 × 10⁻³ m) and intrinsic magnetic properties conferred by the inorganic core, might be suitable for many technological applications discussed in the introduction. In addition, the non-linear optical response combined with the magnetic properties in a final single nano-entity renders it a potent candidate for optical and magneto-optical devices.[62]

As far as bio-applications are concerned (e.g., hyperthermia, drug targeting), although their lability in presence of cations precludes their use in blood-circulating related applications, the possibility of direct injection to the diseased tissue could be promising in the following basis: since the polyelectrolyte arms of the hybrid are strongly bioadhesive,[18] they would be expected to bind on the target tissue after the injection, seconded by the brush collapse upon contact with body fluids. Following hyperthermia or drug release, this may take place by an oscillating external magnetic field. The latter is plausible by previously loading a drug or generally bio-active molecules through interactions with the abundant anionic sulfonate groups.[63]

From the fundamental point of view, considering the number of arms of the hybrids (18 min–36 max, see Supporting Information), one would argue that they lie in the intersection of discrete colloidal particles and hybrid star polymers.[64] Nevertheless, for the time being, their characterization as colloids (such as dense polymer brushes are) appears more appropriate, since arm interactions and interpenetrations, characterizing polymers behavior, are rather improbable. Future work on studying the rheological and viscoelastic properties of sols or films of such hybrids might shed light on the particular matter.

4. Experimental

Synthetic Methods: Poly(sodium 4-styrene sulfonate) of mean M_w = 70000 (M_w/M_n = 1.1) and M_w = 200000, and (NH₄)₂Fe₂(SO₄)₃·6H₂O (ReagentPlus ≥ 99%) were purchased from Aldrich. Hydrochloric acid (37%, ACS reagent) and sodium hydrosulphate in pellets (ACS reagent) were purchased from Riedel de Haen. Anhydrous FeCl₃ and FeCl₄ from Sigma–Aldrich and tetramethylammonium hydroxide was purchased from Alfa Aesar.

For the preparation of the hybrids, (NH₄)₂Fe₂(SO₄)₃·6H₂O (340 mg) was dissolved in a NaPSS (M_w = 70000) aqueous solution (100 mL, 3 wt %). Following, NaOH solution (6 mL, 2 m) was added under stirring in 3 steps of 2 mL, with the first part added at room temperature, the second one at 40 °C and the third one at 50 °C, where the temperature was maintained for 30 min. After the end of the reaction the mixture was centrifuged (3700 rpm, 5 min). The product precipitated and the supernatant containing the excess of NaPSS macromolecules was decanted. The decanted solution was treated with a mixture of ethanol and 1 M HCl in order to precipitate NaPSS (ethanol is a bad solvent for NaPSS) and dissolve any iron oxides. The procedure was repeated twice to secure the purity of the recycled NaPSS and its suitability for use in future experiments. The magnetic product of the reaction was re-suspended in ethanol:water (9:4, 13 mL) and centrifuged in order to remove residual NaPSS and other free ions. The latter procedure was repeated twice. The final product (ca. 75 mg, yield ~85%) was added into H₂O (50 mL), sonicated for 15 min and stirred overnight. The final suspension was centrifuged (4000 rpm, 20 min) and the supernatant, a dark brown aqueous colloid (abbreviated as PSS-Mag) was stored in a glass vial. Solid product could be obtained by condensation in a rotavap to 10 mL and then centrifugation. PSS-5Mag, PSS-7Mag and PSS10-Mag derivatives were
obtained following the same synthesis as for PSS-Mag, but with a 5-, 7-, and 10-fold increase in the initial Fe\textsuperscript{3+} concentration respectively. NaOH addition was accordingly increased.

Neat iron oxide particles, abbreviated as FeO\textsubscript{Q}, were synthesized by adding NaOH (6 mM, 2 mL) into an aqueous (NH\textsubscript{4})\textsubscript{2}Fe(SO\textsubscript{4})\textsubscript{2} \cdot 6H\textsubscript{2}O solution (100 mL, 340 mg). The reaction ended after 30 min stirring at ca. 50 °C.

For comparative reasons, another PSS-Mag product was prepared with NaPSS of \( M_w = 200000 \) and a magenette hydrogel was synthesized following known procedures \[9\], by alkaline co-precipitation of a stoichiometric Fe\textsuperscript{3+}/Fe\textsuperscript{3+} \((1/12)\) aqueous solution.

**Characterization Methods and Instruments**

Powder X-Ray diffraction analysis was performed on a Siemens D-500 diffractometer with Cu K\alpha radiation (1.54 Å). Zeta-potential measurements and dynamic light scattering (DLS) were performed with a Nano Zetasizer Malvern Instrument equipped with a 4 mW He-Ne laser, operating at a wavelength of 633 nm and having an avalanche photodiode as a detector. Scattered light is measured at an angle of 173°. Reported polydispersity index (PDI) values, ranging between 0 for a highly monodisperse sample and 1 for very large size distributions, derive from the formula:

\[
\text{PDI} = \frac{\text{distribution and } \text{size}}{\text{distribution and } \text{size}}
\]

**Results and Discussion**

System – MPMS XL-7, Quantum Design). The hysteresis loops of the investigated sample were recorded at a temperature of 2 K and after each set of measurements to check for undesirable magnetic aggregation effects and/or photo-induced changes. All studied samples were fully transparent during the measurements period. Magnetic measurements were carried out with a Philips CM20 TEM equipped with a Gatan GIF200 that was utilized for electron energy loss spectroscopy (EELS) measurements. Infrared spectra were recorded with a Digilab Excaliber series FTS 3000 spectrometer in a KBr pellet form. The spectra were measured with a resolution of 2 cm\textsuperscript{-1} and were the sum of 64 scans. UV-vis measurements were conducted with a Hitachi, Digilab U-2800 spectrophotometer and chemical analysis with a Carlo-Erba CHNS Elemental Analyzer EA1108. AFM images were prepared with different concentrations in inorganic nanoparticles. For the needs of the NLO measurements several samples were recorded via a Multimode Scanning Probe Microscope (Digital. R. M. Cornwell, U. Schwertmann, *The Iron Oxides*, 2nd ed., Wiley-VCH, Weinheim 2003.


Experiments with NaPSS of different molecular weight (200000) have been performed and the results further corroborate the findings of the work. Specifically, a mean hydrodynamic diameter of 186 nm was recorded in contrast to the value of 113 nm in the case of the 70000 NaPSS macromolecule. The brush layer indeed increased by 73% to 86.5 nm. Studying in more detail the structure and behavior of hybrid brushes with different Mw NaPSS is planned for a forthcoming publication.


