

# Anisotropic Diffusion of Polyelectrolyte Chains within Multilayer Films

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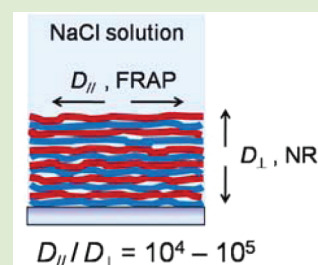
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## S Supporting Information

**ABSTRACT:** We have found diffusion of polyelectrolyte chains within multilayer films to be highly anisotropic, with the preferential chain motion parallel to the substrate. The degree of anisotropy was quantified by a combination of fluorescence recovery after photobleaching and neutron reflectometry, probing chain diffusion in directions parallel and perpendicular to the substrate, respectively. Chain mobility was controlled by ionic strength of annealing solutions and steric hindrance to ionic pairing of interacting polyelectrolytes.



Layer-by-layer (LbL) adsorption of polymers at solid substrates enables construction of multicomponent films or polyelectrolyte multilayers (PEMs). Many potential applications of these films for enhanced photoluminescence,<sup>1</sup> improved antireflection coatings,<sup>2</sup> or multistage, multidrug delivery of therapeutic compounds from surfaces<sup>3</sup> rely on internal film stratification. While PEMs are often considered as inherently nonequilibrium structures, with polymer chains irreversibly bound after assembly,<sup>4</sup> polymer chain mobility can in fact occur during film deposition<sup>5</sup> or post-assembly.<sup>6–8</sup> For example, significant chain mobility was observed within PEMs by atomic force microscopy (AFM) after exposure of LbL films in salt solutions.<sup>6</sup> Polymer diffusion in the direction parallel to the substrate was also detected by fluorescence recovery after photobleaching (FRAP).<sup>8</sup> Increased chain mobility within PEMs can result in chain intermixing and can compromise potential applications that rely on internal film structuring.

Among several parameters controlling chain mobility within PEMs, such as polyelectrolyte type, charge density, and molecular weight, salt concentration has been identified as one of the most important factors promoting chain diffusion.<sup>7,9</sup> Mobility of PE chains within multilayer films has also been tested by applying one of two techniques, either FRAP or neutron reflectometry (NR), which probe molecular motions in directions parallel and perpendicular to the substrate, respectively. For example, salt-induced diffusion of PEs in the direction parallel to the surface was observed with several PEM systems using FRAP,<sup>7,8</sup> while intermixing of polymer layers was studied in different PEM systems using NR.<sup>10–12</sup> Because of the inherently anisotropic structure of PEMs, it is reasonable to suggest that chain mobility might be different in directions parallel and perpendicular to the substrate. However, the

experiments testing this suggestion, as well as the effect of the proposed anisotropic chain motions on film layering have not up to now been carried out.

In this communication, we assess the degree of anisotropy of chain motion within PEMs and experimentally assess by applying a combination of FRAP and NR techniques to the same PEM systems exposed to the same solution stimuli. The degree of anisotropy was assessed from the ratio of PE diffusion coefficients in directions parallel and perpendicular to the surface ( $D_{||}$  and  $D_{\perp}$ , respectively), as quantified by FRAP and NR. We have found that chain motions within PEMs are highly anisotropic, with a preference for chain motion parallel to the substrate.

Experimental systems studied comprise PEMs constructed by LbL deposition of poly(methacrylic acid) (PMAA,  $M_w = 100$  kDa, PDI = 1.12) as a polyanion (PA) and two types of polycations (PCs), a parent poly(2-(dimethylamino)ethyl methacrylate) homopolymer (PDMA,  $M_w = 30$  kDa, PDI = 1.10), synthesized by atom transfer radical polymerization (ATRP) as described elsewhere,<sup>13</sup> as well as a product of its complete quaternization with dimethyl sulfate, abbreviated as Q100M (see Supporting Information for detailed procedures). During deposition, PDMA/PMAA and Q100M/PMAA films showed a linear increase in film thickness at pH 4.5 (Figure S1), with  $\sim 3$  mg/m<sup>2</sup> increase in mass adsorbed per bilayer for both systems.

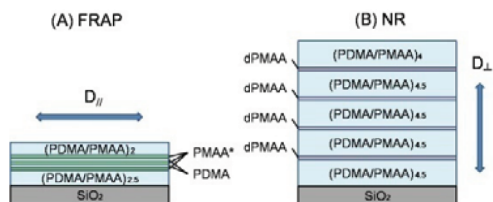
Scheme 1 shows the architecture of the PEM films used in FRAP and NR measurements. For FRAP measurements, PMAA was tagged with an Alexa Fluor 488 every 300th

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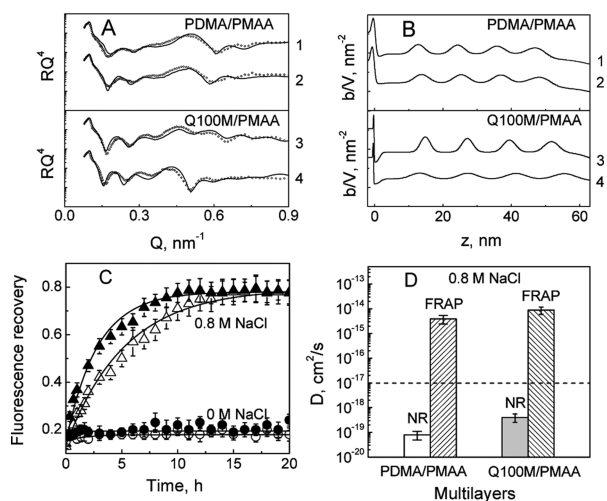
**Scheme 1. Schematic Representation of Multilayers Used in Measurements of Diffusion Coefficients of PMAA Chains within PEM Films in Directions (A) Parallel ( $D_{\parallel}$ ) and (B) Perpendicular ( $D_{\perp}$ ) to the Substrate<sup>a</sup>**



<sup>a</sup>Subscripts denote number of bilayers.

monomer unit to yield PMAA\*. Fluorescently tagged PMAA\* layers were assembled within the central region of the LbL film (Scheme 1A) or within the “bulk” of the film<sup>7</sup> to avoid effects of the solid surface and polymer–water interface on polymer dynamics and film structure. Indeed, our control experiments using FRAP showed that PMAA\* included within the two layers closest to the substrate, or the bilayers closest to the water interface, was about half and twice as mobile, respectively, as layers included within the central film region. At the same time, PMAA\* marker layers included within different layers within the central PEM region demonstrated chain mobility that was consistent within 10%. To probe the degree of film layering using NR, marker layers of deuterated polyanion (dPA), deuterated PMAA (dPMAA,  $M_w = 198$  kDa, PDI = 1.08), were assembled within every fifth polycation/PMAA bilayer.

Figure 1A,B shows NR and related scattering length density profiles for 24-bilayer PDMA/PMAA and Q100M/PMAA films after exposure to buffer solutions with no additional salt (“no-



**Figure 1.** (A) Neutron reflectivity data and (B) corresponding scattering length density profiles for dry [(PC/PA)<sub>4</sub>/(PC/dPA)<sub>4</sub>]/(PC/PA)<sub>4</sub> for PDMA/PMAA and Q100M/PMAA systems (top and bottom, respectively), after annealing for 3 days in 0.01 M phosphate/citrate buffer no-salt and 0.8 M NaCl solutions (labeled 1, 3 and 2, 4, respectively). (C) Fluorescence recovery with (PC/PA)<sub>2</sub>/(PC/PA\*)<sub>3</sub>/(PC/PA)<sub>2</sub> films (PDMA/PMAA system, open symbols; Q100M/PMAA films, filled symbols) in no-salt and 0.8 M NaCl solutions at pH 4.5. (D) Comparison of  $D_{\perp}$  and  $D_{\parallel}$  values for diffusion of PMAA chains within PDMA/PMAA and Q100M/PMAA multilayers in 0.8 M NaCl solutions. Dashed line shows the FRAP sensitivity limit to measurements of  $D_{\parallel}$ .

salt”) or with additional 0.8 M NaCl. Bragg peaks indicate layering within PEMs, but the polymers significantly intermix during deposition, and resultant layers are diffuse (see structural parameters in Table S1). This is consistent with our earlier findings for weak polyelectrolyte multilayers.<sup>12</sup> The internal layering of as-deposited films has not been affected by exposure to no-salt buffer solutions. Annealing in high-salt solutions (0.8 M NaCl) had a different effect on polymer intermixing in the two PEM systems, with a small effect on layering in PDMA/PMAA films, but enhanced salt-induced layer intermixing with the Q100M/PMAA films, in the latter case resulting in an increase of the internal interfacial root-mean-square (rms) roughness  $\sigma_{\text{int}}$  from 39 to 55 Å after 3-day salt annealing (see structural data in Table S1). Salt-induced layer intermixing, resulting from the replacement of a fraction of the polymer–polymer ionic pairs by the salt ion–polymer ionic pairs, has been demonstrated.<sup>12</sup> The difference in PE propensity to intermix in these two systems results from the steric bulk of the methyl groups at the quaternary nitrogen of Q100M. The electrostatic binding energy between amino and carboxylic groups is reduced, as calculated for  $\text{NH}^+(\text{CH}_3)_2(\text{CH}_2\text{CH}_3)/\text{CH}_3\text{COO}^-$  and  $\text{N}^+(\text{CH}_3)_3(\text{CH}_2\text{CH}_3)/\text{CH}_3\text{COO}^-$  ionic pairs by Gaussian 98 using Hartree–Fock SCF modeling and 6-31G split-valence basis (Figure S2, Table S2).<sup>12</sup> Assuming that diffusion of polymer chains follows a Gaussian distribution, the  $D_{\perp}$  was estimated from the equation  $\Delta\sigma_{\text{int}}^2 = 2D_{\perp}\Delta t$ , where  $\Delta\sigma_{\text{int}}$  is the interfacial roughness change of the deuterated layers and  $\Delta t$  is the salt annealing time.<sup>11</sup> Neutron reflectivity curves were collected as-cast and for 3-, 6-, and 9-day anneals on one pair of samples, as well as as-cast and for two 3-day anneals on another pair. From fits to these data,  $D_{\perp}$  of dPMAA for the Q100M/PMAA system was  $(4.0 \pm 1.0) \times 10^{-19}$  cm<sup>2</sup>/s, which was nearly 4-fold larger than the  $D_{\perp}$  of dPMAA in PDMA/PMAA multilayers of  $(1.1 \pm 0.3) \times 10^{-19}$  cm<sup>2</sup>/s. This significant difference in mobility of polyelectrolytes within PEM films is consistent with the above calculations of differences in the ionic pairing energy.

Importantly, as measured using FRAP with the same systems, salt also affected the diffusion coefficient of PMAA chains in the direction parallel to the substrate. Similar to NR studies, assembled chains remained kinetically frozen during annealing in “no-salt” 0.01 M buffer (Figure 1C). After annealing in 0.8 M NaCl salt, the fluorescence intensity of the bleached spot recovered to ~80% of the original value, at the time scale of hours, due to salt-induced lateral chain mobility. Data in Figure 1C could be fitted by an exponential function, with the characteristic half time for fluorescence recovery  $t_{1/2}$ . For steric arguments discussed above, the recovery was twice faster for Q100M/PMAA PEMs. No desorption of PMAA\* from multilayer films was shown in the control experiment (<3% fluorescence decrease for multilayer films over seven-day exposure to 0.8 M NaCl solutions). This is due to strong, multipoint, “zipper-like” binding between PEs within PEMs, a type of binding that induces a large activation energy for desorption, and is well-known in polymer adsorption<sup>14</sup> and interpolyelectrolyte complex formation.<sup>15</sup> In addition, the rms surface roughness of PEM films (9 to 12 nm) was unaffected by salt annealing (Figure S3).

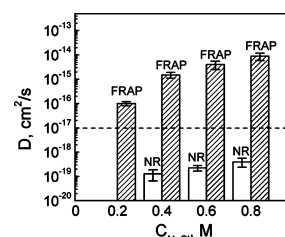
The lateral diffusion coefficients  $D_{\parallel}$  of PEM-assembled PMAA\* calculated as<sup>16</sup>  $D_{\parallel} = \gamma R^2/4t_{1/2}$  (where  $\gamma = 0.88$  is a constant of shape factor for the spherical beam spot and  $R = 0.183$  μm is the radius of the bleaching spot) gave  $(4 \pm 1.5) \times$

$10^{-15}$  cm<sup>2</sup>/s and  $(8 \pm 3) \times 10^{-15}$  cm<sup>2</sup>/s for PDMA/PMAA and Q100M/PMAA systems, respectively. These  $D_{\parallel}$  are of same order of magnitude as those reported for other electrostatically assembled PEMs in 0.1–1 M salt solutions.<sup>7,8</sup>

Surprisingly, however,  $D_{\parallel}$  were 4–5 orders of magnitude higher than  $D_{\perp}$ . From Figure 1D, in particular, diffusion anisotropy ratios  $D_{\parallel}/D_{\perp}$  of  $2\text{--}5 \times 10^4$  can be calculated for diffusion of PMAA within PDMA/PMAA and Q100M/PMAA multilayers in contact with salt solution. We then considered the possibility that such a difference might be at least partially due to frustrated order and accelerated diffusion in the FRAP experiment introduced by the bulky fluorescent labels in the PMAA\* chains. To investigate this possibility, dPMAA rather than hydrogenated PMAA chains were covalently tagged with Alexa Fluor 488, to one label per 300 dPMAA units, similar to PMAA\*. When dPMAA\* was used in FRAP and NR experiments with PDMA/PMAA films in control experiments (Figure S4),  $D_{\parallel}$  and  $D_{\perp}$  were both within the uncertainty of the values found for PMAA\*. Therefore, neither sparse labeling of PMAA with fluorescent dye nor deuteration of PMAA had a significant effect on the observed anisotropy of chain motion.

It is intuitive to think of diffusion of polyelectrolyte chains within layered PEMs as anisotropic, partly because of the anisotropic nature of the films themselves. Indeed, diffusion of polymer chains in anisotropic media, such as nematic solvents, is faster in the direction parallel to the nematic director.<sup>17</sup> The arrangement of polymer chains within an anisotropic structure, such as within a lamellar morphology in block copolymer melts, also leads to faster polymer chain diffusion in the direction parallel rather than perpendicular to the lamellar plane.<sup>18</sup> In both cases, however, diffusion anisotropy is relatively small and its physical origins are very different from those acting within PEMs. Unlike the examples above, internal ordering within PEMs is introduced during film construction and does not represent an equilibrium state. While PE conformations are diffuse and the layers are fuzzy, polymer chains are partially aligned through adsorption at a substrate, and PEs are stitched together through multiple ionic pairings. Highly anisotropic diffusion of polymer chains within PEMs probably results from a high activation barrier of layer intermixing to motion of an adsorbed polymer chain in the direction perpendicular to the substrate, a feature that is known to constrain adsorbed polymer chains within a 2D monolayer at a solid surface.<sup>14</sup> At thermodynamic equilibrium, polymer chain mobility must eventually erase film layering. Yet, demonstrated metastable internal layering can be long-lived and only weakly compromised by PE diffusion along the layer direction. For example, we have observed that long-term (one week) preannealing of PDMA/PMAA films in 0.8 M NaCl solutions leads to  $D_{\parallel}$ ,  $D_{\perp}$ , and  $D_{\parallel}/D_{\perp}$  values similar (within 20% experimental error) to those measured with films not subjected to preannealing.

Figure 2 shows that the observed highly anisotropic diffusion of PA chains within Q100M/PMAA multilayers also is present for films annealed in solutions at a variety of salt concentrations. Corresponding FRAP and NR data related to film annealing in 0.2, 0.4, and 0.6 M NaCl concentrations are given in Figures S5 and S6. As expected, diffusion of polymer chains was progressively enhanced as a higher concentration of extrinsic salt displaces polymer–polymer ionic pairing. Similar to experiments in 0.8 M NaCl, however,  $D_{\parallel}$  remained 4–5 orders of magnitude larger than  $D_{\perp}$  for PMAA chains within Q100M/PMAA multilayers upon exposure to 0.2–0.6 M NaCl solution.



**Figure 2.**  $D_{\perp}$  (open bars) and  $D_{\parallel}$  (filled bars) values for diffusion of PMAA chains within [(PC/PA)<sub>4</sub>/(PC/dPA)]<sub>4</sub>/(PC/PA)<sub>4</sub> and (PC/PA)<sub>2</sub>/(PC/PA\*)<sub>3</sub>/(PC/PA)<sub>2</sub> multilayer films for the Q100M/PMAA system as a function of NaCl concentration in the annealing solution. Dashed line is the FRAP sensitivity limit to measurement of  $D_{\parallel}$ .

In summary, we have measured highly anisotropic diffusion of polyelectrolyte chains within PEM films. This effect was demonstrated with two PEM systems exposed to solutions at various salt concentrations. The large magnitude of diffusion anisotropy reflects weak coupling between polymer chain diffusion in directions parallel and perpendicular to the substrate, and suggests long-lived metastable states in non-equilibrated LbL films. While further theoretical and experimental insights on the dynamic behavior of layered PEMs need to be provided, our experimental finding provides a first experimental motivation for such studies. The observed loss of film internal structure during salt annealing could have important ramifications for applications that rely on persistent stratification of LbL films.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details for polymer synthesis, sample preparation, and fitting of neutron reflectivity curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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