Layer-by-layer assembly of charged poly(phenylacetylene)s with induced macromolecular helicity†

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The macromolecular helicity of charged poly(phenylacetylene)s induced by small chiral guests in water can be retained by the alternative deposition of achiral polyelectrolytes with opposite charges, resulting in optically active multilayer thin films with a macromolecular helicity memory.

The layer-by-layer (LbL) assembly technique is the simplest and most powerful method for the preparation of multilayer thin films consisting of polyanions and polycations.[1] The alternate immersion of charged substrates of any shape or size into solutions of oppositely charged polyelectrolytes can produce tailored multilayer thin films with a controlled thickness and desired composition. Various polyelectrolytes including π-conjugated polymers[2] and biopolymers[3] have been successfully LbL assembled to develop functional thin films with potential applications for separations, catalysis, sensing, and electronic and optical devices. However, LbL multilayer thin films consisting of optically active artificial polymers are rare, although they are expected to be promising materials as enantioseparation membranes.[4] We previously reported the helicity induction in optically inactive, *cis-transoidal* poly(phenylacetylene)s bearing functional groups as the pendants upon complexation with specific chiral guests in water[5] as well as in organic solvents.[6] The complexes showed characteristic induced circular dichroisms (ICDs) in the polymer backbone regions due to the prevailing one-handed helix formation of the polymers. Moreover, the induced macromolecular helicity could be memorized after the chiral compounds were replaced by achiral ones in organic solvents.[6d–g] However, such a macromolecular helicity memory was difficult to realize in water, because the polymer retains the helicity memory only when complexed with achiral molecules such as achiral amines; therefore, the memory in water is lost. We now report our new approach for the macromolecular helicity memory in water through the fabrication of LbL assembled multilayer thin films consisting of induced helical poly(phenylacetylene)s bearing a phosphonate (poly-**1**) or an ammonium (poly-**2**) group as the pendants with chiral guests. The macromolecular helicity of the polyacetylenes can be retained by the alternative deposition of achiral polyelectrolytes with opposite charges, such as the hydrochloride of poly(allylamine) (PAH) or the sodium salt of poly(acrylic acid) (PAA), which results in the formation of optically active multilayer thin films with a controlled helicity (Fig. 1).

The optically inactive poly-**1** was first complexed with (*S*)-phenylalaninol ((*S*)-**3**) ([(*S*)-**3**]/[poly-**1**] = 5, [poly-**1**] = 0.1 mg mL^{-1}, pH 4.0) in water to induce a one-handed helix in the polymer backbone, thus showing a full ICD (the molar circular dichroism of the second Cotton effect ($\Delta\varepsilon_{2nd}$) = −14.8 at 25 °C) in the UV-visible region. The LbL assembly was then conducted on a positively charged quartz plate modified with ammonium groups using the negatively charged poly-**1**–(*S*)-**3** complex and an achiral positively charged PAH ([PAH] = 1.0 mg mL^{-1}, pH 8.0) (Fig. 2). The odd- and even-numbered steps correspond to the poly-**1** and PAH adsorptions, respectively. The multilayer films showed a stepwise increase in their absorption (Fig. 2a and inset) when the quartz plate was immersed in the poly-**1**–(*S*)-**3** solution (odd number layers) because PAH (even number layers) is transparent in this wavelength region (over 220 nm). An almost regular

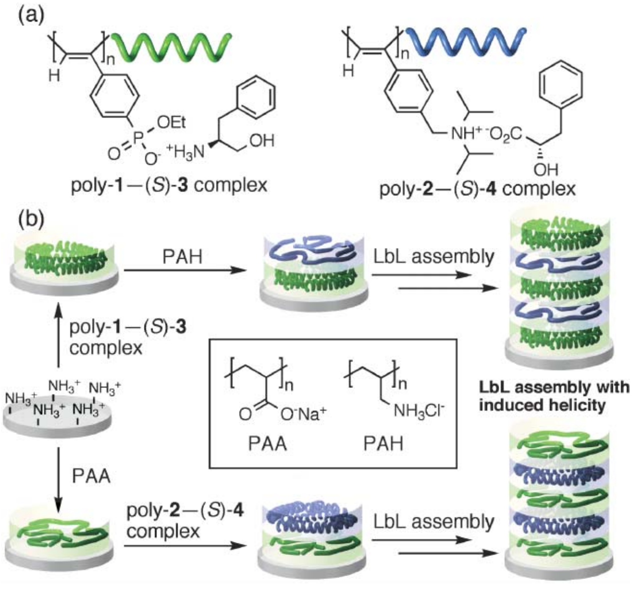

Fig. 1 Schematic illustration of the LbL self-assembly of charged poly(phenylacetylene)s with induced macromolecular helicity. (a) An excess of the one-handed helical sense is induced in poly-**1** and poly-**2**-HCl upon complexation with the optically active (*S*)-**3** and (*S*)-**4**, respectively. (b) An induced helical poly-**1** and poly-**2**-HCl can be LbL assembled with achiral polyelectrolytes with opposite charges (PAA or PAH), resulting in multilayer thin films with an induced macromolecular helicity on a substrate.

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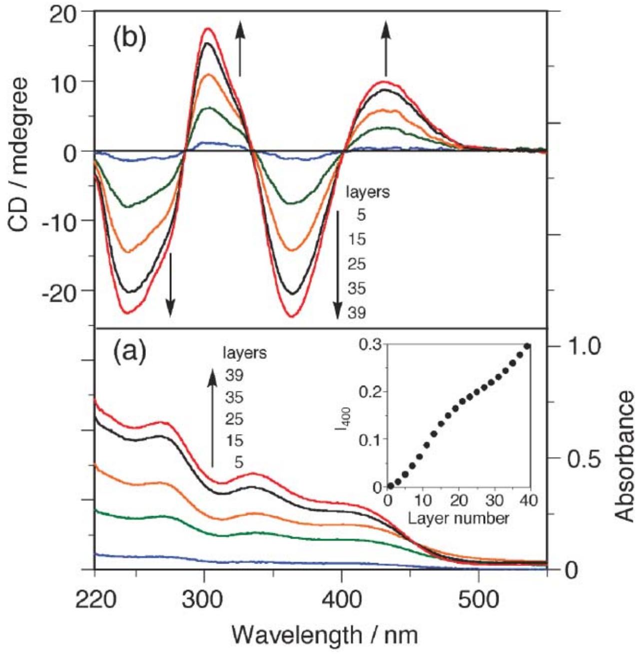

Fig. 2 Absorption (a) and CD spectral (b) changes for the stepwise assembly from the poly-**1**–(*S*)-**3** complex ([(*S*)-**3**]/[poly-**1**] = 5, [poly-**1**] = 0.1 mg mL^{-1}, pH 4.0) containing NaCl (0.024 M) and PAH ([PAH] = 1.0 mg mL^{-1}, pH 8.0) solutions. The inset in (a) shows the plots of the absorbance at 400 nm of the multilayer thin films *versus* the number of deposition cycles.

increment of the absorption intensity at 400 nm was observed except for the initial three layers, indicating that a stepwise assembly regularly occurs with almost equal amounts of deposition in each cycle after three layers. This regular deposition was also confirmed by quartz crystal microbalance (QCM) measurements except for the initial ten layers (see Fig. S1†). Such a smaller increase in the deposition during the initial stage has often been observed in LbL assemblies and is considered to be due to the influence of the substrate.[7] The surface of the film was relatively smooth at the nanometer level as observed by atomic force microscopic (AFM) measurements; the mean roughness (*Ra*) values of the film surface after 20- and 21-step assemblies were 2.3 and 1.6 nm, respectively (see Fig. S4†). The assembled multilayer films exhibited an apparent ICD in the UV-visible region and its intensity also increased with the increasing number of poly-**1** layers (Fig. 2b).[8] The observed Cotton effect patterns were similar to that of poly-**1** induced by (*S*)-**3** in water. These results indicate that the induced helical conformation of poly-**1** was preserved during the LbL assembly process in water. The CD intensity of the film did not change after 52 days at room temperature and at 80 °C for 10 h, suggesting that the helical structure of poly-**1** in the film is stable.

We also prepared multilayer thin films of a positively charged one-handed helical poly-**2**-HCl with an achiral, negatively charged PAA (Fig. 1). A one-handed helicity was induced in poly-**2**-HCl by the sodium salt of (*S*)-phenyllactic acid ((*S*)-**4**) ([(*S*)-**4**]/[poly-**2**-HCl] = 0.5, [poly-**2**-HCl] = 0.5 mg mL^{-1}, pH 3.8, $\Delta\varepsilon_{2nd} = -15.8$ at 25 °C) prior to the LbL assembly. In this case, PAA was first adsorbed on the positively charged quartz plate and then the helical poly-**2** was deposited. A similar regular deposition took place as evidenced by the almost linear relationship of the absorption intensity at 400 nm *versus* the number of layers except for the initial four layers (Fig. 3a inset) (for QCM measurement results, see Fig. S1†). The LbL films also showed ICDs,[8] whose patterns were similar to that of a helical poly-**2**-HCl induced by (*S*)-**4** in water,[5c,d] and the CD intensity increased with an increase in the number of poly-**2** layers (Fig. 3a). These results suggest the formation of PAA–poly-**2** multilayer thin films, in which the poly-**2** is trapped by the PAA layers while maintaining the induced macromolecular helicity.

The LbL assembly from the oppositely charged helical poly(phenylacetylene)s, poly-**1**–(*S*)-**3** and poly-**2**–(*S*)-**4** complexes, was then conducted (Fig. 3b). The regular increase in the absorption intensity suggests that the multilayer thin films consisting of poly-**1** and poly-**2** are uniformly assembled on the substrate (Fig. 3b inset) (for QCM measurement results, see Fig. S1†). The films also exhibited an apparent ICD[8] due to the helical poly(phenylacetylene)s,[5,6] but the intensities were much weaker than those of the poly-**1**–PAH and PAA–poly-**2** films (Fig. 3b).[9] The reason is not clear at the present time, but the induced macromolecular helicity in the poly(phenylacetylene)s may be efficiently maintained with flexible vinylpolymers, but may be lost upon complexation with the rigid-rod poly(phenylacetylene)s of the opposite charge.

As described above, the LbL multilayer thin films of poly-**1**–PAH and poly-**2**–PAA showed an optical activity due to the excess one-handed helical conformations of the poly-**1** and poly-**2**. We are very interested in the origin of the optical activity of the films. During the LbL assembly processes, if the chiral small molecules ((*S*)-**3** and (*S*)-**4**) were replaced by achiral PAH and PAA, their optical activity could be concluded to be due to the memory of the macromolecular helicity. To obtain definitive evidence, we investigated the amount of optically active guest molecules in the

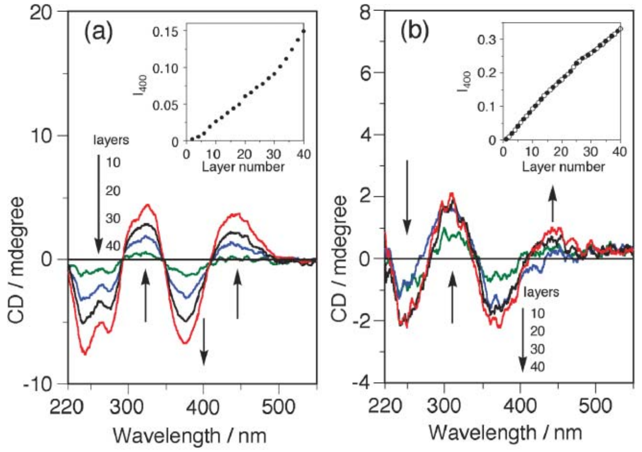

Fig. 3 CD spectral changes for the stepwise assembly from polyanion and polycation aqueous solutions of (a) PAA ([PAA] = 1.0 mg mL^{-1}, pH 5.0) and poly-**2**–(*S*)-**4** complex ([(*S*)-**4**]/[poly-**2**] = 0.5, [poly-**2**] = 0.5 mg mL^{-1}, pH 3.8), (b) poly-**1**–(*S*)-**3** complex ([(*S*)-**3**]/[poly-**1**] = 5, [poly-**1**] = 0.1 mg mL^{-1}, pH 4.0) containing NaCl (0.096 M) and poly-**2**–(*S*)-**4** complex ([(*S*)-**4**]/[poly-**2**] = 0.5, [poly-**2**] = 0.5 mg mL^{-1}, pH 3.8), respectively. The insets show the plots of the absorbance at 400 nm of the multilayer thin films *versus* the number of deposition cycles. In the inset of (b), "●" and "○" represent the outermost layer of poly-**1** and poly-**2**, respectively.

LbL films by size exclusion chromatography (SEC). A standard solution of the poly-**1**–PAH complex ([poly-**1**] = 1.0 mg mL^{-1}, [poly-**1**]/[PAH] = 1) containing a small amount of (*S*)-**3** ([(*S*)-**3**]/[poly-**1**] = 0.01) was also prepared and the solution was injected into an SEC system with alkaline water (pH 12) as the eluent. The peak due to the 0.01 equiv. of (*S*)-**3** was clearly detected (see Fig. S2†). The LbL assembled poly-**1**–PAH film (40 layers) was then dissolved in alkaline water (pH 12) and the solution was injected into the SEC system using the same mobile phase. In the chromatogram, the polymers eluted, but the peak due to (*S*)-**3** was barely detected (see Fig. S2†), indicating that the LbL film exhibiting the intense ICD contains very little (*S*)-**3**, probably less than 0.001 equiv. based on the detection limit. Consequently, the (*S*)-**3** might be completely removed during the LbL assembly process.[10] However, it was difficult to perform the same experiment for the poly-**2**–PAA and poly-**1**–poly-**2** LbL films because they were soluble neither in acidic nor basic water, and therefore, no memory effect could be concluded for the optical activity of these LbL films. To check if a tiny amount (less than 0.01 equiv.) of (*S*)-**3** was still present in the films to induce a CD in the poly-**1**, a cast film was prepared from a poly-**1**–(*S*)-**3** complex solution ([(*S*)-**3**]/[poly-**1**] = 0.01), but the film showed no CD. These results clearly showed that if 0.01 equiv. of (*S*)-**3** would be still present in the LbL film, such a small amount of (*S*)-**3** could not induce any CD in poly-**1** at all. These results also support the macromolecular helicity memory which is the origin of the optical activity of the poly-**1** in the LbL assembled multilayer thin films.

In order to estimate the memory efficiency of the macromolecular helicity in the LbL assembled films, the poly-**1**–(*S*)-**3** and poly-**2**-HCl–(*S*)-**4** films were separately prepared on a quartz plate by casting the dipping solutions used for the LbL assembly experiments, followed by evaporation of the solvent under reduced pressure, and their absorption and CD spectra were then measured.[8] The memory efficiencies of the LbL assembled thin films estimated on the basis of the corresponding cast films were 78, 38, and 6% for the poly-**1**–PAH, poly-**2**–PAA, and poly-**1**–poly-**2** systems, respectively, which were considerably different from each other depending on the combination of polyanions and polycations. A similar dependence of the memory efficiency on the structure of the chaperoning achiral amines was also observed for the macromolecular helicity memory of poly-**1** in DMSO.[6d–f] The proper selection of the counter polyelectrolytes may lead to an increase in the memory efficiency.

In summary, we have found that optically active multilayer thin films consisting of charged poly(phenylacetylene)s with a macromolecular helicity memory can be fabricated by the LbL assembly technique, thus providing the first example of macromolecular helicity memory in water. These optically active multilayer thin films consisting of helical polyelectrolytes will be used as novel chiral materials for enantioseparation and catalysis after the deposition of specific metals. Moreover, we believe that the assembled helical polyelectrolytes with a macromolecular helicity memory may serve as a template for further helicity induction in a different polyelectrolyte with opposite charges.[11] This work is now in progress.

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