



## Hydrogen bond detachment in polymer complexes



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### ABSTRACT

The hydrogen bonded polymer complex bulk and thin film was prepared by solution mixing and layer-by-layer assembly, respectively. Poly(vinylpyrrolidone) (PVPON) and poly(ethylene oxide) (PEO) were hydrogen bonding acceptor polymers while poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) were hydrogen bonding donor polymers. The detachment of hydrogen bond between the chains in polymer complexes was investigated during the dissolution in alkaline solution, ionic liquid and tertiary amine N-oxide. We compared the dissolution process of the polymer complex bulk with the polymer complex thin film, and discussed the polymer chain length, chain entanglement degree and temperature effect on hydrogen bond detachment and dissolution of polymer complexes.

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### 1. Introduction

The concept of hydrogen bond has been put forward for nearly a century [1,2]. Hydrogen bond changes the physical properties of matter, such as melting and boiling points, vapor pressure, heat of vaporization, molar volume, heats of mixing, dielectric properties, and so on. And hydrogen bond affects the supramolecular and crystal structure, for example  $\alpha$ -helix and  $\beta$ -sheet structure motif in protein and double helix in DNA are fixed by hydrogen bonding.

The importance of hydrogen bonding has been realized by physics, chemists, biologist, and materials scientist [3,4]. A huge number of research papers and a serial of monographs on hydrogen bonding have been publishing [5–12]. In material science, most research work is concentrated on hydrogen bond formation and how it affects the structure and properties of material, while there is little work concerning hydrogen bond detachment process. However, hydrogen bond detachment is related to many important processes in science and technology, such as genetic information transfer and dissolution processing of biomass. As fossil fuel exhausted, the petroleum-based material will meet great challenges. Using biomass with a green and economic way will give us

new opportunities [13]. However, the bio-renewable resource such as cellulose, chitin and silk is difficult to be processed because of poor solubility in common solvents due to the tremendous hydrogen bonds in structure [14,15].

For small molecules, the hydrogen bond in one molecule is named as intra-molecular hydrogen bond, while between molecules is inter-molecular hydrogen bond. Generally, polymer is a long chain structure therefore there exist intra-chain hydrogen bonds, such as in  $\alpha$ -helices, and inter-chain hydrogen bonds, like in  $\beta$ -sheets or double helix. Cellulose, the most abundant bio-renewable polymer in the world, has both intra-chain and inter-chain hydrogen bonds [16]. Inter-chain hydrogen bonds can form from the same kind of polymer chain, such as nylon [17], or from two different chains, such as polymer complexes [18–20]. In polymer bulk, there are amorphous region and crystal region, and hydrogen bonds can present both in crystalline state and in amorphous state. Due to complicated chain conformation and multi-scale relaxation, hydrogen bond detachment in polymer systems should be more complicated than that in small molecules. This work is to study hydrogen bond detachment in polymers, and the hydrogen bonded polymer complex is selected as the model system.

We prepare the hydrogen bonded polymer complexes, from PVPON or PEO as hydrogen bonding acceptor polymer and from PAA or PMAA as hydrogen bonding donor polymer. The hydrogen bonded polymer complexes in bulk are produced by mixing donor polymer solution and acceptor polymer solution, while the hydrogen bonded polymer complex thin films are fabricated with layer-by-layer assembly method [21–23]. In early 1990s, Decher

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[21] developed layer-by-layer assembly to prepare thin film basing on coulomb force between polyanion and polycation. Subsequently, Ruber et al. [22] and Zhang et al. [23] used layer-by-layer assembly to prepare thin film basing on hydrogen bonding between two kinds of polymers, i.e. hydrogen-bonded polymer complex thin film on solid substrate. In the polymer complexes, hydrogen bonds formed between two different type polymer chains and these hydrogen bonds are completely in amorphous state. We will investigate the dissolution of hydrogen bonded polymer complex in different solvent and analyze the hydrogen bond breakage mechanism.

## 2. Experimental section

### 2.1. Materials

Poly(vinyl pyrrolidone) (PVPON) (K30,  $M_w = 40,000$ ; K90,  $M_w = 360,000$ ), poly(acrylic acid) (PAA) ( $M_w = 450,000$ ), PAA sodium salt (35% water solution,  $M_w = 15,000$ ), poly(ethylene oxide) (PEO) ( $M_w = 100,000$ ;  $M_w = 600,000$ ), and N-methyl morpholine-N-oxide (NMMO) monohydrate (98%) were purchased from Sigma–Aldrich. Poly(methacrylic acid) (PMAA) ( $M_w = 100,000$ ) was brought from Polysciences Inc. Cellulose pulp ( $\alpha$ -cellulose 95.5%, DP 686) was provided with Baoding glue factory. Ionic liquids 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) were purchased from Chengjie Chemicals Ltd. Sodium hydroxide and other chemicals used in this study were of analytical grade. All chemicals were used as received.

### 2.2. Polymer complex bulk

The polymer complex bulk was obtained by mixing 10.0 mg/mL aqueous solutions of PAA (or PMAA) and PVPON (or PEO) with the same volume. The hydrogen bonding acceptor polymer solution was drop-wisely added into the hydrogen bonding donor polymer solution under magnetic stirring at 25 °C. Before mixing, the pH values of all the solutions were adjusted to 2.0 by adding HCl solution under the monitoring of a pH-meter (Mettler, SR-40). The mixed solution was stirred for 24 h, then the polymer complex was filtered out from the solution, and finally dried at 50 °C under vacuum condition for 24 h. The bulk polymer complex was weighted to calculate the yield.

### 2.3. Polymer complex thin film

The polymer complex thin films were deposited on quartz or silicon substrates. Before the film preparation, the substrates need to be rigorously cleaned. The substrates were immersed in piranha solution ( $H_2SO_4/H_2O_2$ ) mixture (7:3 v/v) for 30 min (*caution: this solution is extremely corrosive*), followed by rinsing with deionized water for 5 times, and dried with a stream of pure  $N_2$  for 3 min. The films were deposited on solid substrate with an automated machine (North Tianfu Ltd. Beijing, China). This machine alternately immersed the substrates into 10.0 mg/mL PVPON solution and PAA solutions, with the interval of three rinses in acidic water (pH = 2.0). The assembling and rinsing time were set to 4 and 1 min, respectively. The pH values of assembling and rinsing solutions were both adjusted to 2.0. In order to improve homogeneity, the as-prepared films were incubated in acidic water (pH = 2.0) at 25 °C for 24 h [24]. After incubation, the wet film was dried with pure  $N_2$  flow for 3 min again, and then preserved in the desiccator. The prepared film was expressed as (PVPON/PAA) $_n$ , which means the film was fabricated from PVPON and PAA through  $n$  assembling cycle(s).

### 2.4. Dissolution of polymer complex bulk

The 10.0 g 4.0 wt% NaOH solution, [AMIM]Cl, [BMIM]Cl or NMMO was put into a glass tube, and then the tube was immersed into the oil bath, which controlled the dissolving temperature. After immersing the tube for 60 min (the temperature of the solvent in the tube is stabilized), 0.5 g polymer complex was added into the tube. The dissolving state of the polymer complex was observed at different time point.

### 2.5. Dissolution of polymer complex thin film

The PVPON/PAA films were immersed into [AMIM]Cl, [BMIM]Cl or NMMO at a certain temperature for different time. When the film was drawn out, the ethanol was used to wash the retarded ionic liquid or NMMO. UV–visible spectrometer, atomic force microscope (AFM), and Fourier-transform infrared (FT-IR) spectrometer were applied to monitor the thin film during dissolving process.

### 2.6. Characterization

Thermal analysis was carried out on a differential scanning calorimeter (TA Instruments, Q20). Aluminum pan containing 5 ~ 10 mg of sample was used in all cases. The scans was carried out across the 50 ~ 250 °C range, under a nitrogen atmosphere. The glass transition temperature ( $T_g$ ) was taken from the second heating scan ( $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ ) as the mid-point of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines.

IR spectra were collected at a spectral resolution of  $4\text{ cm}^{-1}$  on a Nicolet FT-IR spectrometer. The polymer complex bulk was milled with KBr and then pressed into standard disk for IR measurement. The polymer complex thin film is deposited on silicon substrate for IR characterization. Using blank silicon substrate to do base line, then the film deposited on silicon substrate was measured.

AFM images were recorded on an Agilent 5500 instruments in the tapping mode. A commercial silicon probe (model TESP-100) with a typical resonant frequency of approximately 300 kHz was used to scan the film.

UV–visible spectra of polymer complex thin films were recorded on a Shimadzu UV-2550 spectrophotometer (spectroscopic region: 190–900 nm). The thin films were deposited on the UV–visible transparent quartz slides (12 mm  $\times$  45 mm). The measurement was done on transmission mode. The film deposited quartz slide was fixed on sample beam line while the blank quartz slide was put on reference beam line with the film clamp holder.

## 3. Results and discussion

### 3.1. Hydrogen bonding in polymer complex

Poly(carboxylic acid) can form hydrogen bonding polymer complex with neutral polymers such as poly(vinylpyrrolidone) and poly(ethylene oxide). The polymer complex forms due to cooperative hydrogen bonding. The small molecules homologs cannot separate out from the solution to form the complex. There is a critical molecular weight, above which the polymer complex can form [25]. Besides the polymer chain length, pH value, temperature, and solvent affect the hydrogen bonding complexation behavior [18–20]. As the pH value increases, the poly(carboxylic acid) will ionize. From one side, the ionization will decrease the quantity of the hydrogen bonding donor; from the other side, ionization will produce negative charges on polymer chain and charge repulsion will interrupt the hydrogen bonding [26]. Only pH below the critical value, the polymer complex will form and

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