

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.

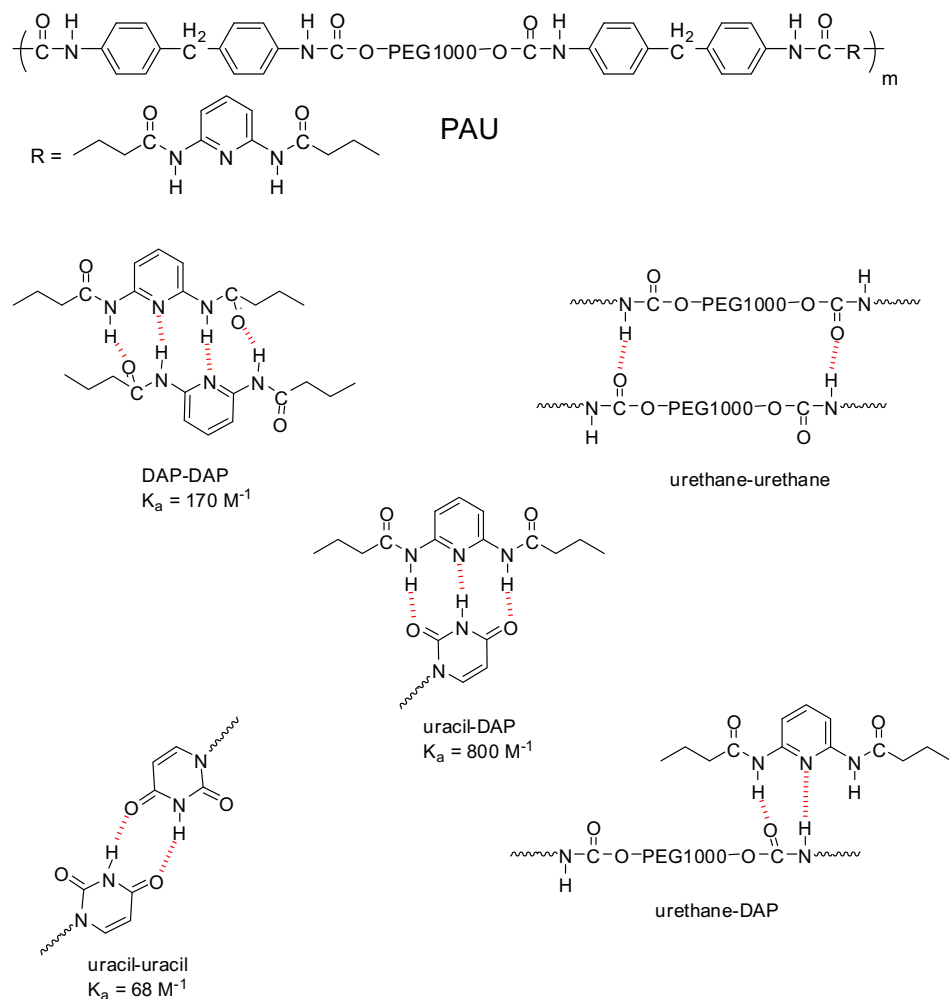
2. Results and discussion

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 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 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 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 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 cm^{-1} . Upon heating, these bands are gradually shifted toward 3315 cm^{-1} , implying that the band at 3315 cm^{-1} represents the free NH group within PAU. The band centered at 3180 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 cm^{-1} , which also reflects the high K_a between the hydrogen bonded DAP NH groups within PAU. Bands at 3262 and 3225 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 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 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 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 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.

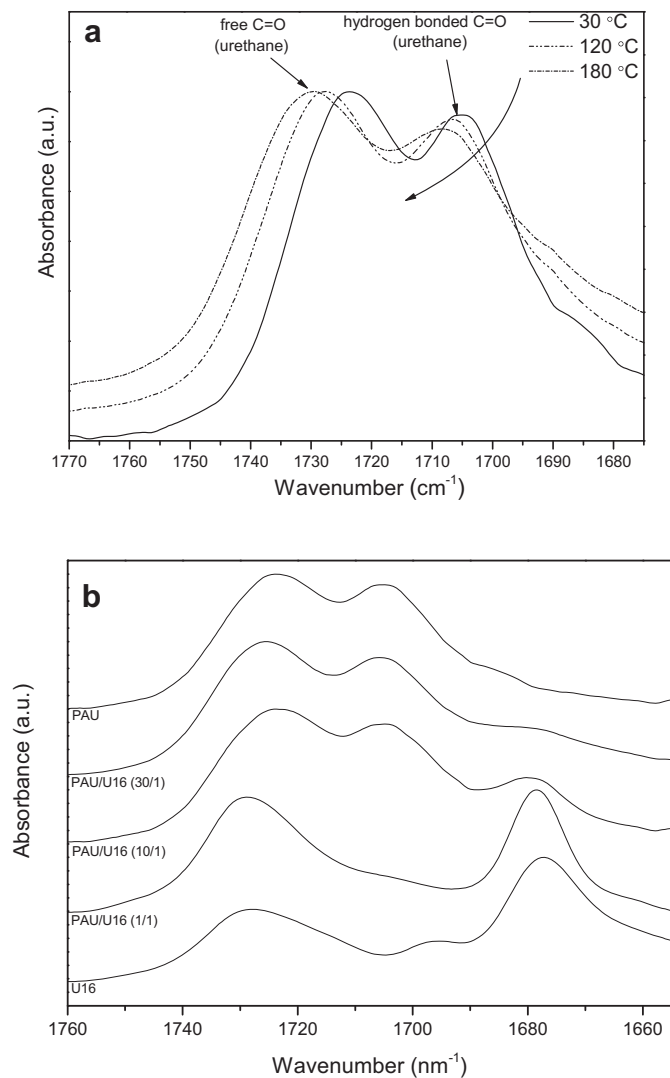


Fig. 1. Normalized FTIR spectra of (a) PAU obtained at various temperatures and (b) PAU, U16, and PAU/U16 blends.

2.2. The change in the microstructure

Fig. 3(a) and (b) illustrates the SAXS and WAXD profiles of the PAU, U16, and PAU/U16 blends, respectively. As shown in Fig. 3(a) and (b), the U16 possesses two series of highly long ranged ordered reflection of q/q^* ratios of 1:2:3, an indication of two series of lamella structures.

According to the simulation from the software (see Supporting information), ChemDraw, the lamella structures with size of 3.9 and 2.4 nm can be attributed to the packed U16 with uniformly stretched and interpenetrated alkyl chains as shown in Scheme 2. In addition, the PAU also exhibits a lamellar structure with relatively larger size and lower degree of order [13]. For the PAU/U16 blend with low U16 content such as PAU/U16 (30/1) blend, the SAXS profile of PAU is not influenced by the incorporation of U16, indicating that the incorporated U16 does not affect the lamellar structure of PAU while the U16 only possesses the lamella structure from its stretched alkyl chain. When the U16 content is increased, the SAXS profile in the low q region of PAU/U16 blend remains unchanged while several peaks corresponding to the change in the packed U16 occur as shown in Fig. 3(a) and (b). As the U16 content is further increased, the PAU lamellar structure still remains and the

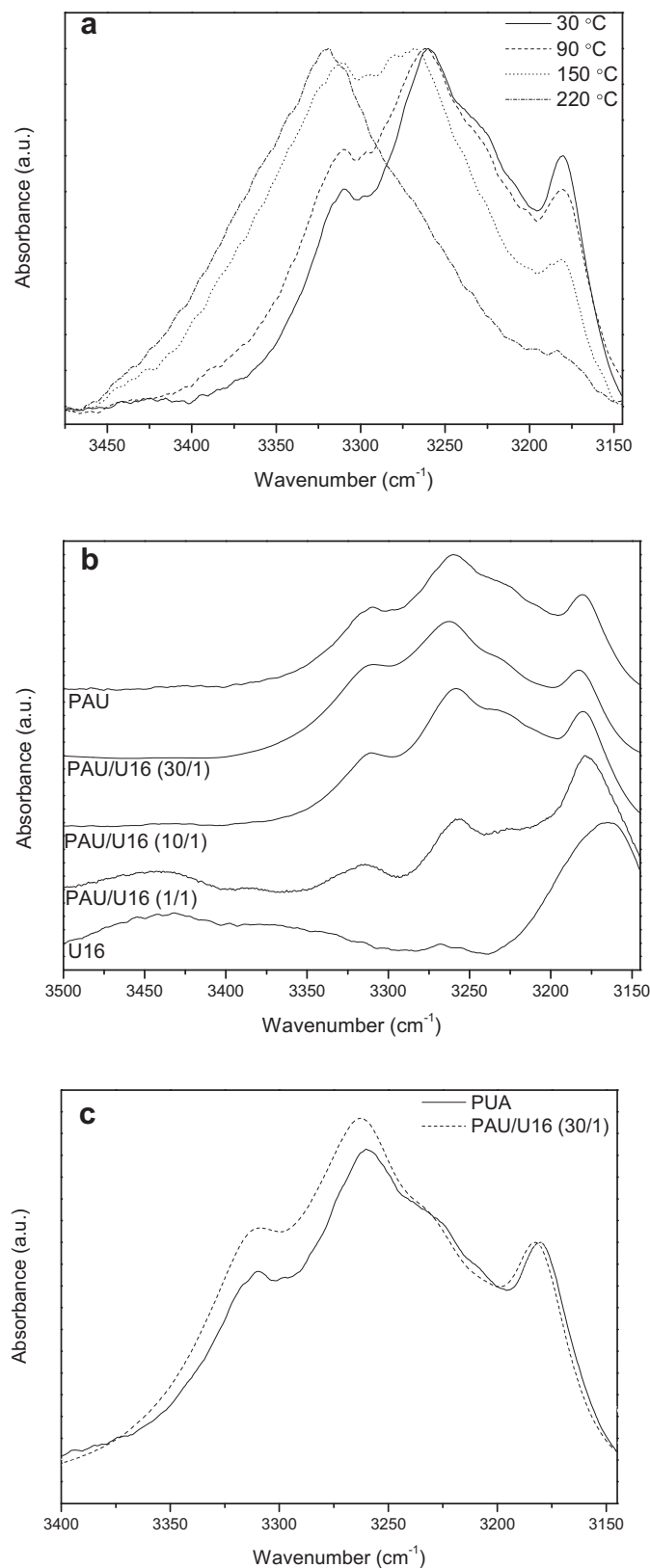


Fig. 2. Normalized FTIR spectra of (a) PAU obtained from variable temperatures, (b) PAU, U16, and PAU/U16 blends, and (c) PAU and PAU/U16 blends (choosing the band at 3179 cm⁻¹ as a reference).

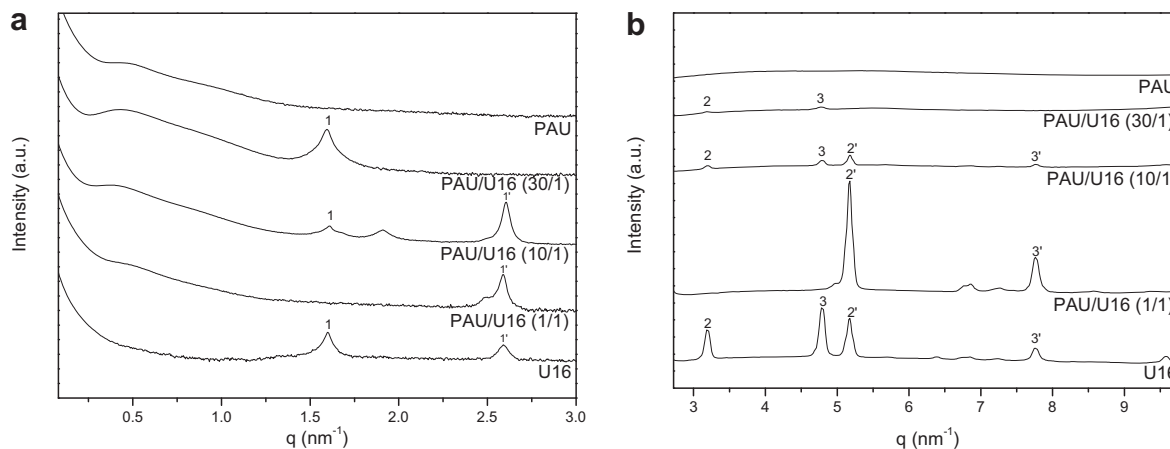
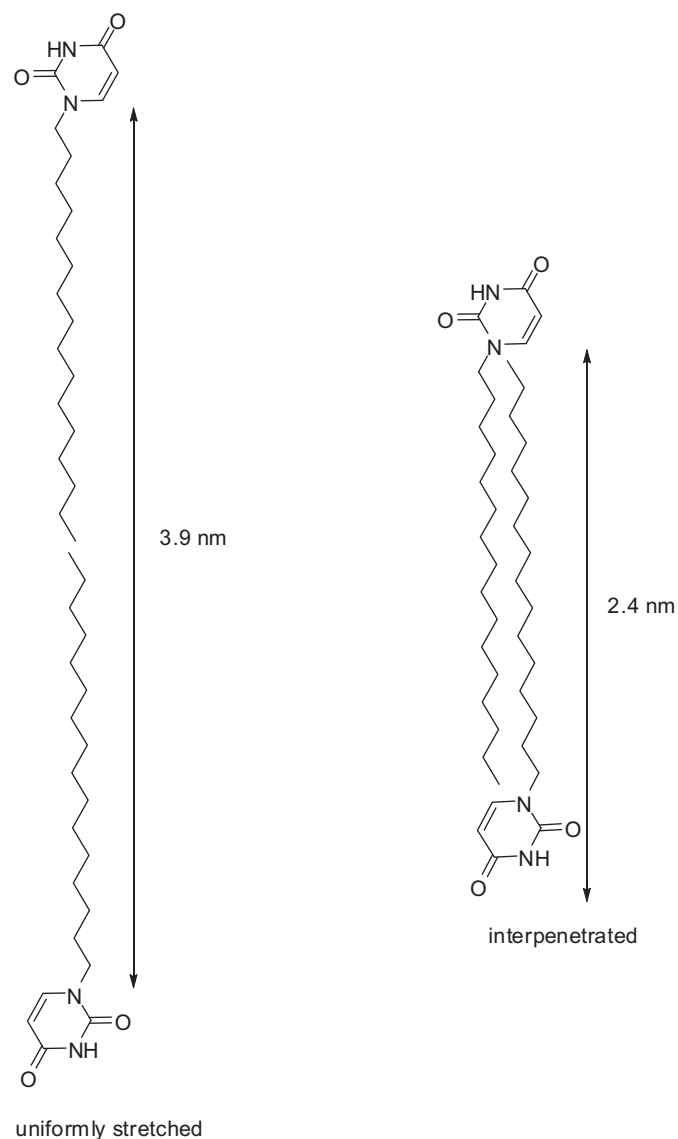


Fig. 3. (a) The SAXS profile of PAU, U16, and PAU/U16 blends and (b) the WAXD profile of PAU, U16, and PAU/U16 blends.

peak at $q = 2.6 \text{ nm}^{-1}$ attributed to interpenetrated structure of the packed U16 (shown in Scheme 2) appears. Besides, the additional peaks appearing in the SAX profile correspond to the intermediates which exhibit structures between the uniformly stretched and interpenetrated structures. For the PAU/U16 (1/1) blend, the long ranged order reflection of U16 is totally transformed from one to the other without the change in the lamellar structure of PAU even with excess of U16. DSC thermograms of PAU, U16, and PAU/U16 illustrated in Fig. 4 also provide evidences that structural change of U16 occurs within the lamellar structure of PAU. As shown in Fig. 4, when the U16 content is gradually increased in the blends, the melting of the U16 becomes clearer and even the melting temperature is slightly higher than the neat U16, indicating that the incorporated U16 is crystallized in confined domains within the PAU lamellar structure without exclusion even there is excess of U16 [12]. Based on the above results, these PAU/U16 blends possess nano-scale lamellar structure of U16 phase within lamellar structure of PAU phase. The nano-scale lamellar structure corresponding to the packed U16 gradually transforms from the stretched form into interpenetrated form because crystallization of the alkyl side chains of hydrogen bonded U16 would stabilize the morphologies [12]. The proposed representations of the structural change are illustrated in Scheme 3. Although the heterodimer recognition



Scheme 2. Graphical representations of different packing of U16 and the corresponding size [16].

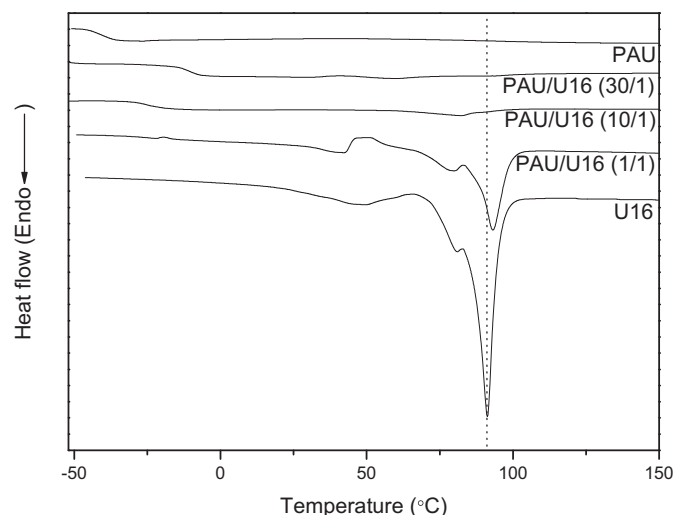
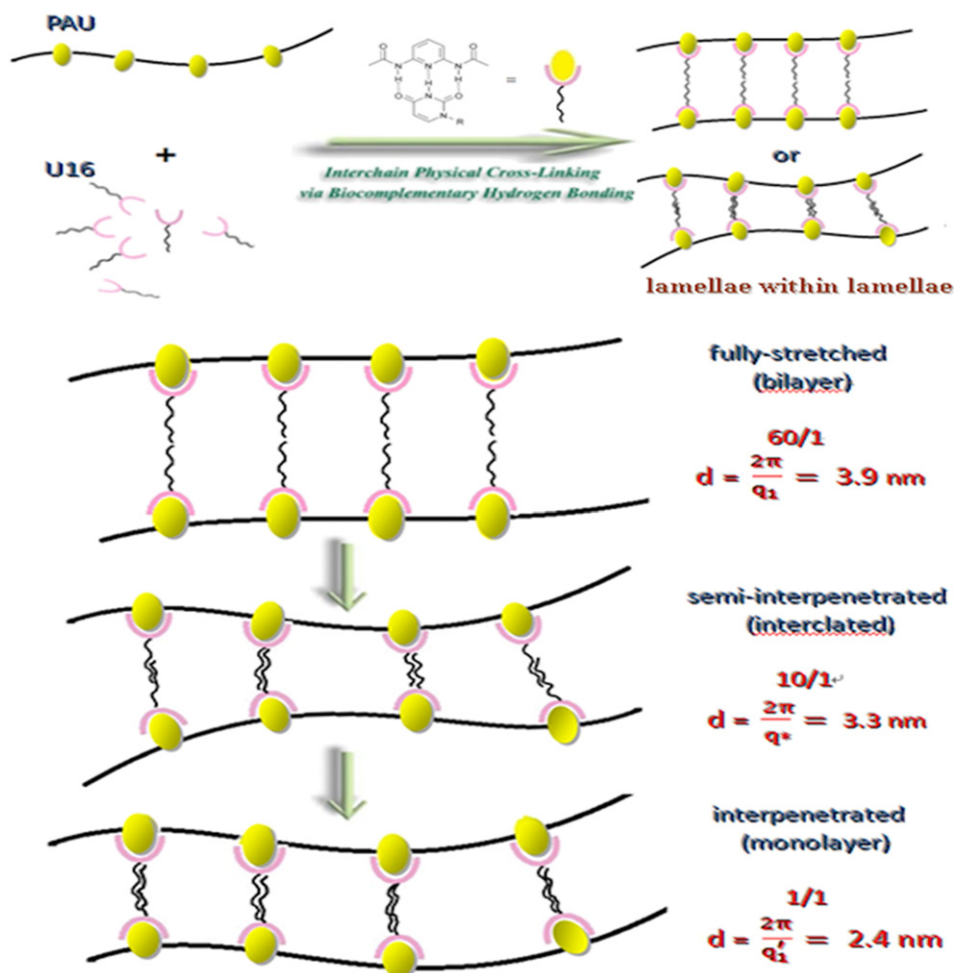


Fig. 4. The DSC thermograms of PAU, U16, and PAU/U16 blends.



Scheme 3. Graphical representations of the change in the lamellar structures with the increase in the content of U16 in the PAU/U16 blends.

coincides with several other hydrogen bonding motifs within the PAU/U16 blends, the plug and play behavior is retained and the microstructure change is similar to the poly[1-(4vinylbenzyl thymine)]/9-hexadecyladenine (PVBt/AC16) blend due to the strongly complementary behavior [12].

To visually investigate the effect of the molecular recognition on morphology, TEM measurement was employed. Since the glass transition temperatures (T_g) of PAU/U16 blends are below room temperature, the cryo-microtome was carried out. The sliced section was placed on copper grids and stained with RuO₄ vapors

(exposing to 2% RuO₄ solution for 1.5 h) to enhance contrast before the TEM measurement. Fig. 5(a) and (b) illustrates the TEM micrographs of PAU and PAU/U16 (10/1). As shown in Fig. 5(a), PAU was microphase separated with long-range order lamellar structure, which was consistent with the SAXS profile. When U16 was incorporated to PAU [Fig. 5(b)], the microphase separation was mediated without the change in the long-range order lamellar structure of PAU matrix. The size of the dark regions is varied from ca. 10 to 20 nm because of the coexistence of these uniformly stretched, semi-interpenetrated, and interpenetrated structures of

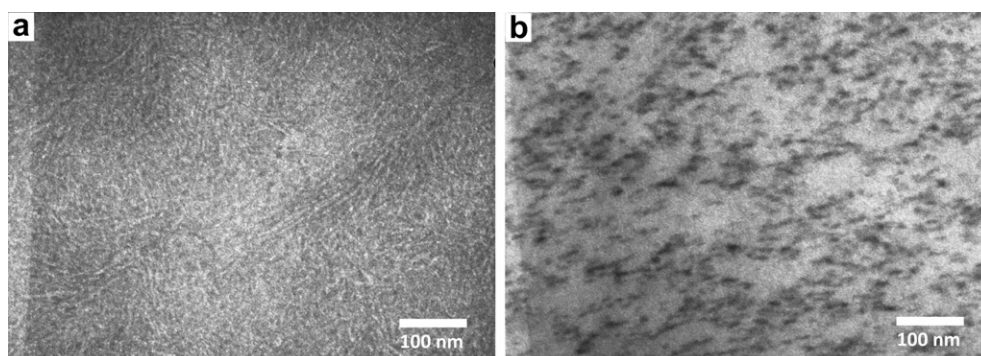


Fig. 5. The TEM micrographs of (a) PAU and (b) PAU/U16 (10/1).

U16 within the lamella structure of PAU as indicated by the SAXS and WAXD profiles.

In addition, tapping-mode AFM measurement was also employed to obtain height imaging data on a scanning probe microscope. As shown in the AFM micrographs in Fig. 6, a strong contrast between domains with higher and lower hardness was obtained. The darker areas are indicative of softer material and lighter areas represent harder material. The lighter spots and region were dispersed in darker areas, resulting from the rigidity difference between different parts of hard segments composed of diaminopyridine (DAP), Methylene di-*p*-phenyl diisocyanate (MDI), uracil groups. From Fig. 6, various hard segments dispersed within

the matrix can be observed, which is similar to those previous studies on polyurethane surface morphology. As U16 was incorporated into PAU [for the PAU/U16 (30/1) blend], these light (hard) spots and regions were separated and less pronounced because the hard phase would be mediated through the U16 incorporation as illustrated in the results of FTIR spectra. In addition, it also displayed the microscale domains dispersed within mesoscale domains as shown in TEM micrographs. Specifically, as the excess content of U16 continuously increased [PAU/U16 (10/1)], there is an increase in the amount of light-colored region because the excess amount of U16 may crystallize or arrange stacked together.

3. Conclusions

In this study, the heterodimer recognition behavior within a poly(amide urethane), was observed through the incorporation of the amphiphilic alkylated nucleobase, 1-hexadecyluracil (U16). The study on the hydrogen bonding interactions and microstructure change indicates that the PAU/U16 blends possess nano-scale lamellar structure of U16 phase within lamella structure of PAU phase. The nano-scale lamella structure of the packed U16 gradually transforms from one to the other with the increase in its content within the blend. In addition, although the system contained several hydrogen bonding motifs, the plug and play behavior is retained and the microstructure change is similar to the poly[1-(4-vinylbenzyl thymine)]/9-hexadecyladenine (PVBT/AC16) blends.

Appendix A. Supporting information

Supporting information associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.polymer.2012.06.040>.

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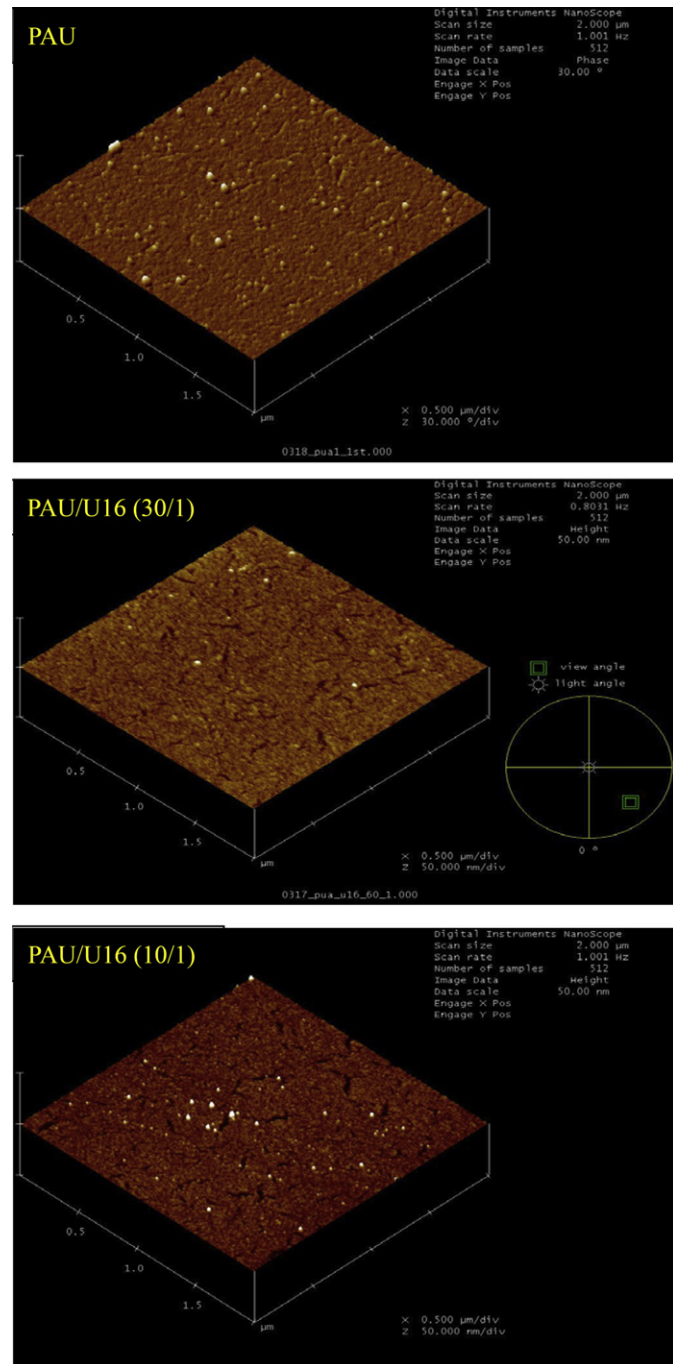


Fig. 6. AFM 3D was used in the investigation of the morphology of the PAU, PAU/U16 (30/1), and PAU/U16 (10/1) with scale of $2 \times 2 \mu\text{m}^2$.

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