

## Molecular recognition within a poly(amide urethane) system

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### ABSTRACT

The heterodimer recognition within a poly(amide urethane) (PAU) has been achieved through the incorporation of the amphiphilic alkylated nucleobase, 1-hexadecyluracil (U16). The heterodimer recognition led the poly(amide urethane) to exhibit the “plug and play” behavior even the heterodimer recognition coincided with several other hydrogen bonding motifs. In addition, the PAU/U16 blends possess nano-scale lamellar structure of U16 phase within lamellar structure of PAU phase. The nano-scale lamellar structure of the packed U16 gradually transforms from one to the other with the change in the U16 content in the blends.

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### 1. Introduction

Polymers with specific structures such as block copolymers are usually formed through covalent linkages in conventional polymer chemistry. Recently, polymers with specific microstructures resulting from directional and strong non-covalent hydrogen bonding interactions have become one of the important fields in the development of polymer materials [1,2]. These new polymers (supramolecular polymers) utilize non-covalent multiple-hydrogen-bonding interactions similar to those found in biomolecules such as protein, DNA, and RNA to direct and modulate their 3-D topology [3]. In addition, the moderately strong and highly directional multiple-hydrogen-bonding interactions also result in unique physical properties, such as high specificity, controlled affinity, and reversibility [3,4]. Until now, studying and controlling the microstructures within supramolecular polymers still remain as a challenging task [5].

In previous reports, the study on the complementary nature and its effect on material properties can be broadly classified into side chain [6] and chain ends types [7]. The amine-functionalized polymer reported by Rotello and co-workers [8] and the quadruple hydrogen-bonded ureidopyrimidone derivatives with donor–donor–acceptor–acceptor (DDAA) proposed by Sijbesma, Meijer, and co-workers [9] were the representative cases of the study on the side chain and chain ends types, respectively. In addition, Ikkala et al. reported supramolecular comb-coil diblock

copolymers [10] and indicated the diverse hierarchical nanostructures within the system [11]. In our previous study, we reported the heterodimer recognition [thymine–adenine (T–A) base pair] between DNA-like side-chains on different polymers, indicating that the *d*-spacing within the well-ordered lamellar complex was influenced by the complementary interaction [12]. In this study, the amphiphilic alkylated nucleobase, 1-hexadecyluracil (U16) was incorporated into poly(amide urethane) [13] containing self-complementary group. The effect of the heterodimer recognition on the microphase separation was investigated, revealing that the heterodimer recognition led the poly(amide urethane) to exhibit the “plug and play” behavior even the heterodimer recognition coincided with several other hydrogen bonding motifs.

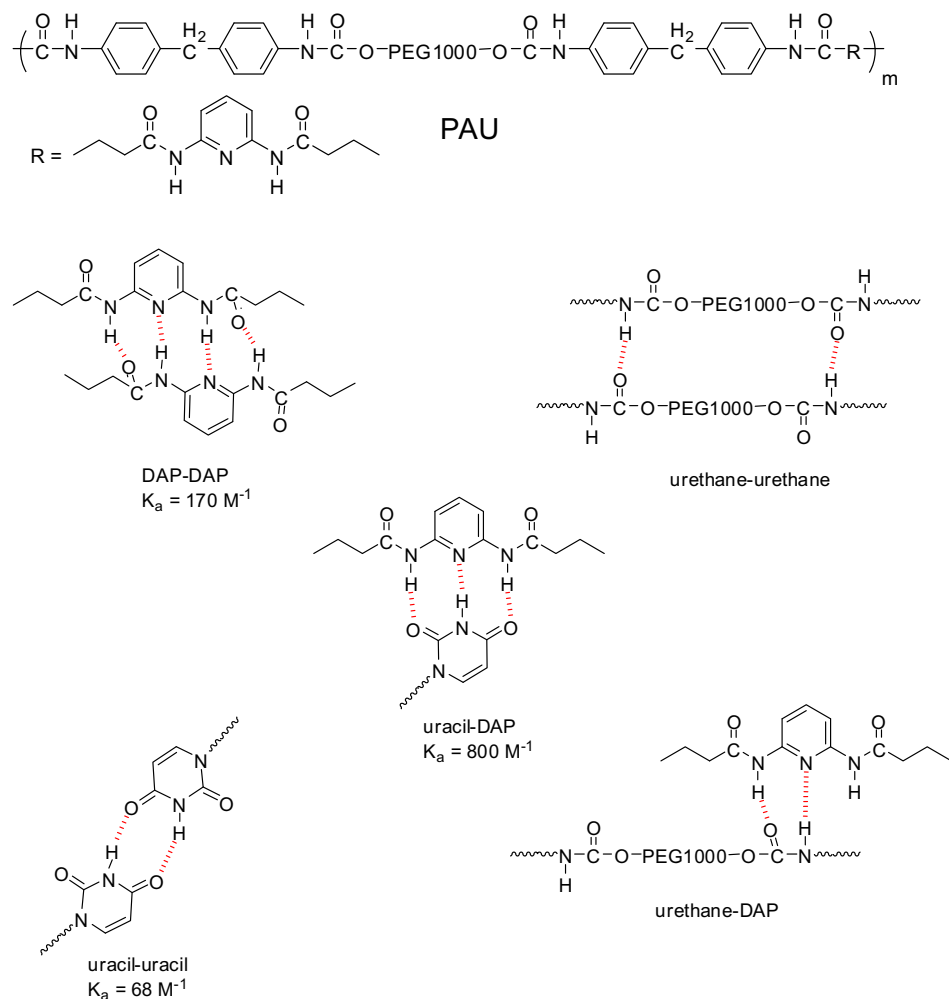
### 2. Results and discussion

#### 2.1. The complementary interaction within the PAU/U16 blends

There are several hydrogen bonding motifs within the PAU/U16 blend as shown in Scheme 1. For PAU, the DAP group has the self-complementary interaction with equilibrium constant ( $K_a$ ) of  $170 \text{ M}^{-1}$  as previously reported [14]. The strength of the self-complementary interaction is relatively stronger as compared with other hydrogen bonding interactions within PAU such as the urethane–urethane interaction and the urethane–DAP interaction because the numbers of the interacted sites play a critical role in determining the strength of the hydrogen bonds [14]. In addition, the uracil group of U16 also possesses self-complementary interaction and the equilibrium constant was calculated to be  $68 \pm 5 \text{ M}^{-1}$  [15]. As U16 is incorporated into PAU, the strongest

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**Scheme 1.** The structure of PAU and hydrogen bonding motifs within the PAU/U16 blend.

interaction, the uracil–DAP interaction, within the system is formed of which  $K_a$  was calculated to be  $800 \text{ M}^{-1}$  in the previous study [14]. Because the uracil–DAP interaction possesses the highest  $K_a$  among all these  $K_a$ s within the PAU/U16 blend, the formation of heterodimer recognition (uracil–DAP interaction) is relatively more preferable.

Fig. 1(a) illustrates the variable temperature FTIR spectra of C=O stretching region of PAU. The peaks centered at 1730, 1704, and  $1685 \text{ cm}^{-1}$  correspond to the free urethane C=O, hydrogen bonded urethane C=O, and amide I groups of PAU, respectively [13]. Upon heating, the intensity of the hydrogen bonded urethane C=O band is gradually decreased. The FTIR spectra of C=O stretching of the PAU, U16, and PAU/U16 blends with different weight ratios are shown in Fig. 1(b). The U16 possesses imide and amide groups centered at 1728 and  $1677 \text{ cm}^{-1}$  which are located almost in the same region of those PAU C=O groups. Obviously, it is very difficult to analyze the hydrogen bonding interactions within this region. FTIR spectra within the NH stretching region of PAU and PAU/U16 blends at different temperatures are shown in Fig. 2(a) and (b), respectively. As shown in Fig. 2(a), the PAU has four bands centered at 3315, 3262, 3225, and  $3180 \text{ cm}^{-1}$ . Upon heating, these bands are gradually shifted toward  $3315 \text{ cm}^{-1}$ , implying that the band at  $3315 \text{ cm}^{-1}$  represents the free NH group within PAU. The band centered at  $3180 \text{ cm}^{-1}$  corresponds to the hydrogen bonded DAP NH group because of its highest  $K_a$  value.

The spectrum obtained at  $220 \text{ }^\circ\text{C}$  still possesses a small band at  $3180 \text{ cm}^{-1}$ , which also reflects the high  $K_a$  between the hydrogen bonded DAP NH groups within PAU. Bands at 3262 and  $3225 \text{ cm}^{-1}$  can be attributed to the hydrogen bonded urethane–urethane and urethane–DAP groups, respectively. As mentioned above, the stronger interaction results in lower wavenumber [12]. In Fig. 2(b), the U16 possesses bands centered at 3164 and  $3433 \text{ cm}^{-1}$  corresponding to the hydrogen bonded and free uracil NH group, respectively. Furthermore, for the PAU/U16 (1/1) blend, the band of the hydrogen bonded uracil NH group shifts to  $3179 \text{ cm}^{-1}$  and therefore we can attribute it to the hydrogen bonded uracil–DAP NH group. In addition, the variable temperature FTIR spectra of the PAU/U16 (10/1) also indicate that the hydrogen bonding interactions within the blend possess similar behavior to that observed in the PAU upon heating (see Supporting information). In order to observe the change from the addition of U16 more clearly, band at  $3179 \text{ cm}^{-1}$  is chosen as a reference and the normalized spectra are shown in Fig. 2(c). As shown in Fig. 2(c), upon incorporating U16 to PAU, the intensities of the bands at 3262 and  $3315 \text{ cm}^{-1}$  corresponding to the urethane–urethane interaction and free NH groups are both increased. The increase in the intensities results from the formation of the uracil–DAP interaction (the highest  $K_a$ ) influencing both DAP–DAP and urethane–DAP interactions. The consequence is consistent with that from the comparison of these equilibrium constants.

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