

Noncovalent Supramolecular Diblock Copolymers: Synthesis and Microphase Separation

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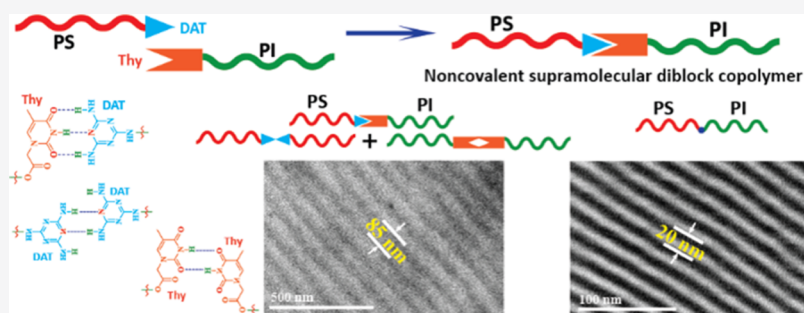
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ABSTRACT: Supramolecular block copolymers (PS-DAT-*sb*-PI-Thy) were synthesized *via* noncovalent hydrogen bonding between well-defined thymine end-functionalized polyisoprene (PI-Thy) and diaminotriazine (DAT) end-functionalized polystyrene (PS-DAT). Three covalently linked block copolymers were also synthesized for comparison with the noncovalent supramolecular block copolymers. The complementary DAT/Thy interaction resulted in the microphase separation of the supramolecular block copolymer system. Detailed characterization of all functionalized homopolymers and block copolymers was carried out *via* proton nuclear magnetic resonance (^1H NMR) spectroscopy, gel permeation chromatography, matrix-assisted laser desorption/ionization-time of flight mass spectrometry, and differential scanning calorimetry. The self-assembly process of supramolecular block copolymers was evidenced by transmission electron microscopy. Small-angle X-ray scattering was also performed to study the microphase separation of supramolecular and covalently linked block copolymers. Comparison of microphase separation images of supramolecular block copolymers and the corresponding covalently linked analogues reveals differences in *d*-spacing and microdomain shape.

INTRODUCTION

Block copolymers have undergone an extraordinary evolution from simple surfactant materials to an expansive class of macromolecules. Self-assembly of block copolymers is considered as an attractive means of generating varieties of nanostructures and patterning over a large area. One way toward complex supramolecular structures is to synthesize the suitable functional homopolymer or block copolymer precursors.^{1–8} Many intermolecular interactions such as π – π stacking, ionic interactions, metal–ligand interactions, and hydrogen bonding can assist in building complex supramolecular architectures.^{9,10} Reversibility, directionality, and self-organization nature make hydrogen bonding one of the most common motifs to design and construct supramolecular polymers with a complex macromolecular architecture. 2,6-Diaminotriazine (DAT) and thymine (Thy) are two of the most common triple hydrogen-bonded systems for the construction of supramolecular structures.^{2,3,5,11–14} Meijer and his group invented the quadruple hydrogen-bonded system to construct complex macromolecular architectures.^{15–18} Moreover, Ikkala et al. used phenolic –OH and pyridine nitrogen to form hierarchical architectures of small

surfactant molecules with block copolymers.^{19–22} In the case of the DAT/Thy system, strong heteroassociation can be formed with the help of three complementary hydrogen bonds between DAT and Thy groups, whereas homoassociation through two hydrogen bonds results in a weak interaction.¹³ This triple hydrogen-bonded system has been used to synthesize linear polymers,² comb-like polymers,^{3,23,24} and polymer networks.²⁵ Incompatibility between the polymer backbones, chain end functionality (DAT/Thy), and crystallization can promote self-assembly.^{12,13} Heteroassociation between DAT and Thy groups is strong enough in the solution to form supramolecular architectures. Small-angle neutron-scattering experiments showed a chain extended structure in solution in DAT and Thy-functionalized

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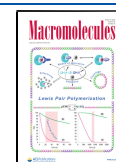


Table 1. Molecular Characteristics of Hydrogen-Bonded Supramolecular Block Copolymers

supramolecular block copolymers	M_n^b , PS (g/mol)	M_n^a , PI (g/mol)	\mathcal{D}^c PS/PI	M_n^b , PS + M_n^a , PI (g/mol)
PS45K-DAT- <i>sb</i> -PI15K-Thy	43,200	14,500	1.06/1.05	57,700
PS21K-DAT- <i>sb</i> -PI7K-Thy	21,500	8000	1.06/1.04	29,500
PS15K-DAT- <i>sb</i> -PI15K-Thy	15,200	14,500	1.05/1.05	29,700

^a M_n determined from NMR spectroscopy (600 MHz, 1,1,2,2-tetrachloroethane- d_2). ^b M_n determined from GPC (THF, 30 °C, PS standards). ^c \mathcal{D} determined from GPC (THF, 30 °C).

polypropylene glycol,²⁶ whereas solid-state complementary DAT/Thy interaction is nearly the same as DAT/DAT interaction.² In general, self-assembly of a system in bulk depends on functionalized group concentration, although it does not follow the pairwise interaction as observed in a dilute solution. Therefore, a new situation can appear in the melt or solid state where the structure and dynamics can be affected by an additional ordering effect such as microphase separation of the respective components. Thus, moderate or weak supramolecular interactions such as hydrogen bonds can show a predominant and significant effect on the properties of the resulted supramolecular system in the melt.¹¹

In this work, we have designed and synthesized DAT end-functionalized polystyrene (PS-DAT) and Thy end-functionalized polyisoprene (PI-Thy) to construct their supramolecular block copolymers *via* noncovalent complementary hydrogen bonding. Different molecular weights of the corresponding homopolymers and different sets of supramolecular block copolymers were prepared to examine the effect in microphase separation. Three different covalently linked block copolymers were also synthesized for comparison with their corresponding supramolecular noncovalent block copolymers.

EXPERIMENTAL SECTION

General Techniques. All polymers were synthesized *via* anionic polymerization high-vacuum techniques. Air- and moisture-sensitive chemicals were used under a nitrogen environment. All solvents used were of analytical grade and carefully dried before use in organic transformations. Polymers were purified by repeated precipitation from methanol.

Materials. *sec*-Butyllithium (1.4 M in cyclohexane, Sigma-Aldrich) was diluted to the appropriate concentration in purified benzene, in a specific custom-made glass apparatus under high vacuum. The same procedure was followed for the protected amine initiator. Styrene (Sigma-Aldrich, 99%) was purified *via* consecutive distillations over CaH₂ (Sigma-Aldrich, 95%) and dibutyl magnesium (1 M in heptane, Sigma-Aldrich) and stored in precalibrated ampoules at -20 °C. Isoprene (Sigma-Aldrich, 99%) was purified *via* continuous distillations over *n*-BuLi, at -10 °C using an ice/salt bath, before the addition to the polymerization reactor. TMEDA (Sigma-Aldrich, 99%) was purified *via* distillations over CaH₂ (Sigma-Aldrich, 95%) and diluted to the appropriate concentration in purified benzene, in a specific custom-made glass apparatus under high vacuum. Benzene (Sigma-Aldrich, 99.8%) was purified *via* distillation over CaH₂ and stored in glass cylinders, under high vacuum. Ethylene oxide (Sigma-Aldrich, 99.5%), used as the end-capping agent, was purified by consecutive distillations over CaH₂ and *n*-BuLi at 0 °C and stored in ampoules under high vacuum. Methanol (terminating agent) was purified by successive distillations over CaH₂ and stored in ampoules under high vacuum. The following compounds were used as received: tetrabutylammonium fluoride solution [Sigma-Aldrich, 1.0 M in tetrahydrofuran (THF)], *N,N*-dimethylformamide (Sigma-Aldrich, over molecular sieve), *O*-(benzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium tetrafluoroborate (Sigma-Aldrich), *N,N*-diisopropylethylamine (Sigma-Aldrich), thymine-1-acetic acid (Sigma-Aldrich), *N,N*-dimethylacetamide (Sigma-Aldrich), and 2-chloro-4,6-diamino-1,3,5-triazine (DAT-Cl) (Sigma-Aldrich).

Instrumentation. Gel permeation chromatography (GPC) equipped with an isocratic pump, Styragel HR2, and HR4 columns in series (300 mm × 8 mm), a refractive index detector, and THF as the eluent, at a flow rate of 1 mL/min, at 30 °C was used to determine the number-average molecular weight (M_n) of PS and polydispersity index (\mathcal{D}) of all synthesized polymers. All the proton nuclear magnetic resonance (¹H NMR) spectroscopy measurements were carried out at room temperature and variable temperatures (25–85 °C) in chloroform-*d* (CDCl₃) and 1,1,2,2-tetrachloroethane-*d*₂ (C₂D₂Cl₄) using Bruker ADVANCED III-600 MHz spectrometers to determine the chemical structure of polymers and supramolecular block copolymers. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry of all polymers was performed using dithranol as the matrix in THF and NaTFA as an ionizing agent on a Bruker Ultraflex III MALDI-TOF (Bruker Daltonik, Bremen, Germany). Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC1/TC100 system under nitrogen atmosphere. The sample was heated from 25–150 °C, cooled to -100 °C, and finally heated again to 150 °C with a heating/cooling rate of 3 °C/min. The hydrogen-bonded supramolecular block copolymers were sectioned with a thickness of 50 nm using a diamond knife (Diatome-45°) under cryogenic conditions, collected over copper grids and stained with an osmium tetroxide (OsO₄). Morphological characterization of stained samples was performed by bright-field transmission electron microscopy (TEM) using an FEI-Technai Twin instrument operated at 120 kV. Small-angle X-ray scattering (SAXS) measurements were performed using Cu *K* α radiation (RigakuMicroMax 007 X-ray generator, Osmic Confocal Max-Flux curved multilayer optics).

RESULTS AND DISCUSSION

Synthesis and Characterization. A series of homopolymers and block copolymers (Table S1) were synthesized *via* anionic polymerization high-vacuum techniques, as described in the Supporting Information (Scheme S1). We have chosen the triple hydrogen bond-forming system, DAT/thymine (Thy), as chain-end groups of the respective polymers. DAT/Thy dimerizes *via* alternating D–A–D/A–D–A interactions of donors and acceptors with an association constant (K_a) of ~900–1000 M⁻¹ in chloroform.^{13,27} The moderate association constant for the DAT/Thy system is strong enough to hold the microstructure in a supramolecular block copolymer. Stadler and co-workers showed that 1–2 mol % of the weakly hydrogen-bonded system was enough to change the mechanical behavior in thermoplastics.^{28,29} To introduce the hydrogen-bonding moieties (DAT and Thy) at the chain ends, an excess of 2-chloro-4,6-diamino-1,3,5-triazine (DAT-Cl) (aromatic nucleophilic substitution) and thymine-1-acetic acid (esterification) were used, respectively. All polystyrene samples were synthesized with amine chain-end groups and modified further to DAT chain-ends. On the other hand, all polyisoprenes with Thy-chain-ends were synthesized from their corresponding hydroxyl (–OH) functionalized precursors. The yield of Thy chain-end functionalization was determined by ¹H NMR spectroscopy, recorded in 1,1,2,2-tetrachloroethane-*d*₂ at 25 °C (Figure S1) and found to be 93–95%. For DAT chain-end functionalization, it was not

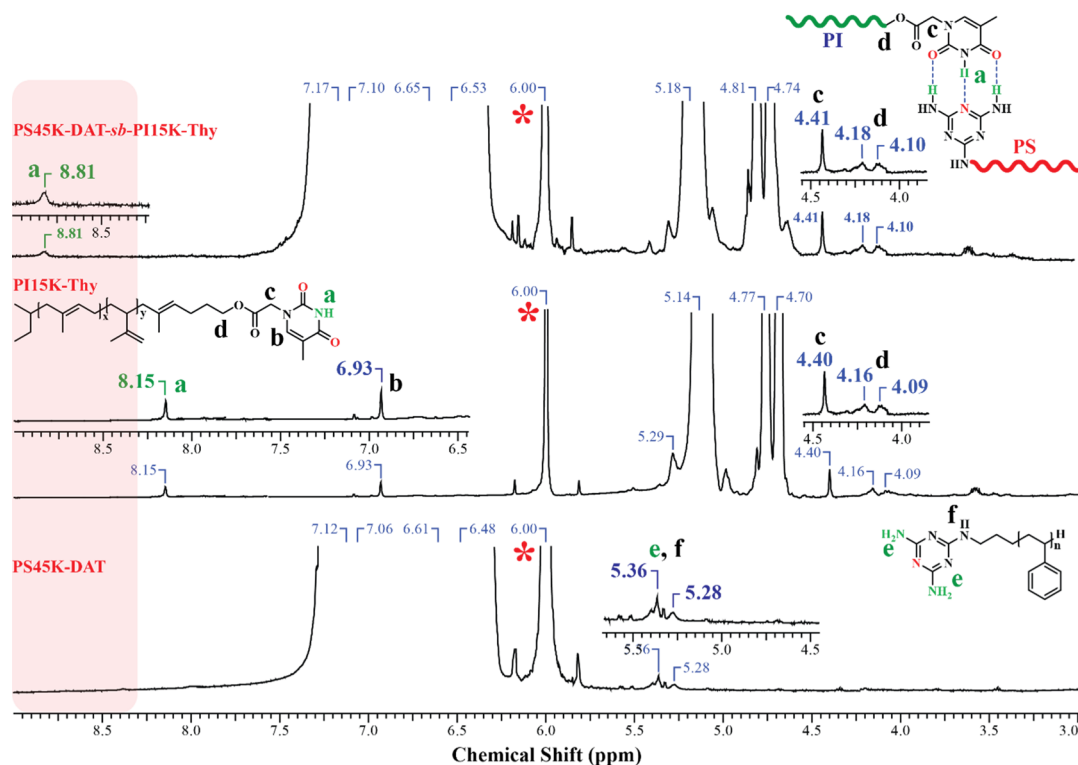
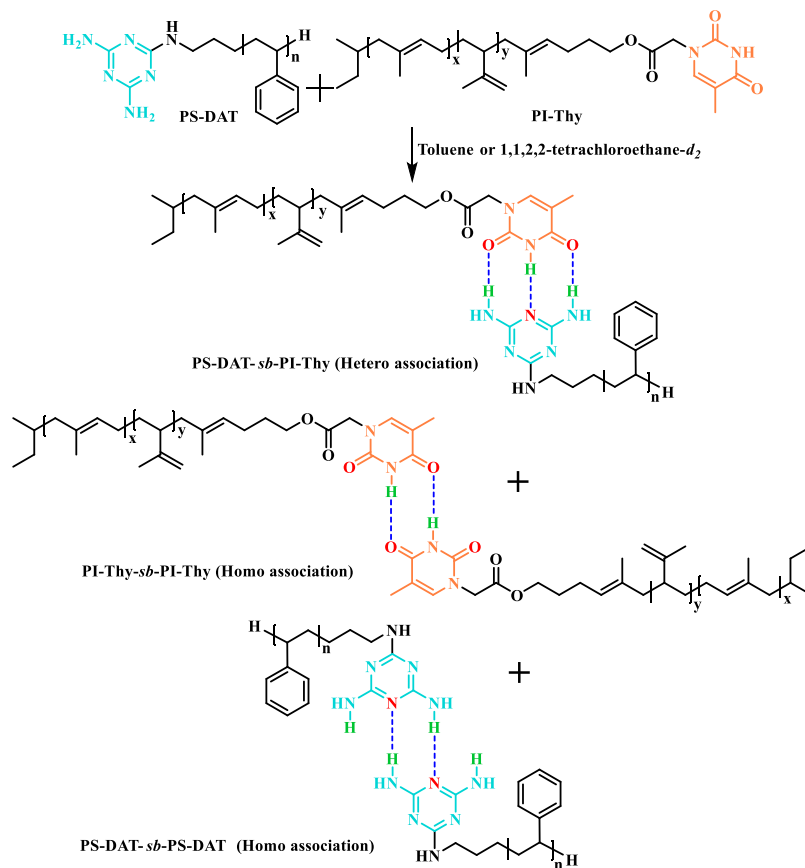


Figure 1. Comparison of the ^1H NMR spectra of PS45K-DAT, PI15K-Thy, and PS45K-DAT-*sb*-PI15K-Thy in 1,1,2,2-tetrachloroethane- d_2 at 25 $^\circ\text{C}$.

Scheme 1. General Scheme for the Formation of the Hydrogen-Bonded Supramolecular Block Copolymer PS-DAT-*sb*-PI-Thy by Heteroassociation and of Homopolymers PS-*sb*-PS and PI-*sb*-PI by Homoassociation



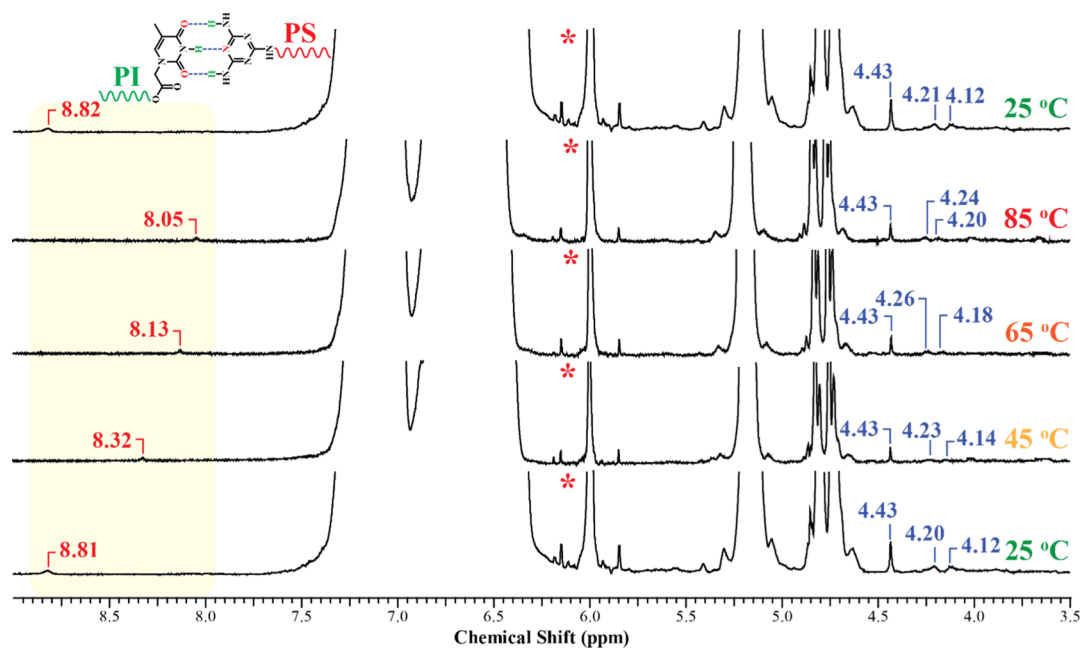


Figure 2. Variable-temperature (25–85 °C) ^1H NMR spectra of PS45K-DAT-*sb*-PI15K-Thy in 1,1,2,2-tetrachloroethane- d_2 .

possible to calculate the yield because the protons of $-\text{CH}_2-\text{NH}_2$ overlap with the CH_2 -DAT protons.

All covalently linked block copolymers and supramolecular block copolymers were named uniformly (e.g., PS15K-*b*-PI15K-OH and PS15K-DAT-*sb*-PI15K-Thy) for simplicity reasons. Their molecular characteristics are presented in Tables S1 and 1, respectively. The non-hydrogen-bonded homopolymer mixtures were prepared and named in a similar way (Table S2) with hydrogen-bonded supramolecular block copolymers (e.g., PS15K- NH_2 -*Mix*-PI15K-OH). The synthetic procedures and molecular characterization (^1H NMR, GPC, and MALDI-TOF) of all final chain-end-functionalized homopolymers and block copolymers are given in the Supporting Information (Schemes S1 and S2 and Figures S1 and S2: ^1H NMR, S3: GPC traces, and S4: MALDI-TOF). DAT-functionalized polystyrenes showed two characteristic proton signals at $\delta = 5.28$ ppm and $\delta = 5.36$ ppm for $-\text{NH}_2$ and $-\text{NH}$ protons from DAT moiety in 1,1,2,2-tetrachloroethane- d_2 , designated as “e” and “f” in Figure 1, respectively. On the other hand, Thy-functionalized polyisoprene showed two characteristic proton signals at $\delta = 8.15$ (± 0.02) ppm and $\delta = 6.93$ ppm for the $-\text{NH}$ and unsaturated $-\text{CH}$ protons from the thymine moiety in 1,1,2,2-tetrachloroethane- d_2 (“a”, and “b” in Figures 1, S1), respectively. Additionally, Thy-functionalized polyisoprene showed one multiplet proton signal at $\delta = 4.16$ ppm (designated as “d” in Figure S1) corresponding to two protons of the ester linkage present in the PI-Thy. Distinguished proton signals as described above confirmed that functionalization reactions were successful in all homopolymers. All the hydrogen-bonded supramolecular block copolymers were prepared (Scheme 1) by dissolving the DAT-functionalized polystyrene and Thy-functionalized polyisoprene in a 1:1 mole ratio in a minimum amount of good solvent at ambient temperature. 1,1,2,2-Tetrachloroethane- d_2 was used directly for the preparation of hydrogen-bonded supramolecular block copolymers for NMR studies. On the other hand, bulk hydrogen-bonded supramolecular block copolymers were prepared by solvent-casting from toluene at

room temperature, followed by further drying in a vacuum oven. ^1H NMR spectroscopy was used for the detailed structural characterization of all supramolecular block copolymers. DAT and Thy can associate *via* hetero- and homocomplementary hydrogen-bonding interactions, as shown in Scheme 1. It is well-known that thermodynamic binding constant of DAT/Thy complementary hydrogen bonding is stronger ($K_{\text{DAT/Thy}} \sim 900 \text{ M}^{-1}$) than homoassociation between DAT/DAT ($K_{\text{DAT/DAT}} \sim 2 \text{ M}^{-1}$) and Thy/Thy ($K_{\text{Thy/Thy}} \sim 4 \text{ M}^{-1}$) in chloroform- d_3 .³⁰ Although there is a chance for the formation of homoassociation, as shown in Scheme 1, ^1H NMR spectra did not show any proton signal corresponding to Thy group homoassociation in 1,1,2,2-tetrachloroethane- d_2 . Unfortunately, as explained later, we cannot detect the DAT homoassociation because the characteristic peak is overlapping with the PI double bond peaks. However, in the solid state, the complementary DAT/Thy is nearly equal with DAT/DAT interaction,² thus leading to a supramolecular organization consisting of hetero- and homoassociation, as well as nonassociated homopolymers.

^1H NMR of PI15K-Thy showed two distinct signals at $\delta = 8.15$ ppm and $\delta = 6.93$ ppm as explained before (“a”, and “b” in Figure 1) in 1,1,2,2-tetrachloroethane- d_2 . PS45K-DAT also showed two signals at $\delta = 5.28$ ppm and $\delta = 5.36$ ppm as described in the previous section (“e” and “f” in Figure 1) in 1,1,2,2-tetrachloroethane- d_2 . Interaction of the Thy group of PI15K-Thy with the DAT group of PS45K-DAT resulted in a downfield shift of the $-\text{NH}$ proton (“a”) of PI15K-Thy from $\delta = 8.15$ ppm to $\delta = 8.81$ ppm in PS45K-DAT-*sb*-PI15K-Thy (Figure 1). The chemical shift of $-\text{NH}_2$ protons for DAT cannot be detected as it interferes with the PI double bond proton signal and the solvent signal. The other two hydrogen-bonded supramolecular block copolymers, PS21K-DAT-*sb*-PI7K-Thy and PS15K-DAT-*sb*-PI15K-Thy, also showed a downfield shift in ^1H NMR at $\delta = 8.68$ (Figure S5) and $\delta = 8.33$ ppm (Figure S6) with respect to their self-hydrogen-bonded Thy groups ($\delta = 8.17$ ppm and $\delta = 8.15$ ppm) in PI7K-Thy and PI15K-Thy, respectively. The downfield shift

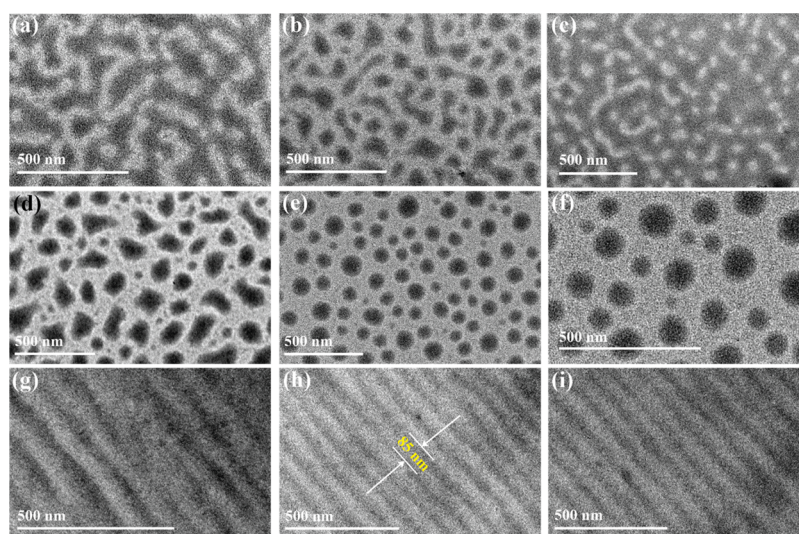


Figure 3. TEM images of (a–c) PS45K-DAT-*sb*-PI15K-Thy, (d–f) PS21K-DAT-*sb*-PI7K-Thy, and (g–i) PS15K-DAT-*sb*-PI15K-Thy.

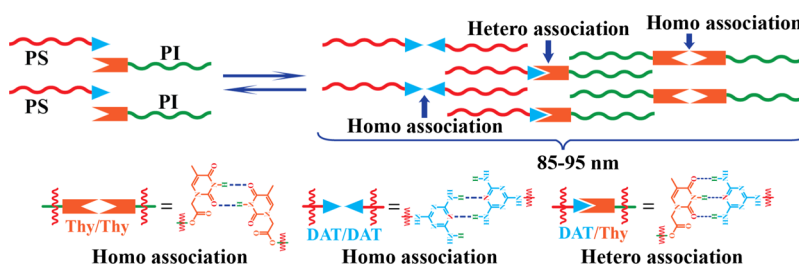


Figure 4. Possible mode of association among Thy/Thy, DAT/DAT, and DAT/Thy of PS15K-DAT-*sb*-PI15K-Thy in the lamellar organization.

of “a” proton in the Thy moiety confirms the successful supramolecular block copolymer formation between PS-DAT and PI-Thy end-functionalized homopolymers.

For further confirmation of hydrogen-bonded supramolecular block copolymers, we have performed variable-temperature ^1H NMR measurements in 1,1,2,2-tetrachloroethane- d_2 . The temperature window was maintained between 25 and 85 $^\circ\text{C}$ for all sets of supramolecular block copolymers. As mentioned above, supramolecular block copolymer PS45K-DAT-*sb*-PI15K-Thy showed a proton signal at $\delta = 8.81$ ppm (labeled as “a” in Figure 1) at 25 $^\circ\text{C}$. Upon heating to 45 $^\circ\text{C}$, an upfield shift was observed for the proton “a” from $\delta = 8.81$ ppm to $\delta = 8.32$ ppm, as depicted in Figure 2 (highlighted with yellow color). Thereafter, the proton “a” was further upfield shifted from $\delta = 8.13$ – 8.05 ppm with a gradual increase in temperature from 65 to 85 $^\circ\text{C}$. The other two supramolecular block copolymers PS21K-DAT-*sb*-PI7K-Thy and PS15K-DAT-*sb*-PI15K-Thy showed a similar trend in ^1H NMR with a gradual increase in temperature, as shown in Figures S7 and S8. No notable change in the chemical shift was observed for “a” proton between 85 and 90 $^\circ\text{C}$. Slightly above 90 $^\circ\text{C}$, the solution turned into pale yellow. The chemical shift of the $-\text{NH}$ proton of the Thy moiety (“a”) again came back to its original position at $\delta = 8.82$ ppm upon cooling from 85 $^\circ\text{C}$ to room temperature (25 $^\circ\text{C}$). The variable-temperature experiment clearly describes that the DAT/Thy complementary hydrogen bond pair is stable up to 85 $^\circ\text{C}$ in solution and fully reversible.

Differential Scanning Calorimetry. Homopolymers PS15K-NH $_2$ and PI15K-OH showed a clear glass transition temperature (T_g) at 92 and -66 $^\circ\text{C}$, respectively. Two distinct

T_g (74 and -64 $^\circ\text{C}$) were obtained for the supramolecular block copolymer PS15K-DAT-*sb*-PI15K-Thy which is comparable to the T_g (72 and -66 $^\circ\text{C}$) of the covalently linked corresponding block copolymer PS15K-*b*-PI15K-OH (Figure S9a). The decrease in T_g of polystyrene from 92 $^\circ\text{C}$ (PS15K-NH $_2$) to 74 $^\circ\text{C}$ in PS15K-DAT-*sb*-PI15K-Thy can be explained by the disruption of polystyrene chain packing in the presence of polyisoprene chains which is similar to the covalently linked block copolymer PS15K-*b*-PI15K-OH, whereas T_g corresponding to polystyrene (84 $^\circ\text{C}$) did not show any significant change in the mixture of two homopolymers without the hydrogen bonding end group (PS15K-NH $_2$ -*Mix*-PI15K-OH). A decrease in T_g was obtained for PS21K-DAT-*sb*-PI7K-Thy and PS45K-DAT-*sb*-PI15K-Thy supramolecular block copolymers, as shown in Figure S9b,c, respectively. The appearance of two T_g of PS15K-DAT-*sb*-PI15K-Thy, PS15K-*b*-PI15K-OH, and PS15K-NH $_2$ -*Mix*-PI15K-OH also suggested the presence of phase-separated morphology, as depicted later in Figures 3, S10 and S11.

Microphase Separation Studies. The microphase separation behaviors of all the hydrogen-bonded supramolecular block copolymers, covalently linked block copolymers, and the corresponding non-hydrogen-bonded homopolymer mixtures were examined by TEM and SAXS measurements. All samples were prepared by dissolving the polymers in toluene (~ 3 wt %), followed by slow evaporation (Supporting Information). Very thin microtomed sections of all vacuum-dried samples were taken on copper (Cu) grids for TEM examination. As shown in Figure 3, all hydrogen-bonded supramolecular block copolymers PS45K-DAT-*sb*-PI15K-Thy, PS21K-DAT-*sb*-PI7K-Thy, and PS15K-DAT-*sb*-

PI15K-Thy showed microphase separation. The dark areas in Figure 3 indicate the polyisoprene phase due to selective staining with osmium tetroxide (OsO_4) and bright areas indicate the polystyrene phase. Variation in the mass fraction ratio of PS:PI from 0.51:0.49 to 0.75:0.25 showed a clear transformation from well-ordered lamellar to disordered irregular interconnected spherical and worm-like domains (Figure 3). The PS15K-DAT-*sb*-PI15K-Thy supramolecular block copolymer showed a lamellar morphology (Figure 3g–i) which is similar to the lamellar morphology of the PS15K-*b*-PI15K-OH block copolymer (Figure S10g–i). However, the PS15K-DAT-*sb*-PI15K-Thy supramolecular block copolymer showed an average *d*-spacing (calculated from TEM) of ~85–95 nm (Figure 3h), which is about four times that of the 20 nm *d*-spacing of the covalently linked block copolymer (PS15K-*b*-PI15K-OH) (Figure S10h). This very large difference in the *d*-spacing between covalent and noncovalent supramolecular block copolymers can be explained on the basis of the homoassociation of the Thy and DAT moiety (Scheme 1, Figure 4) present in the noncovalent system. Thy-functionalized polyisoprene and DAT-functionalized polystyrene can assemble *via* heteroassociation and homoassociation between Thy/Thy or DAT/DAT, as depicted in Figure 4. Homoassociation combines two polyisoprenes or two polystyrenes to create homopolymers that can swell the respective PI and PS layers leading to the larger *d*-spacing in PS15K-DAT-*sb*-PI15K-Thy. Changing the composition of the supramolecular diblock fraction to 0.75:0.25 leads to irregular-shaped PI domains of a range of sizes (50–100 nm), including worm-like cylinders for both PS45K-DAT-*sb*-PI15K-Thy (Figure 3a–c) and PS21K-DAT-*sb*-PI7K-Thy (Figure 3d–f). A decrease in the overall molecular weight of both block components by a factor of about 2 should decrease the length scale of the microphase separation by a factor of $\sim 2^{2/3} - 1.6$ ($M_{n(\text{PS})}/M_{n(\text{PI})} = 45:15$ kDa to 21:7 kDa). However, the scale of the morphology seems to be approximately the same. Again, this may be due to the presence of homopolymers both single chains and homo-associated PS-*sb*-PS and PI-*sb*-PI diblocks. Such a system would tend to macrophase-separate with the PS-*sb*-PI diblocks segregating to the interface regions between the homopolymer species. For a given Flory–Huggins χ parameter ($\chi_{\text{PS-PI}}$), the amount of supramolecular linked material will be higher for blocks with lower molecular weights and for a more symmetric composition (50/50) because the critical value of the degree of segregation ($N_{\text{PS}} + N_{\text{PI}}$) χ for microphase separation is smaller than for more asymmetric compositions (75/25). We presume that the larger scale irregular structures of the noncovalently linked block 75:25 composition copolymers are due to the weaker linking between the two blocks as compared to the covalently linked blocks. The covalently linked block copolymers PS45K-*b*-PI15K-OH and PS21K-*b*-PI7K-OH with similar mass fractions to the supramolecular blocks showed hexagonally packed cylindrical morphology (Figure S10a–f) and defined Bragg peaks in SAXS. As expected, mixtures of non-hydrogen-bonded homopolymers displayed much larger scale macrophase separation because of lack of DAT/Thy complementary interaction (Figure S11). The structure of the supramolecular-bonded system depends on several parameters including $\chi_{\text{PS-PI}}$, the attractive hydrogen bond interaction between the DAT/Thy pair ($\chi_{\text{DAT/Thy}}$), immiscibility among chemically different head groups of PS-DAT and PI-Thy, and the molecular weights of the respective blocks. Therefore, the

finally formed structure depends on the interplay among all miscibility parameters and attractive hydrogen bond interactions to form either the ordered microphase-separated structure similar to the covalently linked block copolymers³¹ (e.g., lamellae, cylinders) or a more disordered, self-aggregated homopolymer-swollen structure because of the formation of homoassociations in addition to the heteroassociations.

Small-Angle X-ray Scattering. SAXS data were collected for all supramolecular block copolymers and covalently linked block copolymers (Figure S12) with all samples prepared in the same way as for the TEM samples (Supporting Information). All covalently linked block copolymers show Bragg scattering with the spacing from the first peak position matching the periodic features observed in the TEM images, whereas the supramolecular block copolymers showed strong low “*q*” scattering but without any evidence of Bragg peaks. From the TEM images in Figure 3a–f, we see that the PS45K-DAT-*sb*-PI15K-Thy and PS21K-DAT-*sb*-PI7K-Thy samples are phase-separated but the domains have various complex shapes and do not show any periodicity, so no Bragg scattering peaks are expected in SAXS. The PS15K-DAT-*sb*-PI15K-Thy sample, on the other hand, shows alternating bright and dark layers in the TEM images, indicative of lamellar ordering. The *d*-spacing in the TEM images varies in the range of 85–95 nm which is much larger than expected for the 15–15 kg/mol supramolecular block copolymer molecular weight. Such a large lamellar periodicity due to domain swelling from the respective associated homopolymers would lead to a Bragg peak at a “*q*” value that is very close to the main beam and likely would not be resolved in SAXS.

CONCLUSIONS

In conclusion, successful microphase separation was obtained in supramolecular block copolymers (PS-DAT-*sb*-PI-Thy), formed *via* noncovalent hydrogen bonding between well-defined thymine end-functionalized polyisoprene (PI-Thy) and DAT end-functionalized polystyrene (PS-DAT). The self-assembly process of supramolecular block copolymers was evidenced through TEM measurement. The DAT/Thy complementary pair is strong enough to couple PS and PI homopolymers from the solution state to the bulk phase. DAT/DAT and Thy/Thy pairs also occur and create homopolymers exhibiting double molecular weight that can influence microphase separation of the supramolecular block copolymers which display differences in *d*-spacings and microdomain size and shape from the corresponding covalently linked block copolymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.9b02326>.

Experimental details, polymer synthesis, polymer functionalization, and polymer characterizations (¹H NMR, GPC, MALDI-TOF, DSC, and TEM) (PDF)

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Notes

The authors declare no competing financial interest.

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