

# A "Plug and Play" Polymer Through Biocomplementary Hydrogen Bonding

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**ABSTRACT:** This article describes a DNA-like polymer that exhibits the ability to self-assemble through hydrogen bonding. We synthesized poly[1-(4-vinylbenzyl)thymine] (PVBT) and 9-hexadecyladenine (A-C16) through an atom transfer radical polymerization (ATRP) and alkylation, respectively. Biocomplementary PVBT/A-C16 hierarchical supramolecular complexes formed in dilute DMSO solution through nucleobase recognition, that is, hydrogen bonding interactions between the thymine (T) groups of PVBT and the adenine (A) group of A-C16; evidence for this molecular recognition was also gained from dynamic light scattering studies.  $^1\text{H}$  NMR titration studies in  $\text{CDCl}_3$  showed that T–A complexes formed rapidly on the NMR time scale with high association constants (up to  $534 \text{ M}^{-1}$ ). Moreover, FTIR spectroscopic, differential scanning calorimetry, wide-angle X-ray diffraction, and small-angle X-ray scattering analyses provided further details into the nature of the self-assembly of these systems. In the bulk state, these complexes self-assemble into well-ordered lamellar structures; the changing *d*-spacing distance (ranging from 4.98 to 2.32 nm) at different A-C16 loadings reveals that the molecular structures of the PVBT/A-C16 complexes are readily tailored. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 6416–6424, 2008

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## INTRODUCTION

DNA self-assembly has attracted great attention recently because novel structural organizations can be formed through highly complementary nucleobase recognition.<sup>1</sup> For example, self-assembly mediated by hydrogen bonding allows DNA-like polymer chains to rapidly form functionalizable materials<sup>2–8</sup> exhibiting unique physical prop-

erties, such as high specificity, controlled affinity, and reversibility.<sup>9–13</sup> Nevertheless, controlling the secondary (and higher) structures of synthetic polymers remains a challenging task.<sup>14</sup> Indeed, the synthesis of well-defined polymer architectures is currently quite inefficient when compared with the level of control found in biomaterials, which efficiently program the formation of higher structures at the molecular level.

Sequential supramolecular polymers are difficult to synthesize through covalent bonds, but similar architectures can be achieved through noncovalent interactions utilizing highly complementary noncovalent bonds.<sup>1</sup> In general,<sup>15,16</sup> this field can be divided into two categories: main-chain and side-chain supramolecular polymers.

Additional Supporting Information may be found in the online version of this article.

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The simplest structures are derived from hydrogen-bonded polymers in that the proton donor and acceptor groups are located in separate polymer main chains, allowing the new supramolecular polymer to be produced without difficult covalent synthesis.<sup>15,16</sup> Generally, for side-chain architectures, the proton donor and acceptor units are appended to polymers that have main chains in the form of homo- or block copolymers, and which the self-assembly occurs via hydrogen bonding, usually in multiple fashion.<sup>2–8</sup> Recently, surface modification via hydrogen bonding has become the motivation for fundamental research into side-chain supramolecular polymers.<sup>17–20</sup> The binding of polymers, nanoparticles, or other nanosized objects onto surfaces, mediated by noncovalent interactions, has become a new area of research in nanotechnology. The Rotello group is one of the leading practitioners of the noncovalent functionalization, mediated by hydrogen bonding, of side-chain polymers with small molecules; they coined the term "plug and play" to describe their modular hydrogen-bonding functionalization strategy.<sup>21,22</sup> The plug-and-play approach toward noncovalent synthesis expands the use of organic polymers into functional composite materials by employing a variety of small molecules that can influence the bulk properties of a material,<sup>23,24</sup> in much the same way as the binary nature of simple electrostatic systems.<sup>25–28</sup> Such side-chain strategies have become a critical component of polymer science and are expected to expand further in the near future.

Recently, we reported that the hydrogen bonding interactions of various polymers<sup>29–31</sup> can be used in an orthogonal fashion to expand their design to lower-surface-energy materials through functionalization based on inter- and intramolecular hydrogen bonds.<sup>32,33</sup> There remain, however, many aspects of the behavior of DNA-like polymers to be transferred to binding and recognition events in fundamental research into noncovalent systems. In this study, for example, we focused on the biocomplementary interactions of a DNA-like side-chain homopolymer with alkylated nucleobases mediated by hydrogen-bonded thymine–adenine (T–A) base pair formation at multiple sites. We devised a strategy of synthesizing a styrenic monomer containing a thymine unit and then converting it—through atom transfer radical polymerization (ATRP)—to a well-defined polymer, poly[1-(4-vinylbenzyl)thymine] (PVBT), containing DNA bases. We prepared an amphiphilic-type alkylated nucleobase A-C16 through the

reaction of adenine with an alkylated halogen. The DNA-like polymer interacts with its complementary alkylated nucleobases, forming a DNA-like side-chain polymer through complementary T–A pairing. We analyzed this self-assembly behavior of this DNA recognition system quantitatively using <sup>1</sup>H NMR spectroscopic titration, dynamic light scattering (DLS), wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering (SAXS).

## EXPERIMENTAL

### Materials

Vinylbenzyl chloride was purchased from Acros Organics (Germany) and distilled prior to use. Thymine, adenine, and ethyl 2-bromobutyrate were obtained from Aldrich (USA). 1-Bromohexadecane was purchased from Fluka (Switzerland) and used as received. *N*-Methyl-2-pyrrolidone (NMP) and *N,N*-Dimethylformamide (DMF) were purchased from TEDIA (USA) and distilled over CaH<sub>2</sub> prior to use. All other chemicals were used as received without further purification.

### 1-(4-Vinylbenzyl)thymine

1-(4-Vinylbenzyl)thymine (VBT) was synthesized from thymine and vinylbenzyl chloride according to a procedure described in the literature.<sup>34,35</sup> The product was crystallized from toluene and collected by filtration. Yield: 52%; m.p. 170 °C.

<sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-DMSO, 25 °C, TMS):  $\delta$  = 11.30 (br, 1H; NH), 7.61 (s, 2H; CH<sub>2</sub>), 7.45 (d, *J* = 8 Hz, 2H; ArCH), 7.26 (d, *J* = 8 Hz, 2H; ArCH), 6.7 (dd, *J*<sub>1</sub> = 11 Hz, *J*<sub>2</sub> = 18 Hz, 1H; CH), 5.8 (d, *J* = 18 Hz, 1H; CH), 5.2 (d, *J* = 11 Hz, 1H; CH), 4.8 (s, 2H; CH<sub>2</sub>), 1.73 (s, 3H; CH<sub>3</sub>) ppm; <sup>13</sup>C NMR (125 MHz, *d*<sub>6</sub>-DMSO, 25 °C):  $\delta$  = 164.4, 151.1, 141.2, 136.7, 136.5, 136.1, 127.8, 126.3, 114.5, 109.0, 49.8, 11.9 ppm; HRMS (EI): *m/z* 242.1058 [M]<sup>+</sup>; ELEM. ANAL: calcd (%) for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.41; H, 5.82; N, 11.56; O, 13.21. Found: C, 68.64; H, 5.83; N, 11.23; O, 14.30.

### Poly[1-(4-vinylbenzyl)thymine]

CuBr (2.87 mg, 0.02 mmol) was dissolved in NMP (3 mL) and then solution was purged with dry argon for 10 min. Tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>TREN; 0.45 g, 1.5 mmol) was added

via syringe, causing the mixture to become homogeneous. The solutions were degassed through three freeze/thaw evacuation cycles. A solution of VBT (0.45 g, 1.5 mmol) in NMP (1 mL) was added via syringe and then the solution was once again degassed through three freeze/thaw evacuation cycles. Finally, ethyl 2-bromobutyrate (0.0029 mL, 0.02 mmol) was added via syringe. All polymerizations were conducted under argon atmospheres, with samples withdrawn at various time intervals. After heating at  $183 \pm 2$  °C for 29 h, the reaction mixture was passed through an aluminum oxide column to remove the Cu(II) catalyst. The final polymer product was purified by precipitation into methanol; it was then filtrated and dried under vacuum. The molecular weight of the PVBT obtained as a slightly gray powder was 14,500 g/mol; its conversion was 93%. A portion of this product was dissolved in DMF; GPC analysis indicated a polydispersity index (PDI,  $M_w/M_n$ ) of 1.45.

$^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, 25 °C, TMS):  $\delta$  = 11.31 (br; NH), 7.44 (br; CH), 6.97 (br; ArCH), 6.38 (br; ArCH), 4.73 (br;  $\text{CH}_2$ ), 1.65 (br;  $\text{CH}_3$ ), 2.0–0.8 (br;  $\text{CH}_2$  and CH) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $d_6$ -DMSO, 25 °C):  $\delta$  = 164.2, 151.1, 144.4, 141.1, 134.2, 128.7, 127.4, 109.1, 49.7, 11.9 ppm.

### 9-Hexadecyladenine (A-C16)<sup>36</sup>

1-Bromohexadecane (2.44 g, 8.00 mmol) and anhydrous potassium carbonate (1.08 g, 7.8 mmol) were added to a solution of adenine (1.00 g, 7.4 mmol) in DMF and then the resulting suspension was stirred at 60 °C for 48 h. The insoluble material obtained was filtrated out, washed with water, and recrystallized twice from ethanol. Yield: 85%; m.p. 120 °C.

$^1\text{H}$  NMR (500 MHz,  $d_6$ -DMSO, 25 °C, TMS):  $\delta$  = 8.11 (d,  $J$  = 2 Hz, 2H; CH), 7.16 (s, 2H;  $\text{NH}_2$ ), 4.10 (t,  $J$  = 7 Hz, 2H;  $\text{CH}_2$ ), 1.80–1.67 (m, 2H;  $\text{CH}_2$ ), 1.40–1.07 (m, 26H;  $\text{CH}_2$ ), 0.83 (t,  $J$  = 7 Hz, 3H;  $\text{CH}_3$ ) ppm; HRMS (EI):  $m/z$  359.3047  $[\text{M}]^+$ ; ELEM. ANAL: calcd (%) for  $\text{C}_{21}\text{H}_{37}\text{N}_5$ : C, 70.15; H, 10.37; N, 19.48. Found: C, 70.15; H, 10.26; N, 19.59.

### PVBT/A-C16 Complexes

The sample was cast onto a Teflon dish and then dried under vacuum at 70 °C for 24 h. Desired amounts of PVBT and A-C16 (70:30, 50:50, and 30:70 weight ratios) were dissolved in DMSO, stirring continuously for 24 h at room temperature.

## Characterization

### FTIR Spectroscopy

Recorded using a Nicolet Avatar 320 FTIR spectrometer; 32 scans were collected at a spectral resolution of  $1\text{ cm}^{-1}$ . The conventional KBr disk method was employed: the sample was dissolved in DMF, then cast onto a KBr disk, and dried under vacuum at 70 °C.

### Nuclear Magnetic Resonance Spectroscopy

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Inova 500 MHz spectrometer equipped with a 9.395 T Bruker magnet and operated at 500 and 125 MHz, respectively. Samples ( $\sim 5$  mg for  $^1\text{H}$  NMR;  $\sim 20$  mg for  $^{13}\text{C}$  NMR) in deuterated solvent were analyzed at room temperature.

### Gel Permeation Chromatography

The weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), and PDI ( $M_w/M_n$ ) were measured using a Waters 410 GPC system equipped with a refractive index detector and three Ultrastayragel columns (100, 500, and 1000 Å) connected in series. DMF was the eluent and the flow rate was 0.6 mL/min. The system was calibrated using polystyrene (PS) standards.

### Elemental Analysis

The carbon, hydrogen, and nitrogen contents of the samples were obtained using a CHN-O-Rapid elemental analyzer (Foss. Heraeus, Germany).

### Gas Chromatography/Mass Spectrometry

GC/MS spectra were acquired using a Micromass Trio 2000 mass spectrometer (Micromass, Beverly, MA). The resulting data were used to identify the real molecular weights of the samples.

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a DuPont 910 DSC-9000 controller operated under an atmosphere of dry  $\text{N}_2$ . Samples were weighed ( $\sim 5$ – $10$  mg) and sealed in an aluminum pan, which was cooled to room temperature, and then scanned from 30 to 200 °C at a scan rate of 20 °C/min. The glass transition temperature was taken as the midpoint of the heat capacity transition between the upper and lower points of

the deviation from the extrapolated glass and liquid lines.

### Wide-Angle X-Ray Diffraction

WAXD spectra of powders were obtained using a Rigaku D/max-2500 X-ray diffractometer. The radiation source was Ni-filtered Cu K $\alpha$  radiation at a wavelength of 0.154 nm. The voltage and current were set at 30 kV and 20 Ma, respectively. The sample was mounted on a circular sample holder; the data were collected using a proportional counter detector over the 2 $\theta$  range from 3° to 60° scanned at a rate of 5°/min. Bragg's law ( $\lambda = 2d \sin\theta$ ) was used to compute the  $d$ -spacing corresponding to the complementary behavior.

### Small-Angle X-Ray Scattering

SAXS data were collected using the BL17A1 wiggler beamline of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The samples were sealed between two Kapton windows (thickness: 12  $\mu\text{m}$ ) and measured at room temperatures. An X-ray beam having a diameter of 0.5 mm and a wavelength ( $\lambda$ ) of 1.1273 Å was used for the SAXS measurement ( $Q$  range: 0.015–0.3 Å<sup>-1</sup>). The  $Q$  values of the SAXS profiles were calibrated using a polyethylene standard, Ag behenate and tripalmitat.

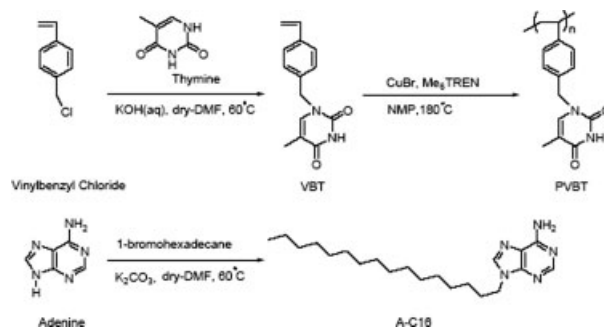
### Dynamic Light Scattering

DLS measurements were conducted using a 90Plus laser particle size analyzer (Brookhaven Instruments Corp., USA), which was calibrated using a 60-nm latex standard. The scattering from a small amount of sample dissolved in DMSO was measured at 90°. The hydrodynamic radius ( $r$ ) of the aggregates was calculated using the Stokes-Einstein equation:  $r = k_B T / 6\pi\eta D$ , where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\eta$  is the solvent viscosity, and  $D$  is the diffusion constant.

## RESULTS AND DISCUSSION

### ATRP Synthesis of PVBT Homopolymer

The VBT monomer, which was synthesized as described previously,<sup>34,35</sup> was subjected to ATRP (Scheme 1) to control the molecular weight and PDI of the polymer (PVBT). Although Shen and Lutz et al. reported the controlled radical poly-



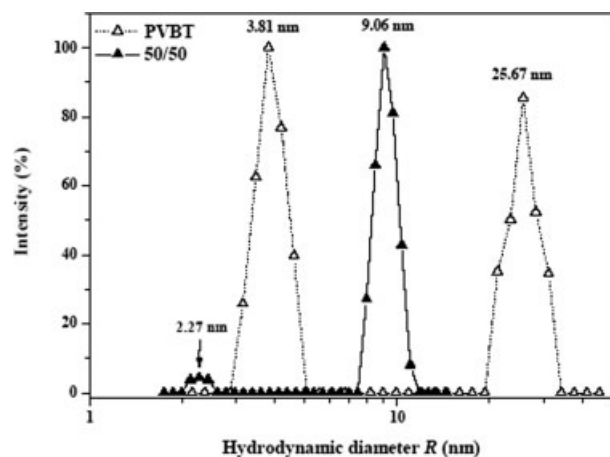
**Scheme 1.** Synthetic procedures used to obtain PVBT and A-C16.

merization of PVBT homopolymer and random copolymer comprising VBT and dodecyl methacrylate (DMA),<sup>37</sup> the living controlled polymerization of VBT to form PVBT in this study has never been reported.

Selecting appropriate reaction conditions is the main challenge for controlled homopolymerization. The outcomes of ATRP experiments often strongly depend on the reaction conditions, especially when the metal catalysts used in this technique can interact with the other constituents of the reaction mixture (e.g., the solvent or the monomer). We examined the influence of the reaction temperature in an attempt to avoid the formation of unfavorable complexes. Fortunately, the polymerization of VBT was controlled at 180 °C, with the resulting PVBT exhibiting high molecular weight ( $M_w = \sim 14,500$ ), acceptable PDI (1.45), and high conversion (93%), as determined through a kinetic experiment (see the Supporting Information).

### Molecular Recognition in Nucleobase PVBT/A-C16 Complexes

Molecular recognition is an interesting phenomenon that can result in various morphological changes.<sup>1</sup> Because PVBT forms complexes with A-C16 through complementary T–A hydrogen bonding, which affords unique capabilities for forming well-ordered structures through bottom-up assembly of PVBT/A-C16 complexes, we investigated the assembly behavior of these complexes using <sup>1</sup>H NMR spectroscopy and DLS. Through <sup>1</sup>H NMR spectroscopic titration, we determined the equilibrium constant ( $K_a$ ) for the complexation of PVBT and A-C16.<sup>38,39</sup> Because PVBT was insoluble in nonpolar organic solvents, such as CDCl<sub>3</sub>, which are often used in <sup>1</sup>H NMR titration



**Figure 1.** DLS analyses of PVBT and PVBT/A-16C (50/50) in DMSO at 20 °C.

experiments, we dissolved A-C16 in the presence of a simple PVBT model, namely 1-hexadecylthymine (T-C16),<sup>36</sup> in  $\text{CDCl}_3$  at 25 °C to calculate the value of  $K_a$  for the T–A complexation event. The chemical shift of the amide proton of thymine in the complex A-C16/T-C16 was monitored to give a value of  $K_a$  of 534  $\text{M}^{-1}$  from Benesi-Hildebrand plots (see the Supporting Information). Previous studies have noted<sup>22,40</sup> that the folding of polymer chain results in low-efficiency recognition for biomolecular functional groups incorporated into polymer matrices. However, the value of  $K_a$  of complementary thymine and adenine recognition units in the model analogues will be understood to the molecular recognition behavior for PVBT/A-C16 blend.

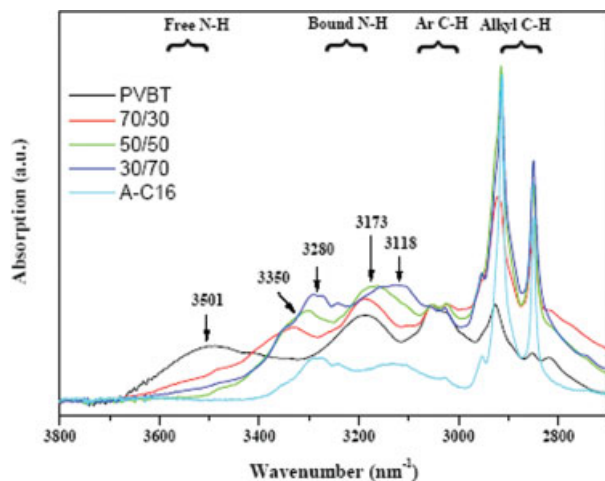
To further investigate the self-assembly, we performed DLS measurements in dilute DMSO solutions at 20 °C (Fig. 1). We attributed the first peak of PVBT, having an  $R$  value of 25.67 nm, to the large aggregates formed through T–T hydrogen bonding. The second peak at 3.81 nm corresponds to the anisotropic structure (or dimer), rather than random coils or spherical globules,<sup>41</sup> because a long, thin anisotropic polymer in dilute solution in conjunction with a large anisotropy in translation diffusion would cause the translational motion to couple, leading to an apparent hydrodynamic diameter of several nanometers. The DLS analysis of the 50/50 PVBT/A-C16 complex exhibited a change in aggregate size distribution, and the signal of anisotropic structure of the PVBT polymer at  $\sim 3.81$  nm disappeared and a narrow distribution having an average particle size of 9.06 nm appeared as a result of the dissociation of the large (25.67 nm) PVBT aggregates; a

peak corresponding to A-C16 was slightly visible at 2.27 nm. The  $^1\text{H}$  NMR spectra and DLS results indicated that the PVBT/A-C16 interaction occurred through strong cooperative hydrogen bonding between PVBT and A-C16, reflecting the highly biocomplementary of this system.

### Self-Assembly of PVBT/A-C16 in Bulk State

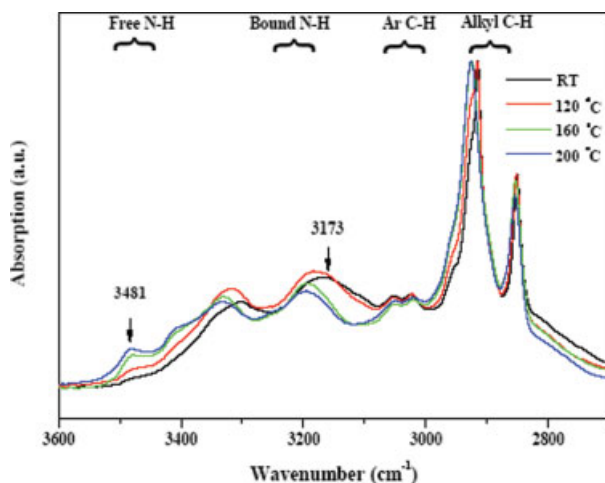
Because PVBT and the amphiphilic A-C16 could form a “plug and play” biocopolymer system, we examined the self-assembly of these complexes in the bulk state using FTIR spectroscopy and DSC. Figure 2 illustrates the N–H stretching region of the FTIR spectra of the PVBT/A-C16 complexes. The characteristic peaks were those of the free amide NH group ( $3500\text{ cm}^{-1}$ ) of PVBT and those involved in T–T ( $3173\text{ cm}^{-1}$ ) and A–A ( $3280$  and  $3118\text{ cm}^{-1}$ ) interactions.<sup>21</sup> The presence of the band at  $3500\text{ cm}^{-1}$  indicates that some of the thymine side groups of the PVBT homopolymer were not involved in T–T interactions.<sup>42–44</sup> The intensity of the free amide N–H stretching vibration at  $3500\text{ cm}^{-1}$  decreased on increasing the amount of added A-C16, indicating that PVBT associated strongly with its complement A-C16, and that A–T interactions were more favorable than either T–T or A–A interactions. FTIR spectra revealed that strong complement of the band at  $3370$  and  $3300\text{ cm}^{-1}$  corresponded to hydrogen-bonded amide N–Hs at 50/50 complex, indicating that the thymine groups of PVBT were highly complementary to the adenine group of A-C16; therefore, we subjected the 50/50 complex to variable-temperature FTIR spectroscopic analyses. Upon heating from room temperature to 200 °C, the signal at  $3173\text{ cm}^{-1}$  corresponding to N–H stretching of the bind shifted to higher wave number, and the free amide N–H stretching vibration at  $3481\text{ cm}^{-1}$  appears gradually for the 50/50 complex in Figure 3, implying that PVBT and A-C16 formed highly stable hydrogen-bonded complexes in the bulk state.

Figure 4 displays DSC traces for the PVBT/A-C16 complexes. The glass transition temperature ( $T_g$ ) of pure PVBT was  $\sim 188$  °C and the melting point ( $T_m$ ) of A-C16 was 120 °C. For the 70/30 complex, the value of  $T_g$  was 102 °C, implying that the highly complementary hydrogen bonding was occurring within the PVBT/A-C16 complex. The value of  $T_g$  was reduced by the presence of the side-chain alkyl groups of A-C16, which constituted a disordered phase; thus, a less nonstoichiometric amount of A-C16 side alkyl chains led

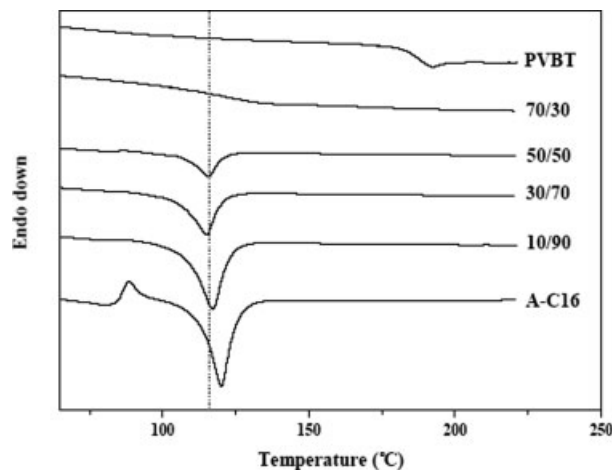


**Figure 2.** FTIR spectra recorded at room temperature in the range of 2700–3800  $\text{cm}^{-1}$  for PVBT in the bulk state in the presence of various amounts of A-C16. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

to a uniform glass transition.<sup>45–51</sup> Increasing the A-C16 content to 50 wt % led to the side-chain alkyl groups of A-C16 forming a more regular crystalline phase, arranged perpendicularly to the amorphous sheets. The crystallization of the alkyl tails occurred in sheets that separated the amorphous regions,<sup>45–51</sup> as we can deduce from the value of  $T_m$  of 115 °C. Furthermore, the value of  $T_m$  decreased slightly to 114 °C for the 30/70 PVBT/A-C16 complex, possibly because of dissoci-



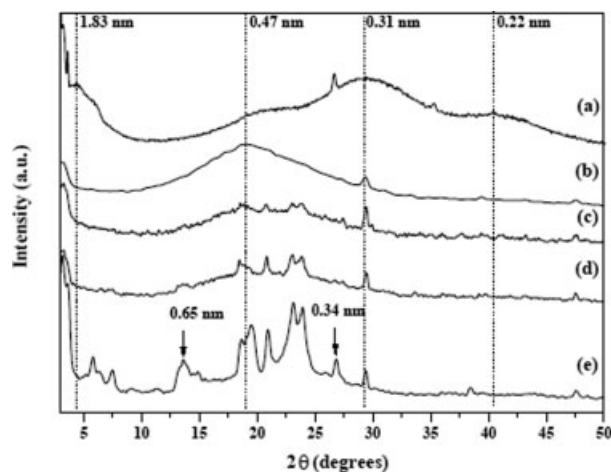
**Figure 3.** Variable-temperature FTIR spectra of PVBT/A-C16 (50/50) recorded in the range of 2700–3600  $\text{cm}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



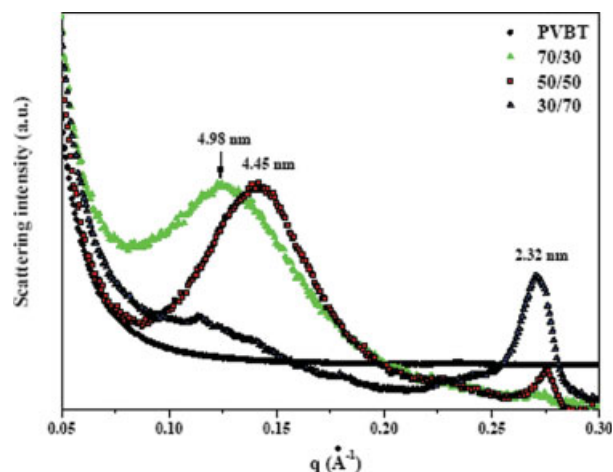
**Figure 4.** DSC curves of PVBT in the presence of various amounts of A-C16.

ation of A-C16 units affected the cocrystallization behavior.<sup>50,51</sup> In a previous report, we noted that DSC analyses revealed cocrystallization on a scale of ~20–40 nm (as sensitivity) for a 30/70 PVBT/A-C16 blend.<sup>52,53</sup> At a 10/90 PVBT/A-C16 weight ratio, the value of  $T_m$  shifted significantly to 117 °C because of the presence of excess A-C16. This intriguing behavior led us to investigate the microstructures of these complexes in more detail through WXR, SAXS, and TEM characterization.

Figure 5 indicates that the WXR diffraction pattern of the A-C16 powder displays two reflection peaks at 13.6° ( $d = 0.65$  nm) and 26.8° ( $d = 0.34$  nm). The reflection peak corresponded to a  $d$ -spacing of 0.34 nm is consistent with the



**Figure 5.** WXR data for PVBT/A-C16 complexes in various weight ratios: (a) PVBT, (b) 70/30, (c) 50/50, (d) 30/70, and (e) A-C16.



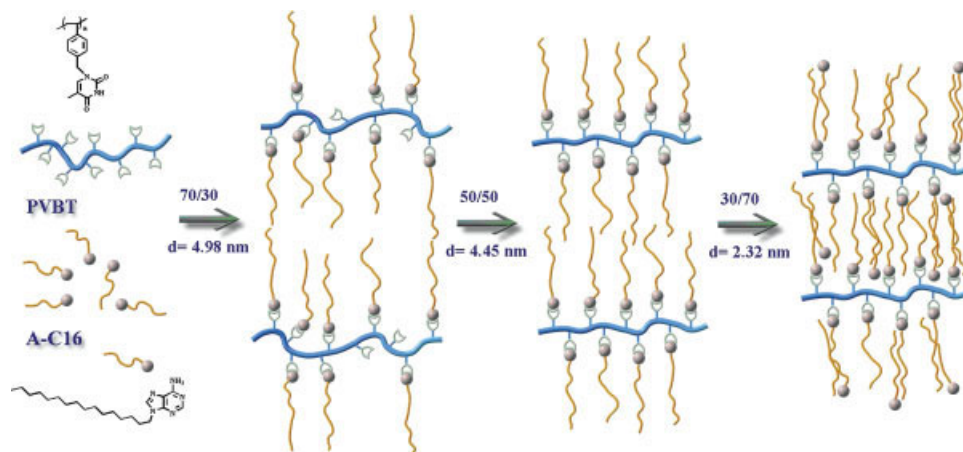
**Figure 6.** SAXS data for PVBT/A-C16 complexes recorded at room temperature.

presence of  $\pi$ - $\pi$  stacking interactions between A-A layers; generally, such interactions occur only in stabilized sheets.<sup>44,54,55</sup> The  $d$ -spacing of 0.65 nm suggests that there are stacks of the nucleobases that are held together through  $\pi$ - $\pi$  interactions within these interaction domain.<sup>54,55</sup> The WAXS pattern of pure PVBT displays several amorphous halos: one centered at a  $d$ -spacing of 4.34° ( $d = 1.83$  nm) and others at 19.0, 29.3, and 40.49° ( $d = 0.41, 0.37,$  and  $0.22$  nm, respectively), corresponding to the distances between the main chains and phenyl rings, respectively.<sup>56-58</sup> Pure PS exhibits a peak at 0.83 nm that corresponds to the interchain distance, and another at 0.45 nm that is attributed to the intrachain distance, that is, the distance between pendent side chains.<sup>58</sup> By

comparing the amorphous halos corresponding to interchain distances of the PVBT and PS samples, we suspect that the introduction of T-T interactions would expand the intermolecular main-chain spacing and reduce the intramolecular distance between the phenyl rings. That is, the intermolecular distance would be expanded because of the size of thymine units attached to the phenyl rings, and the intramolecular distance would be reduced as a result of the repulsion caused by T-T interactions.<sup>59,60</sup>

Each of our PVBT/A-C16 complexes exhibited an obvious shift in their intramolecular amorphous intensity at low values of  $2\theta$  (0.47 nm), indicative of unspecified structural features at a relatively large size scale; the intermolecular main-chain spacing (1.83 nm) and  $\pi$ - $\pi$  interactions (0.65 and 0.34 nm) corresponding to  $d$ -spacings of  $\sim 4.34, 13.6,$  and  $26.8^\circ$  disappeared, implying that the T-A interactions were occurring. Based on the results obtained from the DSC and WAXD analyses, it appears that the alkyl side chains of the A-C16 units in the complexes would form a new regular crystalline phase that differs from that of the crystalline phase of pure A-C16.

Figure 6 displays the SAXS profiles of the PVBT/A-C16 complexes at room temperature. The scattering intensity suggested an amorphous structure for PVBT. The shift in the maximum diffraction peak was particularly large for the 70/30 and 50/50 complexes. In the case of the 70/30 PVBT/A-C16 complex, in which the A-C16 units were distributed uniformly along the polymer backbone, the SAXS profile revealed thick polar layers having a corresponding long period of  $\sim 4.98$  nm. As represented in Scheme 2, the A-C16



**Scheme 2.** Graphical representations of the lamellar structures of the PVBT/A-C16 complexes in bulk state.

layers did not interpenetrate and the A-C16 molecules were uniformly stretched.<sup>61–64</sup> In the case of the 50/50 PVBT/A-C16 complex, however, the long-period distance decreased slightly to 4.45 nm and the tail ends were distributed throughout the layer.<sup>64,65</sup> The long-period profiles indicate that the 70/30 and 50/50 complexes could form well-ordered lamellar structures, although we obtained a relatively inferior ordered structure at higher A-C16 contents, that is, for A-C16 contents greater than 50%. In contrast, in the 30/70 complex, the tail-to-tail layer almost disappeared completely at 4.45 nm and the period decreased to 2.32 nm, which can be explained in terms of an increase in the degree of cocrystallization upon increasing the A-C16 content.<sup>50,51</sup> Consequently, the incorporation of free A-C16 into the crystalline lattice of the alkyl side chains of complexed A-C16 resulted in a cocrystallization packing (Scheme 2). The crystallization of the alkyl side chains gave rise to the novel behavior of the PVBT/A-C16 system. Furthermore, in this study, the *d*-spacing of the lamella morphology could be controlled by changing the A-C16 content.

Crystallization of the alkyl side chains of complexed A-C16 units would stabilize the morphologies of each of the complexes. It would be interesting to investigate the behavior of related biomimetic block copolymers to establish the general fundamental properties of these systems.

## CONCLUSIONS

We have synthesized a PVBT polymer through living controlled ATRP at high temperature. From molecular recognition experiments, we determined that the interactions between PVBT and A-C16 occurred through strong cooperative hydrogen bonding between the thymine group of PVBT and the adenine group of A-C16. In the bulk, the complexes exhibited ordered lamellar structures, with their *d*-spacings being controlled by the degree of crystallization of the alkyl side chains of the complexed A-C16 units. Therefore, these complexes comprising a nucleobase polymer and amphiphilic moieties, could be applied widely as a means of manipulating the morphologies of biomaterials, because hydrogen bonding might provide them with biocompatibility. We are continuing to study these systems to elucidate the factors affecting their morphological control in solution and to develop materials that feature reversible crosslinking networks mediated by

nucleobase hydrogen bonding. Our results will be reported in due course.

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