

Relaxation of Adsorbed Layer Thickness and Electrophoresis of
Polystyrene Latex Particles after Overshooting of Polyelectrolytes with
Different Charge Density

Thi Hai Yen Doan^a, Yasuhisa Adachi^{b}*

*^aGraduate School of Life and Environmental Sciences, University of
Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8572, Japan*

E-mail: haiyendoan90@gmail.com

*^bFaculty of Life and Environmental Sciences, University of Tsukuba,
1-1-1 Tennodai, Tsukuba, Ibaraki 305-8572, Japan*

Corresponding author: *Yasuhisa Adachi,*
adachi.yasuhisa.gu@u.tsukuba.ac.jp

Abstract

Temporal change of hydrodynamic layer thickness (δ_H) and electrophoretic mobility (EPM) of polystyrene sulfate latex (PSL) particles adsorbed by oppositely charged polyelectrolytes were monitored herein to clarify the relaxation behavior after overshooting. Two linear polyelectrolytes with nominal molecular weight of 5 million differing in chain charge density, $\sigma = 100\%$ (PTMA5M) and $\sigma = 4\%$ (PTMC5M), and PSL particles of different diameters were used in the experiment. With the former polyelectrolyte, a remarkably thick layer that is formed at the incubation decays with the time scale of several tens of minutes and the EPM remains constant. The value of δ_H decreases with the increase of particle size, whereas with the latter polyelectrolyte, the initial value of δ_H is several times smaller than that of the former. There is a case wherein the EPM decreases with time,

although δ_H remains constant. The initial δ_H is independent of the particle size. Ascribing the reason for the relaxation phenomena to desorption of overshoot polyelectrolytes attached with meta-stable conformation in the initial stage, we have obtained an approximate picture of the conformational change for the chain of different charge density.

Keywords: polyelectrolyte at interface, hydrodynamic adsorbed layer thickness, kinetically controlled adsorption, relaxation of layer after overshooting, charge density of chain, electrophoretic mobility.

1. Introduction

Dynamics of polyelectrolytes on the oppositely charged surfaces can be regarded as an important basis of flocculation or aggregation of colloid in many applications. Examples of such systems can be found in several practical processes, such as water purification [1-4], papermaking [5], and mineral processing [6]. Colloidal particles in water are stabilized by electrostatic repulsion due to their original surface charge. The adsorption of polyelectrolytes of opposite charge to the colloidal surface induces the reduction or the reversal of charge of colloidal particles. It is also known that the adsorbed polymer/polyelectrolyte generates a polymer layer of considerable thickness around the colloidal particle. Such changes in surface charge and formation of an adsorbed layer have a profound influence on the stability of colloidal suspension [7, 8]. In addition to the change of electrochemical condition, protruding conformation of polymer, which

is in the transient state, is crucial in the analysis of flocculation [9]. Therefore, understanding the surface conformation and charging behavior of colloidal particles is crucial for controlling the flocculation process.

It is well-known that the neutral polymer, whose segment has an affinity to the surface, adsorbs onto the surface, taking a chain conformation of train, loop, and tail [10, 11]. This concept was theoretically developed using a lattice model of mean-field approximation which originally applied to polymer conformation in solution, basically assuming equilibrium conformation. Short range proximate contact of few segment sequences in the segment chain to the surface is assumed to form the part of the train, while other segments remaining Brownian motion of the chain are termed as loop and tail. In the case of polyelectrolytes existing at the oppositely charged surface, long-range electrostatic attractive interactions between charged segments and the colloidal surface are considered to be dominantly operative [10]. In such conditions, the polyelectrolyte chain adsorbs onto the oppositely charged surface in more flattened conformation than that of the neutral polymer.

The charge density of the chain yields a critical difference in determining the conformational change. Polyelectrolyte of high charge density strongly adsorbs onto the oppositely charged surface in flat conformation [12, 13]. In addition to the electrostatic attractive force, non-electrostatic attractive forces such as hydrophobic interaction, hydrogen bonding, chemically specific attractions are operative [14, 15]. Due to these effects, charge reversal is commonly observed by

electrophoretic mobility for the condition of excess dosage. Therefore, the adsorption amount increases with an increase of ionic strength [16]; essentially, flocculation is induced by charge neutralization and additional patch-wise attractive force is considered to play a role [8, 17]. In contrast, the chain with low charge density results in a more protruding structure of loop and tail. The reduction of charge density of the polymer chain results in a thicker and more extended conformation of the adsorbed chain on the surface [18-20]. In this case, flocculation is induced via bridging, which is probably competing with steric stabilization [12].

In the analysis of flocculation, however, non-equilibrium aspects are also important. Hence, upon the onset of flocculation, which is brought under the instant addition of flocculant to the colloidal suspension, the system is placed under the condition far from equilibrium. The enhancement of bridging flocculation depends on the process of polyelectrolyte re-conformation. The re-conformation of a polymer is strongly affected by its molecular weight and polymer concentration [13, 21, 22]. In the case of low molecular weight, the adsorbed polymers re-conform faster into flat chains on the particle surface than in the case of high molecular weight. The increase of polymer concentration induces the interferences between re-conforming chains, resulting in a long time for re-conformation [13]. In a previous study, we reported that a remarkably high initial flocculation rate occurs for an excess dosage of high molecular weight [8]. In a separate study measuring the EPM, we obtained that the adsorption of high charge density polyelectrolytes under low ionic strength is kinetically

controlled [23]. We also confirmed that initially formed layer thickness decays with the time scale of several tens of minutes while the kinetically controlled adsorption detected by electrokinetics is constantly maintained. However, the detail of these phenomena, the reason, the effect of charge density of the polyelectrolyte chain, and the effect of substrate particle size for each condition have remained unclear.

In the present study, based on our previous observation after the event of overshooting [24], we carried out a more comprehensively systematic measurement of hydrodynamic layer thickness and electrokinetics as a function of elapsed time. To clarify the effect of the charge density of polyelectrolyte, we used two polymer samples, which are mostly the same in molecular weight but largely different in charge density. Since we consider that the formation of a remarkably thick layer will be influenced by the space-filling nature of the swollen chain, we also tested the effect of the diameter of substrate particles under two ionic strength conditions. At fixed ionic strength, the δ_H value of PTMA5M after mixing point decreases with the lower PSL particle curvature while that of PTMC5M does not change significantly. Conversely, the behaviors in the PTMC5M adsorption case were similar to those in the PTMA5M adsorption case, i.e., the adsorption was kinetically controlled under the condition of low ionic strength, and the decaying time reflecting relaxation was approximately the same. The δ_H decreases dramatically while the EPM remains constant with time. However, more precisely, there are differences at several points. For instance, the initial value of δ_H of PTMC5M appears several times

smaller than that of PTMA5M. For the case of PTMC5M, relaxation phenomena were found with different polyelectrolyte concentrations under different ionic strength conditions. There is a case under the high ionic strength condition where the δ_H remains constant while the value of EPM decreases with time at high PTMC5M concentration. However, in the same ionic strength, the δ_H value decreases at low PTMC5M concentration. Based on the obtained data, we have drawn an approximate picture of the morphological change of kinetically controlled adsorbed layer, which is different for charge density polyelectrolyte. These results are informative on the coating of colloidal particles by oppositely charged polyelectrolytes in addition to the analysis of the flocculation process.

2. Experimental

2.1 Materials

Monodispersed polystyrene sulfate latex (PSL) particles (Thermo Fisher Scientific, Inc., Waltham, MA, USA) with diameters of 1.2 μm and 2.0 μm with standard deviations of 0.1 μm and 0.052 μm , respectively, were used as substrate colloidal particles. Two linear polycations of different charge densities with mostly the same molecular weight (acquired from Kaya Floc Co. Ltd., Tokyo, Japan) were prepared: a homo-polymer of poly-trimethylamino ethyl methacrylate (PTMA5M) with the nominal molecular weight of 4.9×10^6 g/mol and a co-polymer of trimethylamino ethyl methacrylate and acrylamide (PTMC5M) with a ratio of 1:25 and a nominal molecular

weight of 5.2×10^6 g/mol. The hydrodynamic polyelectrolyte radius was determined by using the viscosity measurement method (Table 1). The chemical structures of both polymers were shown in Fig.1. The stock polyelectrolyte solution with a concentration of 100 mg/L was prepared in the electrolyte solution before application. KCl solution of 0.1 mM and 10 mM were used as an electrolyte for dilution. The dilution was carried out by stirring the solution for 72 h by magnet stirrer and used up within a week. All polymer solutions were placed in a dark and cold place at 5°C for the elimination of light exposure-induced degradation. All solutions and measurements were conducted with ultrapure water, produced from Elix Advantage 5 (Millipore) with electrical conductivity controlled in the neighborhood of $0.6 \mu\text{S}/\text{cm}$. The salt solutions were filtered by $0.2 \mu\text{m}$ cellulose membrane before usage.

Table 1. Hydrodynamic radius of polyelectrolytes with 5 ppm of PTMA5M and PTMC5M concentration was measured by Einstein's viscosity equation at different KCl concentrations.

Hydrodynamic radius (nm)			
Polymer	0.1 mM KCl	10 mM KCl	1 M KCl
PTMA5M	159.32	111.44	77.73
PTMC5M	101.37	100.72	85.95

2.2 Hydrodynamic adsorbed layer thickness by means of particle tracking

An optical microscope (BX50, Olympus) equipped with a CCD video camera (WV-BL200, Matsushita Co. Ltd) was used to record the Brownian motion of a single colloidal particle. The adsorbed layer thickness of polyelectrolytes was determined by the comparison of diffusion constant of colloidal particles with and without a polyelectrolyte layer. Hence, based on the Stokes–Einstein equation, the diffusion constant of a bare particle is given as

$$D = \frac{kT}{6\pi a\mu}, \quad (1)$$

where a is hydrodynamic radius (m), k is Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J/ K), T is the absolute temperature (K), μ is the viscosity of solvent (Pa. s).

While for a particle with adsorbed polymers, the Stokes–Einstein equation becomes as

$$D = \frac{kT}{6\pi(a + \delta_H)\mu}, \quad (2)$$

where a is hydrodynamic radius (m), k is Boltzmann constant ($k_B = 1.38 \times 10^{-23}$ J/ K), T is the absolute temperature (K), μ is the viscosity of solvent (Pa. s), δ_H (m) is the layer thickness of adsorbed polyelectrolytes. The detail of determining D from the displacement of a colloidal particle is given in [21, 22].

The validity of the applied method was confirmed by comparing the measured coefficient variations (CVs) of the hydrodynamic diameters of uniform PSL particles with the supplied values of CVs. For PSL

particles of 1200 nm and 2000 nm diameters, the measured CVs (5.9% and 2.1%) are less than the CVs (6.0% and 2.7%) determined by the transmission electron microscopy (TEM) from the supplier.

2.3 Procedure

Before each measurement, the sonication of PSL suspension was carried out for 20 minutes to eliminate the aggregates. The initial number concentration of PSL particles was adjusted at the number concentration of 1.0×10^8 (particles/cm³) in all experiments. In all adsorption experiments, before the mixing, 5.0 ml of polycation solution was introduced into one side of the forked flask. An equal volume of PSL colloidal suspension with an initial concentration of 1.0×10^8 (cm⁻³) was added to the flask of the other side (see Fig. 2). The samples were mixed for 10 times by an end-over-end apparatus at a fixed frequency of 1 Hz. A detailed description of the end-over-end apparatus was provided in [21]. Elapsed time was determined from the end of the mixing event. All experiments were conducted at room temperature (293 K) controlled by an air conditioner.

Hydrodynamic adsorbed layer thickness

After mixing, the sample was introduced into a 0.2 mm × 2 mm rectangle capillary tube. The Brownian motion of a single spherical particle was observed under an optical microscope with a time resolution of 0.1 s. The diffusion constant was calculated by taking the root mean square value of 500 displacements. The time interval for each displacement is approximately 0.258 s. The focus of the

microscope was manually adjusted to maintain clear images of Brownian motion in recorded videos.

Electrophoretic mobility measurements

A plastic capillary cell filled with the sample was inserted in a laser velocimetry setup Zeta- sizer Nano-ZS (Malvern Instruments, UK) with the electric field of 11.3 V/cm for the electrophoretic mobility measurements. Each sample was measured at least 3 times, with 11 sub-runs for each measurement.

3. Results

Figure 3 demonstrates the temporal changes of δ_H and EPM of PSL particles coated with high charge density polyelectrolyte (PTMA5M) under overshooting conditions; the results were obtained using different ionic strengths and different diameters of PSL particles. The obtained values of δ_H after the onset of PTMA5M adsorption on the PSL particle with 1200 nm diameter in the KCl solution of 1.0×10^{-4} M and 1.0×10^{-2} M were plotted in Fig. 3(a) and 3(b), respectively. These results demonstrate relaxation behavior. However, as shown in Fig. 3(c) and 3(d), the monitored values of EPM in the corresponding conditions of (a) and (b) never indicate relaxation. These sets of data, (a)–(d), exactly reproduce the results reported in our previous measurements using a PSL particle with a diameter of 804 nm [24]. However, the absolute value of δ_H is different, i.e., our detected values are slightly smaller than those previously reported. We infer the reason for this difference is due to the difference in the diameter of substrate particles. Small particles are considered to be advantageous for the adsorption of chains with

large excluded volume by the result of extremely large swelling nature. A highly charged chain in the solution of low ionic strength can be considered to satisfy this condition. As a result, a thicker layer can be formed. This conjecture can be confirmed by the data of a similar measurement of δ_H using a particle with a diameter of 2000 nm demonstrated in Fig. 3(e) - 3(f). As demonstrated in these figures, the initial value of δ_H was smaller than the value obtained with the diameter of 1200 nm. By using a particle with a larger diameter, we obtained a trend in the temporal change of EPM (see Fig. 3(g)–(h)), which is qualitatively similar to our previous measurements [24].

The monitored results of δ_H and EPM after the overshooting of low charge density polyelectrolytes (PTMC5M) are shown in Fig. 4. The alphabet order a-h exactly corresponds to the same condition indicated in Fig. 3. As compared with the result for the case of PTMA5M, several remarkable points should be noted. First, the absolute value of δ_H is a few times smaller than that obtained for PTMA5M. Second, a decrease of initial value with an increase of ionic strength and particle diameter was not detected for the value of δ_H . Third, the value of δ_H obtained for the highest concentration PTMC5M (5 ppm) is found to be more stable against time and ionic strength. As for the value of EPM, the charge reversal is confirmed to take place. However, compared with the case of PTMA5M, the degree of reversal is small, which is probably due to the small charge density of the chain. Under the condition of low ionic strength (1.0×10^{-1} M), kinetically controlled phenomena were also

confirmed for EPM. However, there were also cases wherein the value of EPM changes as a function of elapsed time.

4. Discussion

In this section, we analyze the data demonstrated in the previous section to draw the expected morphology and temporal change of the adsorbed layer of positively charged polyelectrolytes on the negatively charged PSL particles after overshooting. As described in the introduction, expected pictures of the transient process are intrinsically different by the difference of charge density of polyelectrolyte. The analysis should be done separately.

4.1 Layer of high charge density polyelectrolyte on the PSL

In our previous study [24] with PTMA5M, we confirmed the behavior of kinetically controlled adsorption by the measurement of δ_H , but also of the value of EPM. It should be noted that the kinetically controlled adsorption detected by the latter is limited to the condition of lower ionic strength, at least lower than 1.0×10^{-3} M [21, 25], while it is detected by the former irrespective of ionic strength within our studied range. From different behavior of δ_H and EPM, we have proposed a picture of a thin layer, which is thinner than the detection limit ($\delta_H \approx 10$ nm) of the applied method. This thin layer adjacent to the surface determines the value of EPM [8]. EPM of PSL particles coated with PTMA is determined by the electrokinetic structure of this layer. In the presence of a sufficient amount of counter ions, the formation process

of this thin layer is not kinetically controlled. However, under the condition of low ionic strength, chains can be considered stiff, and the absence of counter ions strongly enhances the approach of oppositely charged segments of chain and surface. Around this layer, a hydrodynamically detected layer is present. The thickness of this layer will decrease as a function of time, although the electrokinetic properties (EPM) are maintained constant. The dependency of the thickness on the diameter of the substrate particle can be referred qualitatively to the numerical calculation of Stoll et al. [26].

On the basis of these discussions together with the result on the effect of PSL particle diameter, we draw an approximate picture of the morphology of adsorbed layer of PTMA5M on the PSL particle as shown in Fig. 5.

4.2 Layer of low charge density polyelectrolyte on the PSL

It is known that the adsorbing conformation of the equilibrium state of low charge density polyelectrolyte has a tendency of loop-train-tail structure, reflecting the weak electrostatic effect. However, our result can be regarded as providing some important points before forwarding the detailed analysis. For instance, in the case with high charge density polyelectrolyte, most result demonstrated that the EPM remains constant although the value of δ_H decays to zero. This result can be interpreted as the EPM being controlled by a thin layer adjacent to the surface of the particle. The detection of kinetically controlled phenomena of EPM under lower ionic strength, 1.0×10^{-4} M, demonstrated in Fig. 4(c) and 4(g) also supports this interpretation.

However, due to the low charge density, the thickness of the EPM control layer can be expected to be not as compressed as is predicted for the case of high charge density polyelectrolyte. It should be also noted that the resulted thickness formed with PTMC5M concentration of 5 ppm maintain its initial value of approximately 100 nm, while the value of EPM changes significantly. By the application of Ohshima-Kondo theory on the electro-osmosis of soft-particle [27, 28], the reason for the reduction of EPM can be ascribed to the decrease of charge density of the adsorbed layer. Our idea to explain these results is to predict the layer structure as an alignment of chains to the direction perpendicular to the surface, as illustrated in Fig. 6. Thus, we can explain the reduction of EPM keeping δ_H constant.

5. Conclusions

We have reported a comprehensive measurement of temporal change of hydrodynamic layer thickness and electrophoretic mobility of polystyrene latex particles coated with an excess dosage of oppositely charged polyelectrolyte chains. To clarify the effect of charge density of the chain, we tested two polyelectrolytes – a homo-polymer of poly-trimethylamino ethyl methacrylate (PTMA5M) with a nominal molecular weight of 4.9×10^6 g/mol and a co-polymer of trimethylamino ethyl methacrylate and acrylamide (PTMC5M) with a ratio of 1:25 and a nominal molecular weight of 5.2×10^6 g/mol. From the systematic data, we have gained insights into the relaxation behavior of polyelectrolytes on the surface of oppositely charged colloid surface. That is, the randomly sequential attachment to the oppositely charged

surface of particle is expected for the chain of high charge density while chains of low charge density will adsorb aligning to the direction of perpendicular to the particle surface.

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Conflict of Interest

The authors declare that they have no conflict of interest associated with this article.

Figure captions

Fig.1. Chemical structures of the monomers: (a) PTMA5M ($\sigma = 100\%$) and (b) PTMC5M ($\sigma = 4\%$).

Fig.2. Schematic drawing of the mixing event by using the end-over-end apparatus.

Fig.3. Temporal changes of δ_H and EPM of PTMA5M on PSL particles with different ionic strength and different diameters of PSL Particles. (a) δ_H , in 0.1 mM KCl solution using PSL particle with 1200 nm diameter. (b) δ_H , in 10 mM KCl solution using PSL particle with 1200 nm diameter. (c) EPM in 0.1 mM KCl solution using PSL particle with 1200 nm diameter. (d) EPM in 10 mM KCl solution using PSL particle with 1200 nm diameter. (e)–(h) are exactly same data obtained using PSL particle with 2000 nm diameter as indicated in (a)–(d) except PSL particle diameter. PTMA5M concentrations: 5 ppm (\blacklozenge), 2.5 ppm (\blacksquare), 1 ppm (\blacktriangle), 0 ppm (\bullet). The error bars show the deviations of different runs.

Fig.4. Temporal changes of δ_H of PTMC5M on PSL particles with the different diameters. The meaning of (a)–(h) and symbols are exactly same as those of Fig. 3.

Fig.5. Schematic presentation of the relaxation behaviors of PTMA5M adsorbed layer on PSL particles under over shooting condition. Initially formed layer is essentially composed of two regions. The first is the proximate region where positively charged segments have directly interact to form relatively thin EPM determining zone. The formation of this zone is kinetically controlled.

Fig.6. Schematic presentation of the relaxation behaviors of PTMC5M adsorbed layer on PSL particles under over shooting condition (the polyelectrolytes which will be desorbed are presented in the green dashed circles).

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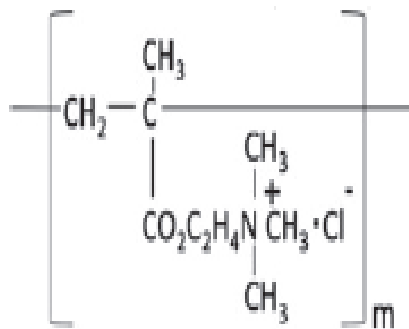
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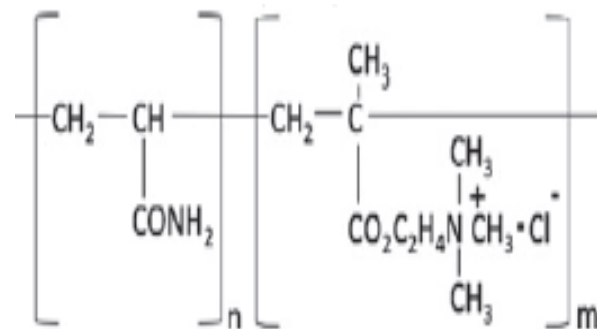
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(a)



(b)

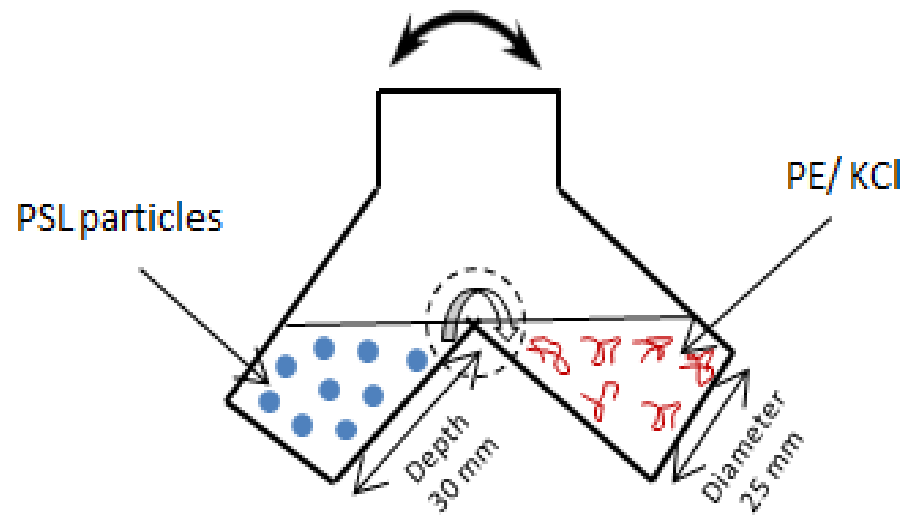


Fig.2

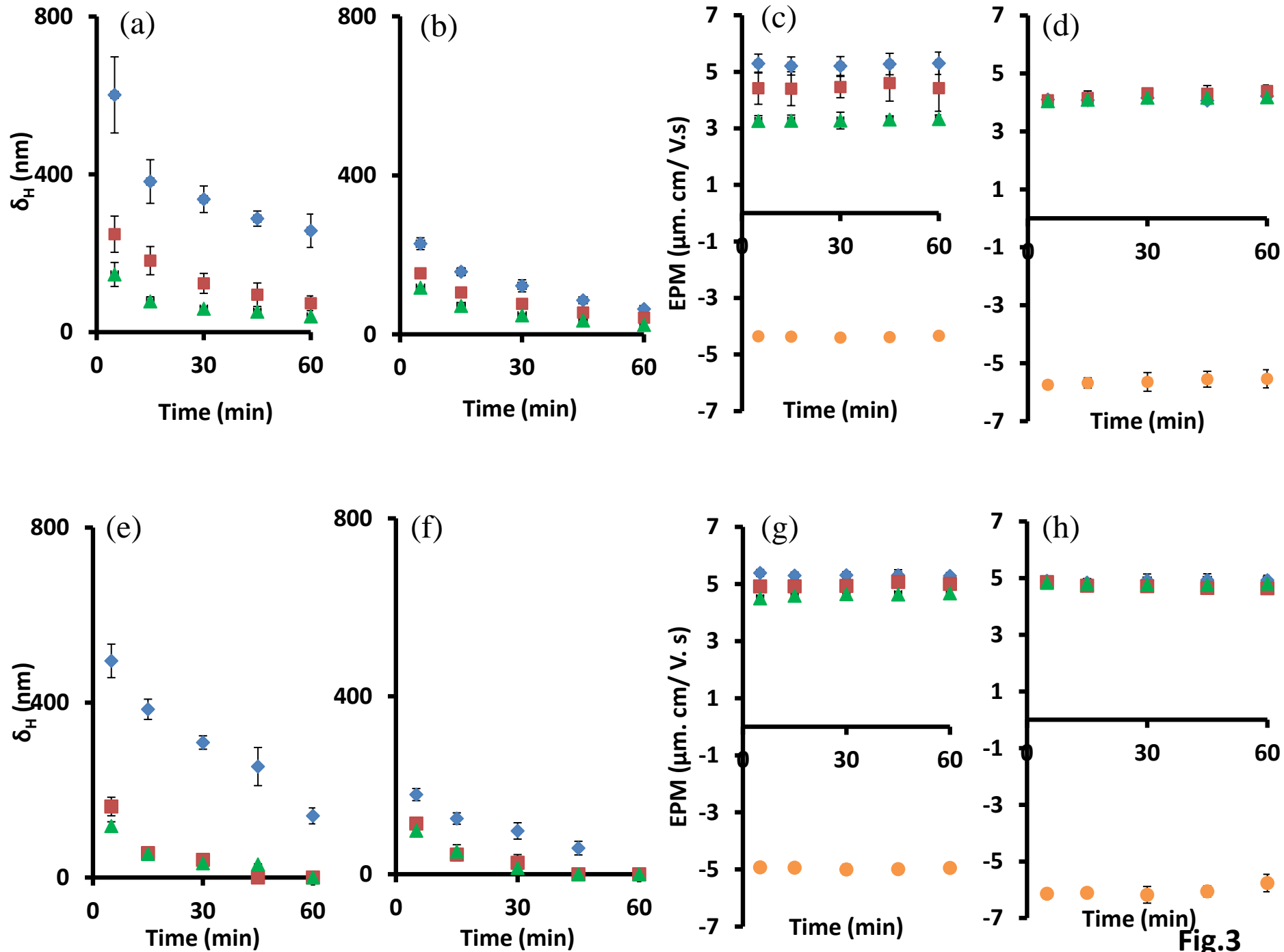


Fig.3

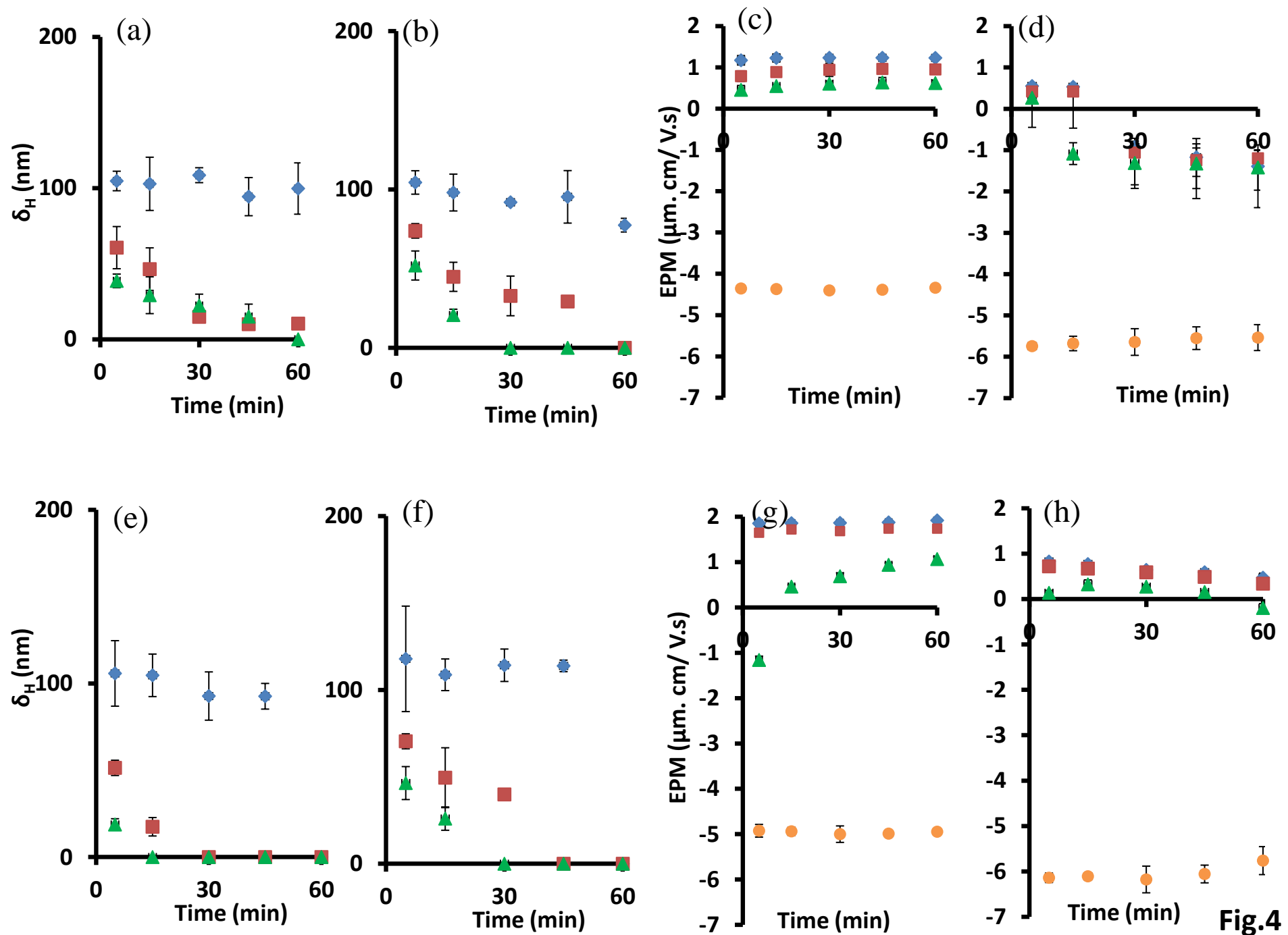


Fig.4

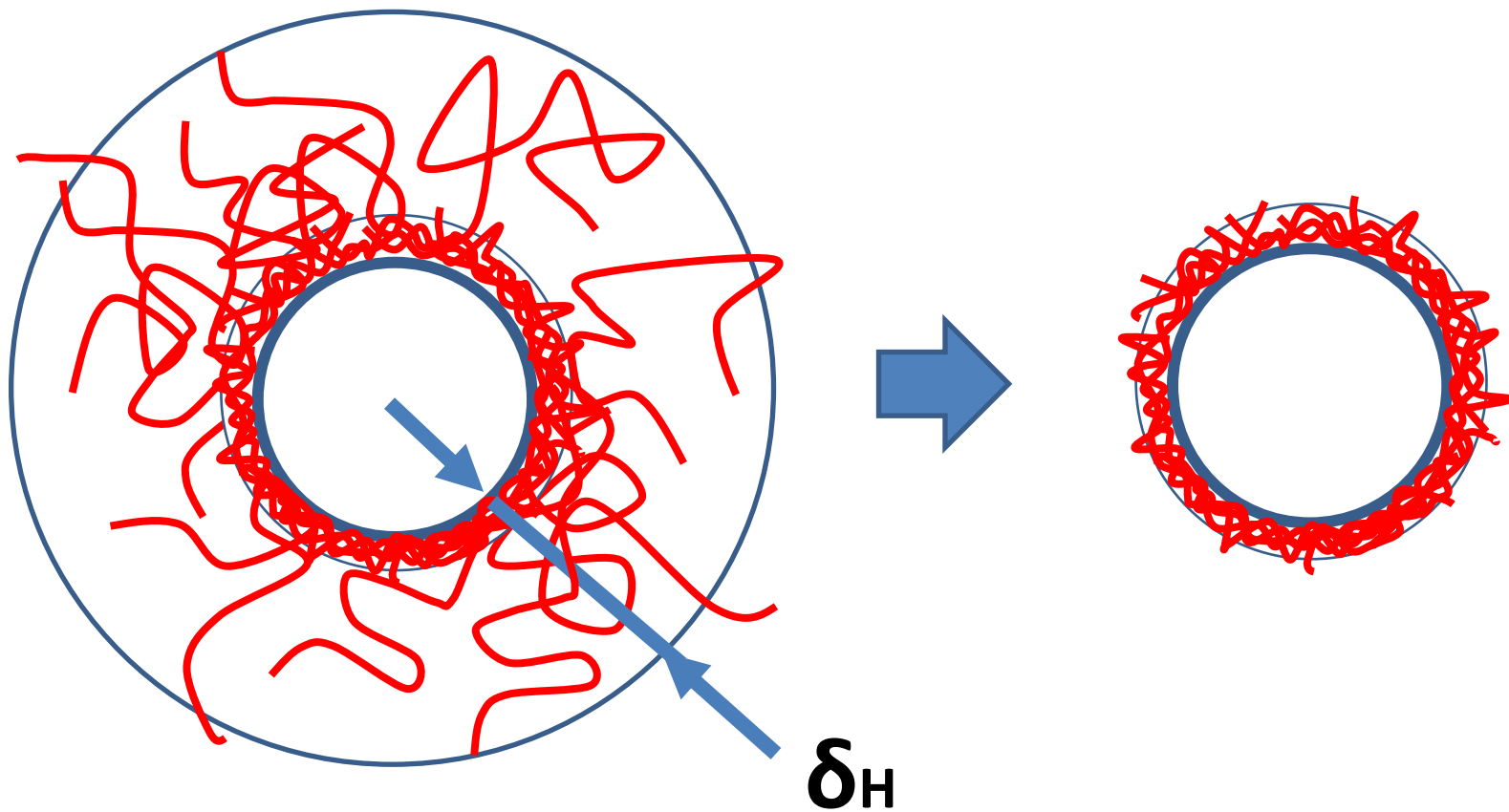


Fig.5

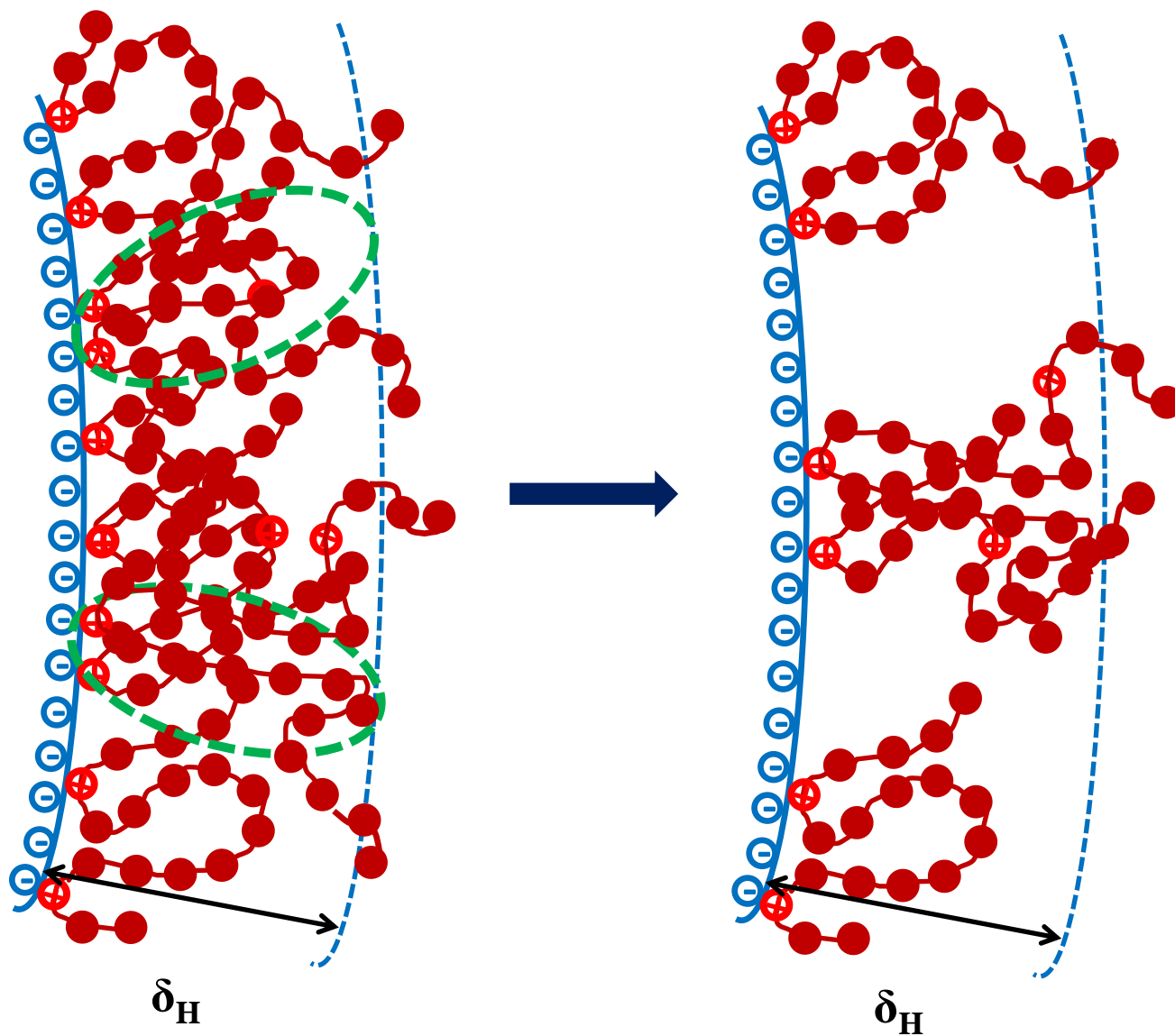


Fig.6

Highlights

1. Temporal change of δ_H and EPM of PSL particle coated with oppositely charged polyelectrolyte after over dosage incubation was monitored.
2. Charge density of polyelectrolyte chain is confirmed to have significant influences on the morphological relaxation of adsorbed polyelectrolytes.
3. Effects of the diameter of particle and ionic strength were clarified.

CRedit author statement

Yasuhisa Adachi: Conceptualization; investigation; methodology; project administration; supervision; validation; visualization. **Thi Hai Yen Doan:** formal analysis; resources, software. **Thi Hai Yen Doan and Yasuhisa Adachi:** data curation; writing—original draft, writing—review and editing. All authors reviewed and approved the manuscript.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: