

It should be emphasized that, although the high-strength DN gel has some similarities with regard to the preparation process to IPNs, it is different in concept. IPN structure is usually induced to combine various properties of each component material, such as adhesion to cells, water-absorbing ability, biocompatibility, biodegradability, etc.; these IPN hydrogels do not exhibit any notable improvement in mechanical strength in comparison to their original single-network structure.^[10] The DN gel differs also from a fiber-reinforced hydrogel, which consists of a mechanically tough “dry” component (hydrophobic plastics) and mechanically weak “wet” component (hydrophilic gel), in that the mechanical properties of the composite are basically determined by the tough “dry” component while the hydrophilic component behaves as a water absorber, playing practically no role in improving the mechanical strength.^[11] The high strength of the DN gels is not due to a linear combination of two component networks, like the common IPN or fiber-reinforced hydrogels, but due to a nonlinear effect of the binary structure. Although both of the two individual networks are mechanically weak, that is, the first one is stiff and brittle and the second soft and ductile, their combined DN gels are stiff but not brittle, ductile but not soft.

Experimental

DN hydrogels were synthesized by a (two-step) sequential network formation technique. For example, the first network of the PAMPS-1-4/PAAm-2-0.1 DN gel was synthesized from an aqueous solution of 1 M 2-acrylamido-2-methylpropanesulfonic acid (AMPS) containing 4 mol-% crosslinking agent, *N,N'*-methylenebisacrylamide (MBAA), and 0.1 mol-% initiator, 2-oxoglutaric acid, in a reaction cell consisting of a pair of glass plates with 2 mm spacing. This gel (first network) was then immersed in an aqueous solution of 2 M acrylamide (AAm), containing 0.1 mol-% MBAA and 0.1 mol-% 2-oxoglutaric acid, for one day until equilibrium was reached. The second network was subsequently synthesized in the presence of the first network. The gel thus prepared consists of two polymer networks entangled with each other. Details of the sample preparation are described in [2].

The compressive stress-strain measurements were performed on water-swollen gels using a tensile-compressive tester (Tensilon RTC-1310A, Orientec Co.). The cylindrical gel sample of 9 mm diameter and 4 mm thickness was set on the lower plate and compressed by the upper plate, which was connected to a load cell, at a strain rate of 0.1 %/min. A tensile tester (Tensilon RTC-1150A, Orientec Co.) was used to carry out uniaxial stretching on specimens of 50 mm length, 5 mm breadth, and 3 mm height at a strain rate of 10 %/min. The strain λ under compression (or stretching) is defined as the change in the thickness (or length) relative to the freestanding thickness (or length) of the specimen. Details are described in [12].

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Enantioselective Discrimination of D- and L-Phenylalanine by Chiral Polyaniline Thin Films**

By Jiaxing Huang, Veronica M. Egan, Hailan Guo, Jeong-Yeol Yoon, Alejandro L. Briseno, Iris E. Rauda, Robin L. Garrell, Charles M. Knobler, Feimeng Zhou, and Richard B. Kaner*

Polyaniline is unique in the conjugated polymer family in that it undergoes a non-redox reversible doping/de-doping process based on simple acid/base chemistry.^[1] Doping of polyaniline with a strong acid preferentially protonates the imine nitrogens, leading to an increase in conductivity from the insulating to the metallic regime.^[2] The positive charge created along the backbone by protonation is counter-balanced by negatively charged counter-ions created from the doping acid, which causes a physical rearrangement of the polyaniline chains to accommodate them. The counter-ions make very important contributions to the properties of polyaniline through their interactions with the polymer backbone and/or their effects on the packing and orientation of polymer chains. Counter-ions can be used to improve solubility, processability, and conductivity by using functionalized protonic acids.^[3-7] Wallace and co-workers^[8,9] and Havinga et al.^[10] demonstrated that chiral counter-ions can induce optical activity in achiral polyaniline. The polyaniline backbone is believed to adopt a helical conformation in the presence of chiral dopants.^[10]

Inspired by our previous experience in gas and liquid separations using polyaniline,^[11,12] we suggested the possibility of using chiral polyaniline for enantiomeric recognition.^[13] The key concept is that the chiral chain conformations induced by the dopants are retained^[14] when the dopants are removed from solid films,^[13,15] thus creating a novel chiral polymer capable of recognizing a single enantiomer of an amino acid (Fig. 1). Here, we present visual, circular dichroism (CD), and

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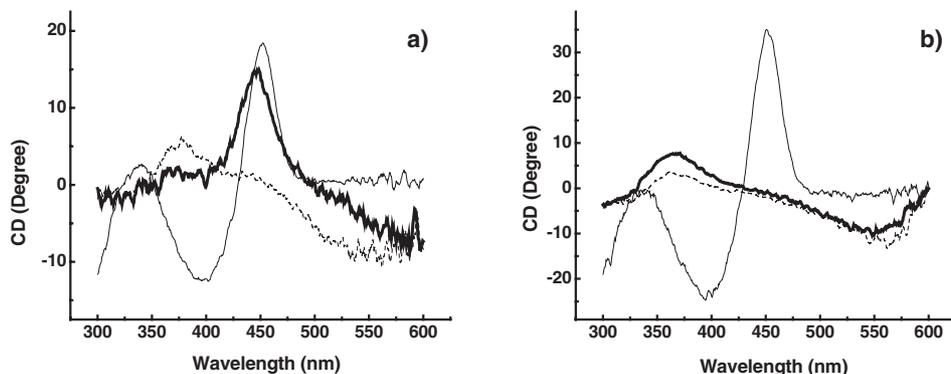


Fig. 1. Enantioselective recognition of D- and L-phenylalanine by chiral polyaniline thin films indicated by changes in their CD spectra. Thin solid lines: (R)-CSA doped films; dashed lines: films de-doped with $\text{NH}_3 \cdot \text{H}_2\text{O}$; thick solid lines: de-doped films after interacting with a) L-phenylalanine; b) D-phenylalanine. Note that for the film interacting with L-phenylalanine, the 450 nm peak in the CD spectrum is restored; while for the film interacting with D-phenylalanine, there is essentially no change at 450 nm in the CD spectrum.

UV-vis evidence for chiral discrimination between D- and L-phenylalanine by (R)-camphorsulfonic acid ((R)-CSA) de-doped polyaniline. Kinetic studies using a flow-injection quartz crystal microbalance demonstrate quantitatively the enantioselective incorporation of L-phenylalanine over D-phenylalanine. These results support a re-doping type interaction between the de-doped polymer and L-phenylalanine.

In a typical experiment, (R)-CSA doped polyaniline thin films are cast from polyaniline/(R)-CSA *N*-methyl-pyrrolidone (NMP) solutions. The as-cast (R)-CSA doped polyaniline thin films appear green (Fig. 2a), as expected for doped polyaniline in its emeraldine salt form. The films are then de-doped with 0.1 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ resulting in an instant color change from green to blue (Fig. 2b). The blue color indicates a transformation of polyaniline to its de-doped emeraldine base form. X-ray photoelectron spectra (XPS) of de-doped polyaniline thin films show no detectable sulfur, confirming that the CSA dopant is completely removed by base. De-doped films subsequently exposed to L-phenylalanine change from blue to green (Fig. 2c), while films exposed to D-phenylalanine remain blue (Fig. 2d). Depending on the thickness of the films, the time for a visually distinguishable color change varies from hours to days. The photos in Figure 2 were taken after the films were immersed in phenylalanine solutions for one week. Corresponding changes in the UV spectra before and after interaction with the L- or D-enantiomers are shown in Figure 3. For de-doped films immersed in D-phenylalanine solution, no color or UV spectral changes are observed even after one month. For the films immersed in L-phenylalanine, two shoulders appear at 440 nm and 860 nm in the UV spectra. These are the characteristic absorption bands of polyani-

line in its doped state (as can be seen by comparing with the (R)-CSA doped polyaniline spectrum in Fig. 3b) corresponding to electronic transitions from the valence band to the polaron band.^[16] These changes in the UV spectra indicate that the de-doped polyaniline films are partially re-doped by L-phenylalanine. This re-doping effect is also apparent in the CD spectrum (Fig. 1b).

In control experiments, *un*-doped achiral polyaniline thin films (i.e., films that had never been doped) were tested for chiral recognition. No color change or changes in the UV-vis spectra were observed for films immersed in either D- or L-phenylalanine for one month. Un-doped polyaniline thin films are chemically identical to (R)-CSA de-doped chiral

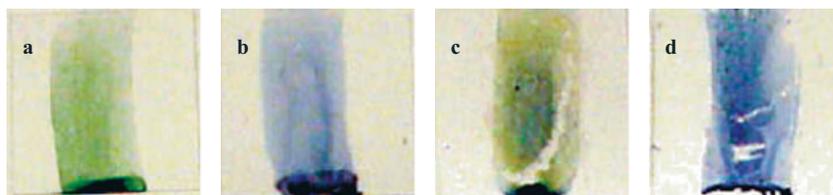


Fig. 2. Colors of polyaniline films on glass slides: a) a green (R)-CSA doped polyaniline thin film; b) a blue (R)-CSA de-doped polyaniline thin film; c) a de-doped polyaniline thin film turns green after exposure to L-phenylalanine; d) a de-doped polyaniline thin film stays blue after exposure to D-phenylalanine. Scratches on the films in (c) and (d) were made to identify the coated side of the glass slide.

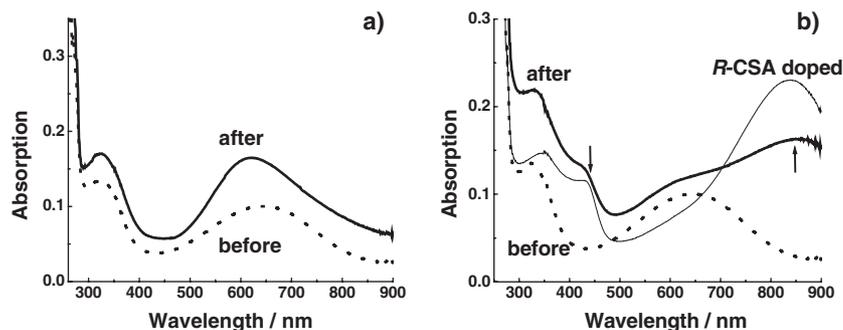


Fig. 3. UV-vis spectra of de-doped polyaniline thin films before (dotted line) and after (thick solid line) exposure to a) D-phenylalanine and b) L-phenylalanine. A UV-vis spectrum of (R)-CSA doped polyaniline film (thin solid line) is shown in (b) for comparison.

polyaniline thin films, except for their doping/de-doping history. Therefore, the chiral recognition ability of the de-doped films must be attributed to the chiral sites produced from incorporating and then removing the (*R*)-CSA dopants.

Normally, in order to dope emeraldine base polyaniline with an acidic dopant, the pH of the solution must be < 4 .^[2] Because the isoelectric point of phenylalanine is only 6.3–6.4, an aqueous solution of phenylalanine alone is not acidic enough to dope the emeraldine base form of polyaniline. When un-doped polyaniline thin films are immersed in either *D*- or *L*-phenylalanine solutions, no color change is observed, indicating no phenylalanine uptake. However, when polyaniline is first doped with the chiral acid (*R*)-CSA and then de-doped, the films are selectively re-doped by *L*-phenylalanine. While (*R*)-CSA doped polyaniline films change color immediately upon interacting with 0.1 M $\text{NH}_3 \cdot \text{H}_2\text{O}$, *L*-phenylalanine re-doped films stay green for up to three hours after exposure to base. The robustness of the *L*-phenylalanine re-doped films against de-doping suggests that *L*-phenylalanine is partially trapped by the chiral sites in the polymer film. Ionic interactions, hydrogen bonding, and π - π stacking along with size and shape selectivity between polyaniline and *L*-phenylalanine may contribute to this trapping effect. This explains why *L*-phenylalanine diffuses out much more slowly than a typical strong acid dopant.

The preferential uptake of one enantiomer over the other by a chiral recognition thin film can be detected using a quartz crystal microbalance (QCM).^[17–19] In this work, real-time frequency changes of two de-doped polyaniline coated quartz crystals were recorded and compared after injecting *D*- and *L*-phenylalanine using a flow-injection system (Fig. 4). For both enantiomers of phenylalanine, there is a sharp decrease in the QCM resonance frequency within the first 300 s following injection. For *D*-phenylalanine, this frequency drop is about 17 Hz, which then stabilizes within 3 Hz for the remaining 55 min of interaction with the *D*-phenylalanine solution. For *L*-phenylalanine, the frequency also drops sharply within the first 300 s, by about 24 Hz, but then continues to drop 16 Hz more until injection ends. The sharp frequency drop in the first 300 s for both *D*- and *L*-phenylalanine may be explained by non-specific adsorption driven by interactions such

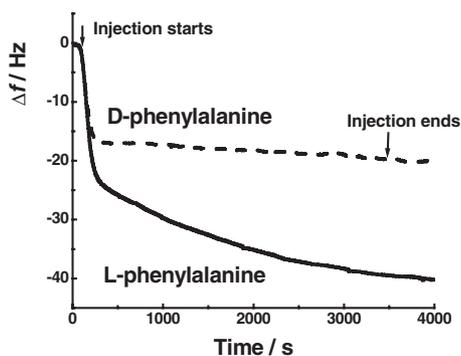


Fig. 4. Frequency change (Δf) of two 10 MHz crystals coated with the same amount of de-doped polyaniline after injecting *D*-phenylalanine and *L*-phenylalanine, respectively.

as π - π stacking and hydrogen bonding. The rate of *L*-phenylalanine uptake decreases after this initial period, consistent with a slower diffusion process into the chiral cavities in the films. *D*-phenylalanine can not re-dope the polymer so no significant decrease in resonance frequency is observed after the non-specific surface adsorption. Using flow-injection QCM, chiral recognition of other amino acids and their derivatives are currently under investigation. Similar QCM responses have been observed after injecting *D*- and *L*-alanine, and *D*- and *L*-glutamic acid.

Thus, enantioselective interactions between (*R*)-CSA de-doped polyaniline thin films and *L*-amino acids such as phenylalanine are demonstrated. Although this effect may appear to be analogous to molecular imprinting,^[20,21] here the imprinted chiral “seeds” (dopants) can be fully recovered, through simple acid/base chemistry. Since doping/de-doping is not a precise imprinting process involving forming and breaking covalent bonds, the structure of the seeds and targets can be quite different, such as (*R*)-camphorsulfonic acid and *L*-phenylalanine. Therefore, polyaniline could potentially serve as a more general matrix to host various chiral dopants, and be used as an enantiomeric sensor or separation material for a range of chiral molecules.

Experimental

Chiral Polyaniline Thin Films and Enantiomeric Recognition: Aniline (Fisher, 99.9%), (1*R*)-(-)-10-camphorsulfonic acid (Aldrich, 98%), *L*-phenylalanine (Aldrich, 99.8%), and *D*-phenylalanine (Aldrich, 99.8%) were used as received. Polyaniline was synthesized via oxidation of aniline with ammonium peroxydisulfate in 1.0 M HCl at 0 °C [1]. Since films cast from hydrated chiral polyaniline solutions [22] adhere to glass slides better than films cast from anhydrous solution do, hydrated polyaniline/(*R*)-CSA solutions were used in this study. To prepare a hydrated polyaniline/(*R*)-CSA solution, the polyaniline emeraldine base powder was first immersed in 10 mL deionized water for 24 h, and then vacuum filtered for 15 min. Differential scanning calorimeter (DSC) measurements indicate that the weight ratio of water in such hydrated powder is about 50%. The hydrated powder was then mixed with *R*-CSA in NMP, with a weight ratio of polyaniline/(*R*)-CSA = 2:1. The solution was kept at room temperature for at least 48 h before filtering. Polyaniline/(*R*)-CSA thin films were cast using the filtrate on quartz slides, and dried either in a 60 °C oven or under a heat lamp. The films were de-doped in 0.1 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ before interacting with *D*- or *L*-phenylalanine solution (concentration: 5 mg mL⁻¹). For control experiments, “un-doped” polyaniline (emeraldine base) thin films were made in the same manner, except that no (*R*)-CSA, only pristine polyaniline emeraldine base powder was used to prepare the solution. UV spectra of (*R*)-CSA doped polyaniline and de-doped films before and after interacting with *D*- or *L*-phenylalanine were recorded on a Beckman DU 640 spectrophotometer. CD spectra were taken on a Jasco J715 CD Spectropolarimeter. Films for CD were immersed in *D*- or *L*-phenylalanine solution for up to 45 days to ensure complete interaction.

QCM Studies: A custom-built flow-injection quartz crystal microbalance (FI-QCM) [23] was employed to monitor the real time interactions between polyaniline and *D*- and *L*-phenylalanine. The QCM was controlled by a CHI 440 Electrochemical Workstation (CH Instruments, Inc.) which determines the frequency difference between the working crystal and a reference crystal. An acrylic QCM flow cell (International Crystal Manufacturer Co. Inc.) with an internal volume of ca. 70 μL was used in conjunction with a six-port rotary valve (Valco Instruments Co., Houston, TX). The QCM cell and the oscillator circuit box were housed in a Faraday cage (Elchema Inc.). 10 MHz AT-cut crystals (International Crystal Manufacturer Co. Inc.) with polyaniline/(*R*)-CSA thin films pre-coated on polished gold electrodes, in a “brush-painting” manner, were used in these experiments. Before the flow-injection starts, frequencies (f) of the crystals were measured at three stages with a Hewlett Packard LF impedance analyzer (4192 A, ~5–13 MHz): before coating with polyaniline/(*R*)-CSA (f_1), after coating (f_2), and after de-doping the films (f_3). Since the frequency

change of a QCM crystal is proportional to the mass loaded on its gold electrodes [24], the difference between f_2 and f_1 ($f_2 - f_1$), is proportional to the mass of polyaniline/R-CSA thin films on the electrodes, while the difference between f_3 and f_1 ($f_3 - f_1$), is proportional to the mass of de-doped polyaniline. Since only the de-doped polyaniline thin films have chiral recognition ability, two crystals containing about the same amount of de-doped polyaniline, i.e., same values of ($f_3 - f_1 = 400$ Hz), were used in each pair of trials comparing L-phenylalanine and D-phenylalanine. In a typical experiment, a 1000 μL sample loop was loaded with D- or L-phenylalanine while the flow rate was set at 1 mL h^{-1} , so that the total interaction time between polyaniline and D- or L-phenylalanine was 60 min. The six-port valve was used to switch between "loading" and "injecting" phenylalanine solutions. A pre-coated crystal was first de-doped with $0.1 \text{ M NH}_3 \cdot \text{H}_2\text{O}$, and then assembled in the flow-injection cell so that the pre-coated side was exposed to liquid, while the other side is open to air. The injection of D- or L-phenylalanine (concentration: 5 mg mL^{-1}) did not start until the baseline stabilized within 1 Hz for at least 10 min. A computer was used to monitor the real time frequency change (Δf) of the crystal, and collect one data point per second.

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Electrospinning of Continuous Carbon Nanotube-Filled Nanofiber Yarns**

By Frank Ko,* Yury Gogotsi, Ashraf Ali, Nevin Naguib, Haihui Ye, Guoliang Yang, Christopher Li, and Peter Willis

Although tremendous progress has been made in the synthesis and characterization of single wall carbon nanotubes (SWNTs),^[1–4] a major challenge remains in the search for an effective means to bridge the dimensional and property gap between nanotubes and engineering materials and structures.^[5,6] In order to translate the superior properties of SWNT to meso- and macro-scale structures, considerable effort has been devoted to the development of linear and planar SWNT assemblies.^[7–9] This paper describes an electrospinning process capable placing SWNTs into a continuous nanoscale composite fibril. This composite fibril shows superior mechanical properties and can be used, as a reinforcement, for a variety of composites. Alignment of SWNT bundles in the fiber has been successfully achieved. Upon heat treatment, the composite fibrils are carbonized at 1100°C to form the SWNT/carbon yarns. SWNT structure has been maintained after carbonization. The latter process has a potential to produce advanced carbon fibers for the reinforcement of composites.

Electrospinning is an electrostatically induced self-assembly process wherein ultra-fine fibers are produced.^[10] In the electrospinning process, a high voltage is generated between a negatively charged polymer fluid and a metallic fiber collector for random orientation or nanoscale fibril alignment as shown in Figure 1.

The polymer fluid is contained in a polymer reservoir with a capillary tip. The electrospinning of polymer solutions allows the formation of nanoscale ($< 100 \text{ nm}$) fibrils.^[10–12] Incorporation of random carbon nanotubes (CNT) into these fibrils is expected to improve the thermal conductivity, electrical conductivity, and mechanical properties of the fibrils, and to provide a means for development of CNT/polymer composites^[7,13–15] and reinforced carbon fibers with improved properties.

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