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Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules via a Michael Addition

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ABSTRACT: The synthesis and characterization of novel complementary multiple hydrogen-bonded poly(styrene) (CMHB-PS) oligomers possessing controlled molecular weights and narrow molecular distributions are described. Novel CMHB-PS oligomers comprising terminal heterocyclic base units were synthesized in a controlled fashion via derivatization of well-defined hydroxyl-terminated PS. The heterocyclic-terminated oligomers were synthesized via a Michael addition of the corresponding heterocyclic compounds such as adenine, thymine, and 2,6-purine with acrylated PS. The acrylated PS precursors were prepared in a quantitative fashion via reaction of hydroxyl-terminated PS with acryloyl chloride in the presence of triethylamine. Terminal heterocyclic bases were introduced via a Michael addition in the presence of potassium *tert*-butoxide (*t*-BuOK). Novel CMHB-PS aggregates were prepared via subsequent solution blending of PS with complementary heterocyclic base units. ^{1}H NMR analysis confirmed that a 1:1 mixture of adenine-PS or purine-PS with thymine-PS formed complementary multiple hydrogen bonding and exhibited thermoreversibility. In addition, ^{1}H NMR analysis confirmed that complementary hydrogen bonds dissociated at 95 °C in deuterated toluene.

Introduction

Multiple hydrogen bonding in molecular design has recently received significant attention due to the propensity to form new supramolecular structures that exhibit thermoreversible characteristics. In addition, reversible molecular recognition is also attainable due to relatively weak noncovalent bonds compared to covalent bonds.[1−7] Multiple hydrogen bonding scaffolds are classified into two different families: (1) self-complementary multiple hydrogen bonds (SCMHB), which are formed between identical hydrogen bonding units and (2) complementary multiple hydrogen bonds (CMHB), which are formed between dissimilar hydrogen bonding units containing complementary donor and acceptor sites. Meijer et al. recently reported the versatility of SCMHB between 2-ureido-4[1*H*]-pyrimidone (UPy) units, which strongly self-dimerize through four hydrogen bonds arranged in donor−donor−acceptor−acceptor sites.[8−17] The aggregated molecules containing SCMHB units exhibited polymer-like properties including shear thinning in the melt phase, viscoelastic behavior in the solid state, and glass transition temperatures. Supramolecular structures possessing CMHB units have also received significant attention in the literature.[18−22] In particular, heterocyclic base pairing between adenine, guanine, thymine, uracil, and tyrosine in DNA and RNA are well-known as tailored CMHB pairs in biological systems. Recent research efforts in this rapidly evolving area have focused on the design of supramolecular structures consisting of tailored CMHB with extremely high dimerization constants. Initial supramolecular systems based on CMHB were reported by Lehn,[24−29] Kato and Fréchet,[30−35] and Whitesides.[36−39] These diverse efforts focused on the selective formation of discrete supermolecules from complementary receptor-substrate hydrogen bonding pairs, such as bartituric acid and triaminopyrimidine units, 2,6-diaminopyridine and 2,6-pyridinedicarbonyl units, and carboxylic acid and pyridine units.

Other recent research efforts have focused on the introduction of SCMHB or CMHB with relatively high dimerization constants into macromolecules to improve mechanical properties. Coates et al. reported the incorporation of SCMHB containing UPy units into elastometric nonpolar poly(1-hexene) and their reversible nature.[40] Strong dimerization was observed in nonpolar solvents. Chino et al. prepared poly(isoprene) thermoplastic elastmers via derivatization of a maleic anhydride modified poly(isoprene) with 3-amino-1,2,4-triazole.[41] Interestingly, the SCMHB networks exhibited similar mechanical properties to vulcanized rubber, and thermoreversible dissociation occurred at approximately 185 °C. Our earlier research efforts have involved the synthesis of well-defined SCMHB polymers, such as glassy poly(styrene) (PS), rubbery poly(isoprene) (PI) and microphase separated PS-*b*-PI block copolymers with well-defined molecular weights and narrow molecular weight distributions.[42−45] The relationship between end group structure and physical properties, such as glass transition temperature, melt viscosity and morphology were reported.[42,43] In addition, the synthesis and thermoreversible nature of poly(alkyl acrylates) comprising pendant SCMHB units were also reported.[44,45]

Macromolecules containing CMHB units based on nucleic acid heterocyclic bases have also received significant attention.[46−49] Inaki et al. reported the synthesis and characterization of graft copolymers containing nucleic acid heterocyclic bases and L-amino acids on poly(ethylene imine).[46] The synthesis of poly(alkyl methacrylate)s containing nucleic acid bases and subsequent photochemical processes were reported.[47] Kalra et al. have described the synthesis and characterization of

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block copolymers based on poly(ethylene glycol) (PEG) and a nucleoside pendant alkyl methacrylate monomer, which was prepared via selective acylation of the nucleoside.[48] Most CMHB-containing polymers were obtained via a combination of nucleic acid bases and synthetic polymers that contain hydrophilic units, such as sugars, poly(ethylene imine), PEG, or poly(peptides). Limited selective synthetic methodologies and solubility of nucleic acid bases and resulting polymers account for this earlier focus. Thus, the introduction of CMHB based on nucleic acid derived heterocyclic bases into nonpolar polymers is particularly interesting because the nonpolar polymer does not interfere with these tailored, directional, hydrogen bonds.

Our current efforts have focused on the introduction of CMHB via addition of terminal heterocyclic base units, such as adenine, thymine, and 2,6-purine, into well-defined macromolecules. This report deals with the unprecedented synthesis and characterization of CMHB-PS with terminal heterocyclic base functionality using living anionic polymerization in combination with quantitative Michael addition strategies. In addition, a detailed study of thermoreversibility in novel CMHB-PS was performed in order to fully elucidate the nature of novel CMHB macromolecules.

Experimental Section

Materials. Cyclohexane (Aldrich) was washed with 95% sulfuric acid and distilled from elemental sodium prior to use. Styrene (S) was distilled from calcium hydride at reduced pressure (0.5 mmHg) using a classic freeze−thaw method. Ethylene oxide (EO) was distilled from *n*-butyllithium (*n*-BuLi) prior to functionalization. DMSO was distilled from calcium hydride at reduced pressure (0.5 mmHg). Chloroform was refluxed and distilled over "DRIERITE" under a nitrogen atmosphere. Triethylamine (TEA) (Aldrich) was refluxed and distilled from calcium hydride. Acryloyl chloride, adenine (6-aminopurine; mp > 360 °C) (Aldrich), 2,6-diaminopurine (DAP; mp > 300 °C) (Aldrich), thymine (2,4-dihydroxy-5-methylpyrimidine; mp 316−317 °C) (Aldrich), and potassium *tert*-butoxide (*t*-BuOK) (Aldrich) were used as received.

Synthesis of Acrylated PS. Hydroxyl-terminated PS (PSOH) was prepared in a similar fashion as reported in the earlier literature.[42,43,50,51] Acryloyl chloride (3.2 mL, 39.4 mmol) in a 10.0-fold molar excess compared to the hydroxyl end group in the polymer was added dropwise to a solution of PSOH (10.0 g, 4.0 mmol (hydroxyl end group)) in 100 mL of $CHCl_3$ and 10 mL of triethylamine.[52] The reaction was stirred for 24 h at 23 °C. The solution was then precipitated into excess MeOH (500 mL), redissolved in $CHCl_3$, reprecipitated in MeOH three times, and finally dried at 50 °C under reduced pressure (0.5 mmHg) for 24 h (yield: 92%). ^{1}H NMR (400 MHz, 30 °C in $CDCl_3$, δ): 0.6−0.9 ppm ($CH_3CH_2CH(CH_3)$: 9H), 1.0−2.8 ppm (poly(styrene) backbone: 3H × repeating units), 3.5−4.0 ppm ($-CH_2C\mathit{H}_2OOC-CH=CH_2$: 2H), 5.8−6.3 ppm ($-OC-C\mathit{H}=C\mathit{H}_2$: 3H), 6.3−7.5 ppm (aromatic protons: 5H × repeating units). $M_n = 2800$, $M_w/M_n = 1.20$ (GPC with DRI), $M_n = 2800$ (calculated from the relative ^{1}H NMR integrals associated with the repeating unit such as aromatic protons at 6.3−7.5 ppm compared to the methylene in the acrylated end group ($-CH_2C\mathit{H}_2OOC-CH=CH_2$) at 3.5−4.0 ppm, the vinylic group ($-OOC-C\mathit{H}=C\mathit{H}_2$), and the *sec*-butyl end group at 0.6−0.9 ppm).

Synthesis of Heterocyclic-Terminated PS via Michael Addition of Acrylated PS.[53−55] Acrylated PS (1.0 g), heterocyclic compounds such as adenine, thymine, and 2,6-purine (1.0 g), and a catalytic amount of potassium *tert*-butoxide (10 mg) were dissolved in 25 mL of DMSO. The mixture was stirred for 24 h at 60 °C. The DMSO solvent was removed under reduced pressure (0.5 mmHg/60 °C). The crude product was dissolved in chloroform, filtrated, and precipitated into methanol three times and finally dried at 50 °C under reduced pressure (0.5 mmHg) for 24 h.

Adenine-PS. ^{1}H NMR (400 MHz, 30 °C in d_8-toluene, δ): 0.6−0.9 ppm ($CH_3CH_2CH(CH_3)$: 9H), 1.0−2.8 ppm (poly(styrene) backbone: 3H × repeating units), 3.7 ppm ($-OC\mathit{H}_2$-CH_2-: 2H), 3.8 ppm ($-C\mathit{H}_2N-$: 2H), 5.4 ppm ($-N\mathit{H}_2$: 2H), 6.3−7.5 ppm (aromatic protons: 5H × repeating units), 7.5 ppm ($-C=N-C\mathit{H}=N-$: 1H), 8.6 ppm ($-N=C\mathit{H}-N-$: 1H). $M_n = 3010$, $M_w/M_n = 1.18$ (GPC with DRI), $M_n = 3000$ (calculated from the ^{1}H NMR integration ratio of aromatic protons compared to $-N=C\mathit{H}-N-$ at 8.6 ppm, $-C=N-C\mathit{H}=N-$ at 7.5 ppm, $-N\mathit{H}_2$ at 5.4 ppm, and *sec*-butyl at 0.6−0.9 ppm).

Purine-PS. ^{1}H NMR (400 MHz, 30 °C in d_8-toluene, δ): 0.6−0.9 ppm ($CH_3CH_2CH(CH_3)$: 9H), 1.0−2.5 ppm (poly(styrene) backbone: 3H × repeating units), 3.5 ppm ($-OC\mathit{H}_2$-CH_2-: 2H), 4.3 ppm ($-C\mathit{H}_2N-$: 2H)), 5.1 ppm ($-C=C(N\mathit{H}_2)-N=$: 2H), 6.3−7.5 ppm (aromatic protons: 5H × repeating units, $-N=C(N\mathit{H}_2)-N=$: 2H, $-N=C\mathit{H}-N-$: 1H), $-N=C(N\mathit{H}_2)-N=$ and $-N=C\mathit{H}$-$N-$ were observed in $CDCl_3$. $M_n = 2820$, $M_w/M_n = 1.17$ (GPC), $M_n = 2920$ (calculated from the ^{1}H NMR integration ratio of aromatic protons at 6.3−7.5 ppm compared to $-OC\mathit{H}_2CH_2-$ at 3.5 ppm, $-C\mathit{H}_2N-$ at 4.3 ppm, $-C=C(N\mathit{H}_2)-N=$ at 5.1 ppm, *sec*-butyl at 0.6−0.9 ppm).

Thymine-PS. ^{1}H NMR (400 MHz, 30 °C in d_8-toluene, δ): 0.6−0.9 ppm ($CH_3CH_2CH(CH_3)$: 9H), 1.0−2.5 ppm (poly(styrene) backbone: 3H × repeating units), 3.3 ppm ($-C\mathit{H}_2N-$: 2H), 3.8 ppm ($-OC\mathit{H}_2CH_2-$: 2H), 6.3 ppm ($-C(CH_3)=C\mathit{H}-$: 1H), 6.3−7.5 ppm (aromatic protons: 5H × repeating units), 8.9 ppm ($-CO-N\mathit{H}-CO-$: 1H), $M_n = 2970$, $M_w/M_n = 1.19$ (GPC), $M_n = 3000$ (calculated from the ^{1}H NMR integration ratio of aromatic protons at 6.3−7.5 ppm, $-CO-N\mathit{H}$-$CO-$ at 8.9 ppm, $-C(CH_3)=C\mathit{H}$- at 6.3 ppm and *sec*-butyl at 0.6−0.9 ppm).

Preparation of CMHB-PS Blends. CMHB-PS was prepared via solution blending from a 1:1 mixture of adenine-PS and thymine-PS (adenine-PS/thymine-PS), and a mixture of purine-PS and thymine-PS (purine-PS/thymine-PS) in toluene or chloroform solution at room temperature, and the solvent was subsequently evaporated. In addition, solution blends were prepared in d_8-toluene or *d*-chloroform for ^{1}H NMR characterization (end group concentration = 1.6×10^{-2} M, 40 mg/mL).

Characterization. Instrumentation. ^{1}H NMR spectra were recorded in various deuterated solvents using a Varian UNITY 400 spectrometer at 400 MHz at constant concentration (end group concentration = 1.6×10^{-2} M, 40 mg/mL). Molecular weights were determined at 40 °C in ACS grade THF at a flow rate of 1.0 mL/min using a Waters SEC (515 pump, 717 auto sampler) with an external 410 refractive index detector. Multiangle laser light scattering (MALLS) permitted absolute molecular weight determination using an in-line Wyatt Minidawn.

Results and Discussion

Synthesis and Characterization of CMHB-PS. CMHB-PS homopolymers were synthesized via a four-step synthesis as shown in Scheme 1. The first step involved the synthesis of well-defined PSOH (**I**), which was prepared using living anionic polymerization and subsequent quantitative termination with EO in a similar fashion as reported earlier.[42,43,50,51] In the second step, well-defined acrylated PS (**II**) was prepared via reaction of PSOH (**I**) with acryloyl chloride. In the third step, heterocyclic-terminated PS was synthesized via a Michael addition of the acrylated PS (**II**) with various heterocycles such as adenine, thymine, or 2,6-purine in the presence of *t*-BuOK. Finally, CMHB-PS blends were subsequently prepared in toluene or chloroform at room temperature.

Well-defined PSOH (**I**) and acrylated PS (**II**) were synthesized in a similar fashion as reported earlier.[42,43,50−52] A comparison of the ^{1}H NMR spectra for

Scheme 1. Synthetic Strategy for Novel CMHB-PS from Well-Defined PSOH

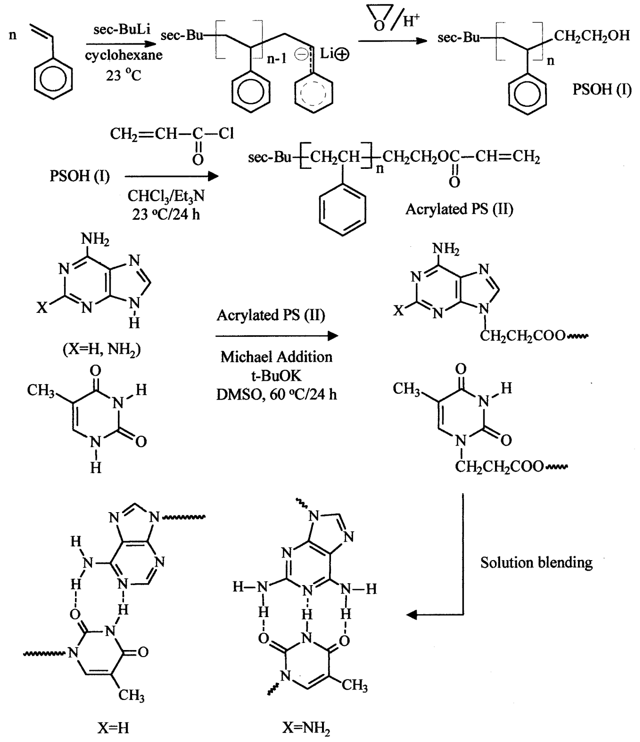

Table 1. Reaction Conditions and Reaction Conversions for Michael Additions of Acrylated PS with Heterocyclic Compounds

run	heterocyclic compounds	reaction condition		conversion (%)[b]
		catalyst	solvent	
1	adenine	Na	EtOH[a]	no reaction
2	adenine	no catalyst	DMSO	no reaction
3	adenine	no catalyst	DMF	no reaction
4	adenine	*t*-BuOK	DMSO	100
5	2,6-purine	*t*-BuOK	DMSO	100
6	thymine	*t*-BuOK	DMSO	100

[a] Heterogeneous reaction. [b] Determined using ^{1}H NMR spectroscopy.

PSOH (**I**) and corresponding reaction product revealed that the signal at 3.3−3.5 ppm, which was assigned to $-CH_2CH_2OH$, disappeared, and new reasonances attributed to $-CH_2CH_2OOC-CH=CH_2$ (3.5−4.0 ppm: 2H) and $-OOC-CH=CH_2$ (5.8−6.3 ppm: 3H) were observed. GPC measurements confirmed that molecular weights did not appreciably change upon derivatization of PSOH with acryloyl chloride. Heterocyclic-terminated PS (adenine-PS, purine-PS, and thymine-PS) were produced via a quantitative Michael addition of acrylated PS (**II**) with heterocyclic compounds as shown in Scheme 1. Table 1 summarizes the reaction conditions and the conversions for the Michael addition of acrylated-PS (**II**) with various heterocycles. Michael additions of adenine in the presence of base (sodium ethoxide) in ethanol, DMSO and DMF with acrylated PS (**II**) were performed as described in previous reports for adenine and a low molar mass methyl acrylate adduct.[54,55] However, the polymer modification did not proceed to completion under these reaction conditions (experiments 1−3). On the contrary, modifications of acrylated PS (**II**) with three types of heterocyclic compounds occurred quantitatively in the presence of a catalytic amount of *t*-BuOK. It is presumed that a weak base catalyst such as *t*-BuOK accelerated the Michael addition through the homogeneous formation of a more nucleophilic heterocyclic base.

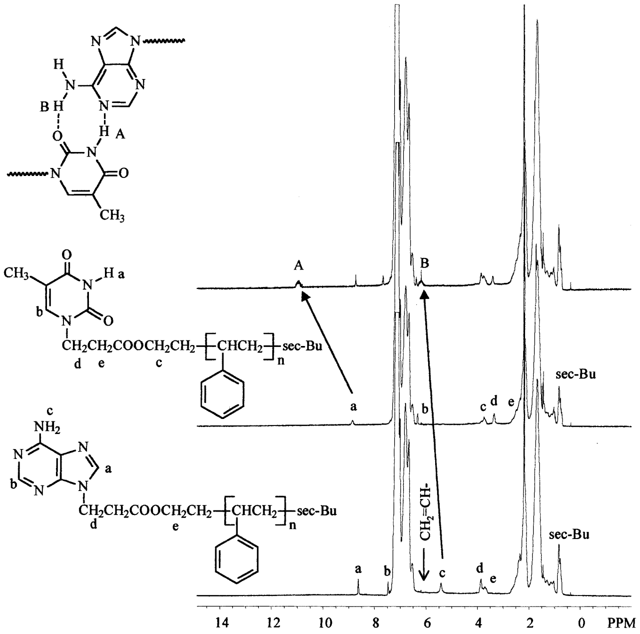

Figure 1. 400 MHz ^{1}H NMR of adenine-PS, thymine-PS, and their mixture (1:1 molar ratio) in d_8-toluene at 30 °C (end group concentration = 1.6 × 10^{-2} M (40 mg/mL)).

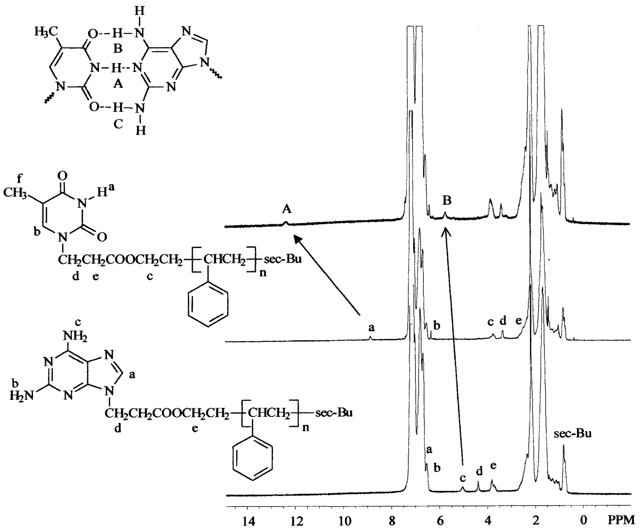

Figure 2. 400 MHz ^{1}H NMR of purine-PS, thymine-PS, and their mixture (1:1 molar ratio) in d_8-toluene at 30 °C (end group concentration = 1.6 × 10^{-2} M (40 mg/mL)).

Figures 1 and 2 depict a comparison of ^{1}H NMR spectra for reaction products (adenine-PS, thymine-PS, and purine-PS) and 1:1 mixture of adenine-PS or purine-PS with thymine-PS measured in d_8-toluene. Molecular weights and molecular weights distributions of the reaction products (adenine-PS, thymine-PS, and purine-PS) are also shown in Table 2. ^{1}H NMR analysis of adenine-PS showed that the signal at 5.8−6.3 ppm, which was assigned to $-OC-CH=CH_2$, completely disappeared and resonances associated with adenine units were observed at 8.6 ppm (a, $-N=CH-N-$), 7.5 ppm (b, $-C=N-CH=N-$), 5.4 ppm (c, $-NH_2$). Other resonances were observed at 3.7 ppm (d, $-OCH_2CH_2-$) and 3.8 ppm (e, $-CH_2N-$). In addition, number-average molecular weights were calculated from the ^{1}H NMR

Table 2. Molecular Weights and Molecular Weight Distributions of PSOH, Acrylated PS, Heterocyclic Terminated PS, and CMHB-PS

	SEC		
	DRI[a]		^{1}H NMR[b]
sample	M_n	M_w/M_n	M_n
PSOH	2500	1.10	2600
acrylated PS	2800	1.20	2800
adenine-PS	3010	1.18	3000
purine-PS	2820	1.17	2920
thymine-PS	2970	1.19	3000
adenine-PS/thymine-PS	3000	1.20	3000
purine-PS/thymine-PS	2920	1.20	2950

[a] THF at 40 °C and 1.0 mL/min using polystyrene standards. [b] Calculated from the relative intensities of reasonances associated with the repeating units such as $-C_6H_5$. *sec*-Bu, $-CH_2N-$, $-CH_2CH_2OOC-$, and heterocycles units.

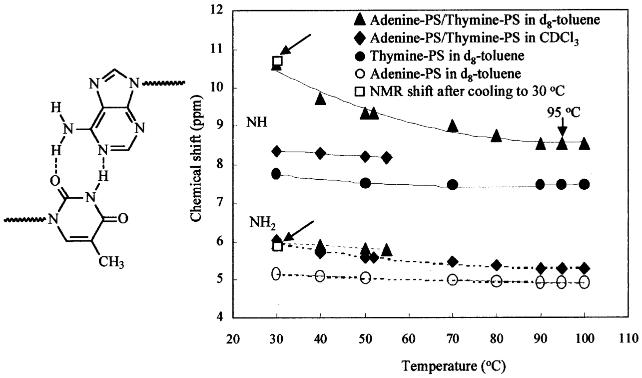

Figure 3. Temperature dependence on chemical shift of NH and NH_2 (adenine-PS/thymine-PS) measured in $CDCl_3$ and d_8-toluene (end group concentration = 1.6×10^{-2} M (40 mg/mL)).

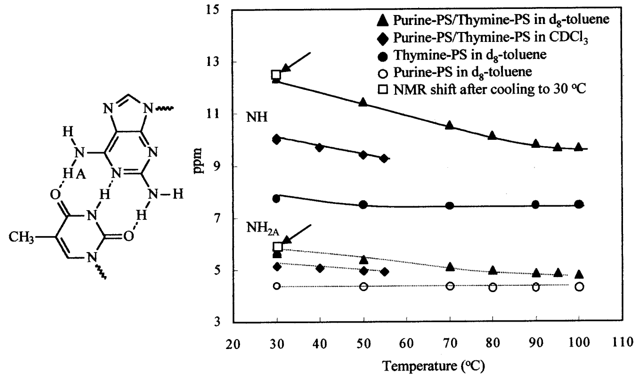

Figure 4. Temperature dependence on chemical shift of NH and NH_2 (purine-PS/thymine-PS) measured in $CDCl_3$ and d_8-toluene (end group concentration = 1.6×10^{-2} M (40 mg/mL)).

integration ratios of aromatic protons at 6.3−7.5 ppm compared to $-N{=}CH-N-$ at 8.6 ppm, $-C{=}N-CH{=}N-$ at 7.5 ppm, $-NH_2$ at 5.4 ppm, and *sec*-butyl at 0.6−1.0 ppm, and excellent agreement with GPC values as shown in Table 2 were observed.

^{1}H NMR analysis of purine-PS as shown in Figure 2 revealed that the signal at 5.8−6.3 ppm, which was assigned to $-OC-CH{=}CH_2$, disappeared and new characteristic resonances assigned to purine units were observed at 5.1 ppm (c, $-NH_2$), 4.3 ppm (d, $-CH_2N-$) and 3.5 ppm (e, $-OCH_2CH_2-$). The other specific resonances such as $-N{=}C(-NH_2)-N{=}$ (a, 2H) and $-N{=}CH-N-$ (b, 1H) overlapped with aromatic proton signals in d_8-toluene; however, these resonances were detected in $CDCl_3$. Furthermore, number-average molecular weights were calculated from the ^{1}H NMR integration ratios of aromatic protons compared to $-OCH_2CH_2-$ at 3.5 ppm, $-CH_2N-$ at 4.3 ppm, NH_2 at 5.1 ppm, and *sec*-butyl at 0.6−0.9 ppm and revealed good agreement with GPC values. ^{1}H NMR spectrum of thymine-PS also revealed that new characteristic resonances assigned to thymine units were observed at 8.9 ppm (a, $-CO-NH-CO-$), 6.3 ppm (b, $-C(CH_3){=}CH$-), 3.8 ppm (c, $-OCH_2CH_2-$), and 3.3 ppm (d, $-CH_2N-$). Number-average molecular weights based on NMR were in good agreement with GPC. In addition, ^{1}H NMR spectra of adenine-PS, thymine-PS, and purine-PS did not show other resonances, which could be attributed to regioisomers formed via an isomerization of heterocyclic anion as reported in the earlier literature for the Michael reaction of methyl acrylate and adenine in the absence of catalyst in DMSO.[55] In our work, it is presumed that isomerization of heterocyclic units did not proceed via a Michael reaction in the presence of *t*-BuOK. Despite the ambident nature of the heterocyclic bases, ^{1}H NMR confirmed that only the NH_2 in adenine and NH in thymine participated as nucleophiles under these reaction conditions.

Thin-layer chromatography (TLC) results in chloroform did not detect either the PSOH or acrylated PS. In chloroform, PSOH and acrylated PS ascended to the top of the plate; however, heterocyclic-terminated PS remained at the origin in chloroform. This observation confirmed that end group modification proceeded in a quantitative yield. On the other hand, in a polar solvent such as THF, all polymers ascended the plate, indicating that heterocyclic-terminated PS did not noncovalently bind to silica in the presence of a polar solvent. Thus, end group modification proceeded quantitatively in the absence of any polymerization of acrylated PS and other undesirable side reactions. In addition, GPC measurements in THF also suggest complete dissociation in polar solvents at GPC analysis concentrations (1 mg/1 mL).

NMR Analysis for Formation of Complementary Multiple Hydrogen Bonds. ^{1}H NMR analysis of 1:1 mixture of adenine-PS or purine-PS with thymine-PS measured at 30 °C in d_8-toluene is presented in Figures 1 and 2. A comparison of NMR spectra of a 1:1 mixture of adenine-PS and thymine-PS indicated that the NH_2 (c) in adenine-PS was shifted to lower field from 5.4 ppm (c) to 6.0 ppm (B), and NH (a) in thymine-PS was also shifted to lower field from 8.9 ppm (a) to 10.8 ppm (A) upon solution blending (Figure 1). In addition, Figure 2 also indicates that the NH_2 (c) in purine-PS was shifted to lower field from 5.1 ppm (c) to 5.8 ppm (B) and the NH (a) in thymine-PS was also shifted from 8.9 ppm (a) to 12.2 ppm (A) upon solution blending. It is presumed that this is due to the formation of CMHB. In addition, the molecular weights and molecular weight distributions of a 1:1 mixture such as adenine-PS/thymine-PS and purine-PS/thymine-PS did not appreciably change during solution blending. GPC analysis confirmed complete dissociation in polar solvents at GPC concentrations (1 mg/1 mL).

NMR study of Dissociation Temperature for CMHB-PS. Figures 3 and 4 summarize the temperature dependence of the chemical shift of NH_2 and NH in the adenine-PS/thymine-PS and purine-PS/thymine-PS blends to confirm the dissociation temperature of CMHB. The NH_2 in adenine-PS, purine-PS, and NH in thymine-PS did not appreciably change as temperature increased from 30 to 100 °C when measured in the absence of the complementary groups. This phenomenon suggests that heterocyclic-terminated PS did not form hydrogen bonds in the absence of corresponding complementary groups. On the other hand, the peaks assigned to NH_2 and NH in the 1:1 mixture were shifted to higher field below 95 °C in both $CDCl_3$ and d_8-toluene. On the basis of the temperature dependence of the ^{1}H NMR analysis of adenine-PS/thymine-PS measured in d_8-toluene (Figure 3), the peaks assigned to NH_2 in the adenine-PS/thymine-PS were shifted to higher field from 6.0 to 5.3 ppm, and the NH resonance in the adenine-PS/thymine-PS was also shifted from 10.8 to 8.5 ppm when the temperature was increased from 30 to 95 °C. In addition, ^{1}H NMR analysis of purine-PS/thymine-PS also indicated that the peaks assigned to NH_2 in the purine-PS/thymine-PS were shifted to higher field from 5.8 to 5.0 ppm, and the NH resonance in the purine-PS/thymine-PS was shifted from 12.2 to 9.8 ppm below 95 °C. Interestingly, the peaks assigned to NH_2 and NH in the adenine-PS/thymine-PS (Figure 3) and the purine-PS/thymine-PS (Figure 4) were relatively constant above 95 °C. This phenomenon is attributed to the dissociation of the CMHB. Therefore, the dissociation temperature of CMHB is proposed to be 95 °C.

Thermoreversibility of CMHB-PS was demonstrated using ^{1}H NMR analysis as shown in Figures 3 and 4. On the basis of the temperature dependence of the ^{1}H NMR analysis of adenine-PS/thymine-PS and purine-PS/thymine-PS, the peaks assigned to NH_2 and NH in both 1:1 mixtures, which were measured at 30 °C after cooling from 100 °C (denoted as □ points at 30 °C in Figures 3 and 4), were consistent with the original sample measured at 30 °C. This demonstrated thermoreversibility of CMHB-PS consisting of adenine-PS/thymine-PS and purine-PS/thymine-PS. However, if a 1:1 mixture of adenine-PS/thymine-PS and purine-PS/thymine-PS completely dissociated at 95 °C, then the resonances assigned to NH_2 and NH in adenine-PS/thymine-PS and purine-PS/thymine-PS should approach the NH_2 and NH resonances in heterocyclic-terminated PS in the absence of corresponding complementary group at 95 °C. However, the chemical shifts of NH_2 and NH in 1:1 mixtures measured above 95 °C remained higher than individual adenine-PS, thymine-PS, and purine-PS. An explanation for the difference in chemical shift above 95 °C remains under investigation; however, GPC analysis indicated that there was not an appreciable change in molecular weight and molecular weight distribution upon heating. It was presumed the well-defined hydrogen bonded assembly was dissociated at 95 °C; however, future studies will probe the possibility of a less defined and weaker aggregated state at higher temperatures. Further investigations of dissociation behavior of CMHB-PS using ^{1}H NMR in high temperature solvents, and melt rheological characterization of CMHB poly(isoprene), which has substantially lower glass transition temperature compared to PS (−60 °C), will be addressed in a future publication to fully understand the dissociation behavior of CMHB.

Conclusions

Novel CMHB-PS polymers, adenine-PS, thymine-PS, and purine-PS, were synthesized in a controlled fashion via derivatization from well-defined PSOH. The PSOH were prepared using living anionic polymerization and subsequent quantitative termination with EO. CMHB-PS polymers were synthesized via a quantitative Michael addition reaction of acrylated PS. Acrylated PS was prepared via reaction of PSOH and acryloyl chloride. Acrylated PS was subsequently derivatized with heterocyclic compounds such as adenine, thymine or 2,6-purine in the presence of *t*-BuOK via a Michael addition. CMHB-PS was obtained via solution blending. ^{1}H NMR analysis demonstrated that these mixtures formed CMHB and exhibited thermoreversibility. In addition, CMHB-PS composed of adenine-PS/thymine-PS and purine-PS/thymine-PS both dissociated at 95 °C in toluene.

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Supporting Information Available: Text giving the synthesis of hydroxyl-terminated PS and figures showing ^{1}H NMR spectra of PSOH and acrylated PS (Figure 1S), ^{1}H NMR spectra of 1:1 mixture of adenine-PS and thymine-PS measured at different temperatures (Figure 2S), and ^{1}H NMR spectra of 1:1 mixture of adenine-PS and purine-PS measured at different temperatures (Figure 3S). This material is available free of charge via the Internet at http://pubs.acs.org.

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