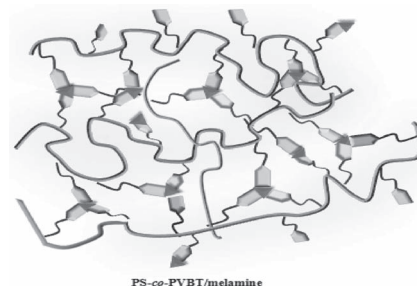


High-Heteronucleobase-Content Polystyrene Copolymers Prepared Using Click Chemistry Form Supramolecular Structures With Melamine Through Complementary Multiple Hydrogen-Bonding Interactions

Kai-Wei Huang, Shiao-Wei Kuo*

Free-radical copolymerization is used to synthesize poly[styrene-*co*-(4-vinylbenzyl azide)] (PS-*co*-PVBN₃), followed by click chemistry to react it with propargyl thymine (PT) to obtain a series of high-performance polystyrene derivatives, poly[styrene-*co*-(4-vinylbenzyltriazolyl-methylmethylthymine)] (PS-*co*-PVBT). The presence of the thymine units on the side chains of the PS copolymers allows specific intermolecular association through self-complementary T–T interactions. In addition, the thermal and dynamic rheological properties of PS-*co*-PVBT increase significantly when it is blended with melamine (M) because of the strong, complementary, multiple hydrogen-bonding interactions that occur between the T units and this low-molecular-weight compound (M).



1. Introduction

Incorporating specific functional groups into a polymer can influence its physical, mechanical, and rheological properties. Functionalizing polymers with nucleic acid bases (DNA bases) is of particular interest because of the potential to form complexes through multiple hydrogen-bonding interactions of complementary bases. Multiple hydrogen-bonding arrays play a fundamental role in complex biological systems (e.g., DNA complexation); they are influential structures in polymer science, where they are often presented as

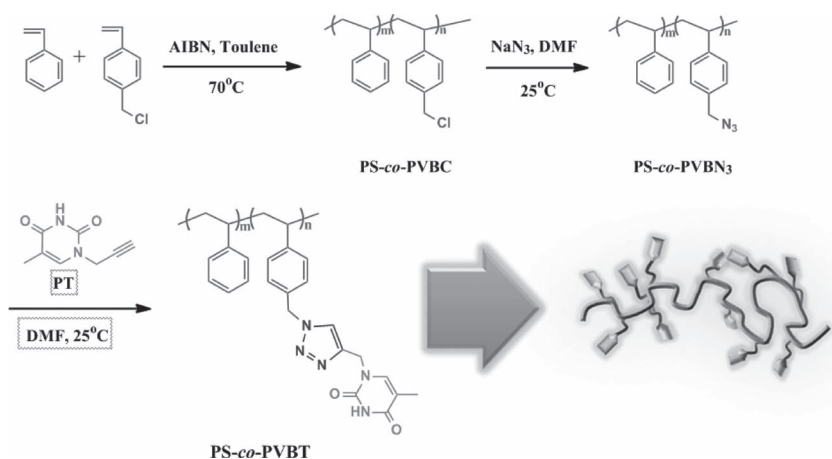
defined macromolecules possessing near-perfect molecular structures.^[1] As a result, the preparation of synthetic polymers that mimic DNA remains an important challenge in polymer science.^[2–7]

Artificial polymers bearing nucleobase moieties are very appealing macromolecules because they can potentially combine the advantages of synthetic functional polymers (low cost, high-yield preparation) with the supramolecular properties of DNA.^[8] Hence, such synthetic macromolecules are very promising candidates for applications in molecular nanotechnology^[9–12] or biotechnology.^[13–15] Taylor et al.^[16] introduced 4-(vinylbenzyl)thymine (VBT) as a versatile monomer featuring an amide group ($pK_a = 9$), two C=O groups available for hydrogen bonding, an aromatic ring for π -stacking, and a photoreactive olefinic bond.^[16] In previous studies, we used free-radical copolymerization to prepare poly(methacrylate-*co*-vinylbenzyl thymine) with various thymine (T)-functionalized vinylbenzyl monomers, but

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obtained only 7–24% functionality.^[17–20] The free-radical copolymerization was difficult to use for the synthesis of copolymer chains featuring high contents of heteronucleobase because of the significantly different polarities of the heteronucleobase monomers with respect to styrene or methacrylate monomers.^[21] Thus, we sought a different synthetic method that would provide copolymer chains with high contents of heteronucleobases. Overberger et al. reported the synthesis of polyethyleneimine derivatives bearing adenine (A) and T groups on the polymer backbone, obtaining 35–100% functionality.^[22,23] Using a similar method, poly(*l*-lysine) was functionalized with various nucleic acids (T, A, and uracil), reaching 8–93 mol% base contents.^[24] Using free-radical polymerization, polyacrylate, polymethacrylate, and poly(methyl methacrylate) derivatives presenting T functionalities (4–100 mol%) have been synthesized from various T-functionalized acrylate monomers.^[25] As a result, all the high T-functionalized copolymer should prepare through chemical modification of the side-chain groups of the copolymer chain, not only by free-radical copolymerization.

Click chemistry is used extensively because of its high (often quantitative) yields, high tolerance toward functional groups, and insensitivity to variations in solvents.^[26] The reaction between a terminal alkyne and an azide to form a triazole, first studied by Huisgen, is the most popular click reaction.^[27] These reactions have been applied widely in polymer science^[11] for the synthesis of linear,^[28–30] dendritic,^[31,32] cyclic,^[33] and star polymers,^[34,35] they have also been employed to prepare functionalized surfaces,^[36–38] sugars,^[39] probe biological systems,^[40,41] and nanoparticles.^[42] In this study, we used a combination of free-radical copolymerization and click chemistry to prepare high-performance copolymers featuring high contents of heteronucleobases. First, we employed free-radical copolymerization to synthesize poly[styrene-*co*-(vinylbenzyl chloride)] (PS-*co*-PVBC) copolymers with various VBC contents and then converted them to poly[styrene-*co*-(4-vinylbenzyl azide)] (PS-*co*-PVBN₃) copolymers through reactions with NaN₃. Finally, we used click chemistry to react PS-*co*-PVBN₃ with propargyl thymine (PT) to yield poly[styrene-*co*-(4-vinylbenzyl-



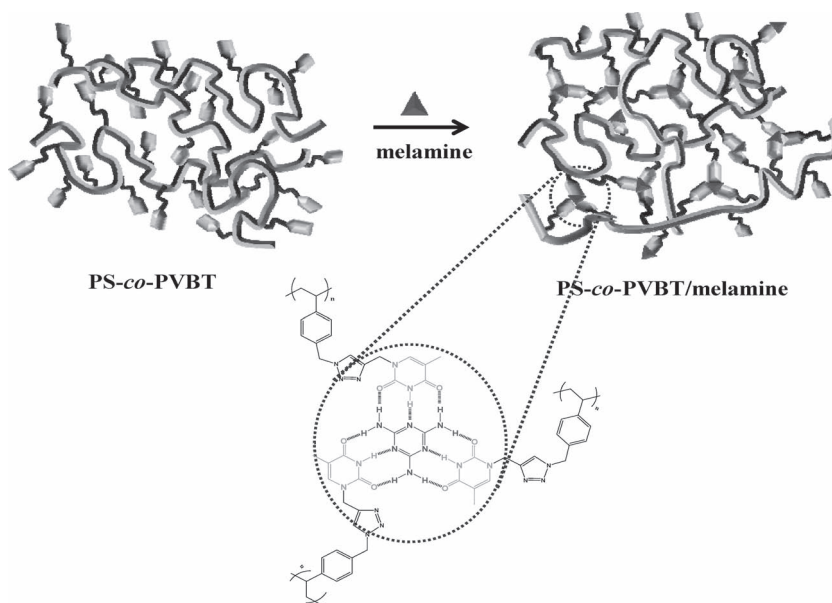
Scheme 1. Syntheses of PS-*co*-PVBC, PS-*co*-PVBN₃, PT, and PS-*co*-PVBT.

triazolylmethylmethylthymine)] (PS-*co*-PVBT) copolymers (Scheme 1). We then used Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and dynamic rheology to investigate the supramolecular structures and thermal and rheological properties of PS-*co*-PVBT when blended with the low-molecular-weight compound melamine (M) to form strong complementary multiple hydrogen bonds (Scheme 2).

2. Experimental Section

2.1. Materials

Prior to use, styrene and 4-vinylbenzyl chloride (Aldrich, USA) were passed through an alumina column and then vacuum



Scheme 2. Supramolecular structure of PS-*co*-PVBT/melamine complex through strong complementary multiple hydrogen bonding.

distilled from CaH_2 under reduced pressure. 2,2'-Azobisobutyronitrile (AIBN) was recrystallized from MeOH. Sodium azide was purchased from Aldrich. Thymine (99%) and K_2CO_3 were purchased from Showa. Propargyl bromide (80% in toluene, stabilized with MgO) was purchased from Alfa. Copper(I) bromide (CuBr, 98%) and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Aldrich. Toluene and dimethylformamide (DMF) were distilled from CaH_2 under vacuum prior to use. All other chemicals were of reagent grade and used as received without further purification.

2.2. PT

Propargyl bromide (11.9 g, 100 mmol) was added dropwise to a solution of T (5.00 g, 40.1 mmol) and K_2CO_3 (8.30 g, 60.1 mmol) in DMF (100 mL) in an ice-cooled 250 mL two-neck round-bottom flask equipped with an Ar inlet and a rubber septum. After stirring the mixture at room temperature overnight, the precipitate was filtered off and the solvent was evaporated from the filtrate. The residue was purified through column chromatography (*n*-hexane/EtOAc, 1:2) to obtain a pale-yellow powder (9.31 g, 85.0%). ^1H NMR (CDCl_3 , δ): 1.79 (3H, **CH₃**), 2.48 (1H, **CH** of propargyl), 4.55 (2H, **CH₂-N**), 7.30 (1H, **H-6** of T), 9.21 (1H, **NH**). ^{13}C NMR (CDCl_3 , δ): 11.82 [NCHC(CH₃)CO], 36.81 (CHCCH₂N), 75.13 (CHCCH₂N), 76.21 (CHCCH₂N), 110.96 [NCHC(CH₃)CO], 138.68 [NCHC(CH₃)CO], 150.36 (NHCON), 164.06 (NHCOC).

2.3. PS-co-PVBT

The solution copolymerization of styrene (1.50 g, 14.3 mmol) and 4-vinylbenzyl chloride (0.720 g, 4.78 mmol) was performed in toluene (50 mL) at 70 °C under an Ar atmosphere within a glass reaction flask equipped with condensers. AIBN (9.7 mg, 0.059 mmol) was employed as the initiator; the mixture was stirred for approximately 24 h. The product was dissolved in toluene and then poured into excess MeOH under vigorous agitation to precipitate the copolymer. The resultant solid was filtered off and dried in a vacuum oven (24 h) to give PS-co-PVBC (1.8 g, 81%). PS-co-PVBC (0.41 g, 2.43 mmol of 4-vinylbenzyl chloride repeating unit) was then dissolved in DMF (50 mL), which was added sodium azide (0.78 g, 11.9 mmol). The reaction mixture was stirred at room temperature for overnight and then precipitated into water. The product was redissolved in dichloromethane and reprecipitated in methanol. The resultant solid was collected by filtration and dried overnight in a vacuum oven for 24 h to give PS-co-PVBN₃ (1.0 g, 87%). PS-co-PVBN₃ (0.42 g, 2.39 mmol of 4-vinylbenzyl azide repeating units), PT (8.10 mg, 0.49 mmol), and CuBr (2.40 mg, 0.163 mmol) were dissolved in DMF (50 mL) in a flask equipped with a magnetic stirrer bar. After one brief freeze/thaw/pump cycle, PMDETA (4.20 mg, 0.163 mmol) was added and then the reaction mixture was carefully degassed through three freeze/thaw/pump cycles at 60 °C and stirred for 24 h. The resulting mixture was passed through a neutral alumina column to remove Cu catalysts and then poured into excess EtOAc under vigorous agitation to precipitate the copolymer, which was filtered off to provide a brown solid. ^1H NMR (DMSO-*d*₆, δ): 4.87 (2H, NCHCCH₂N), 5.45 (2H, ArCH₂N), 6.29, 6.90 (9H, ArH), 7.54 (2H, ArCH₂NCHCCH₂N), 8.14 [1H, NCHC(CH₃)CO], 11.31 (1H, NH of T). ^{13}C NMR (DMSO-*d*₆, δ): 11.82 [NCHC(CH₃)CO], 31.04,

42.43 (CH₂CH₂Ar), 36.10 (ArCH₂NCHCCH₂N), 52.63 (ArCH₂N), 109.14 [NCHC(CH₃)CO], 123.57 (ArCH₂NCHCCH₂), 127.53, 132.40, 150.89 (Ar), 141.20 [NCHC(CH₃)CO], 142.98 (ArCH₂NCHCCH₂), 162.44 (NHCON), 164.73 (NHCOC).

2.4. Supramolecular Complexes

Supramolecular complexes of PS-co-PVBT and M were prepared through solution blending. DMF solutions containing the polymer and monomer (molar ratio: 3:1) were stirred for 6–8 h; the solvent was then evaporated slowly at room temperature for 24 h. The complex films were then dried at 50 °C for 2 d.

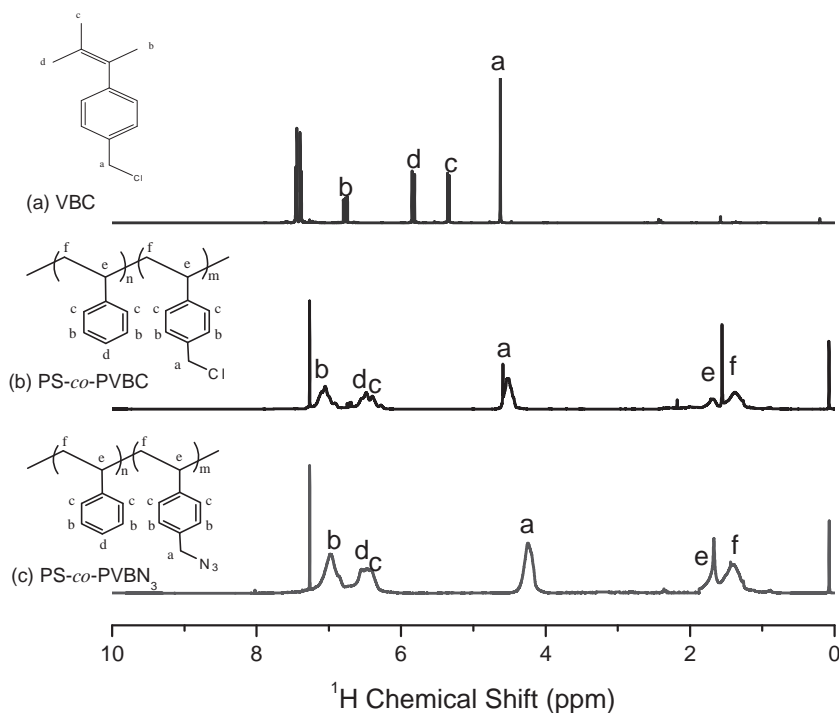
2.5. Characterization

^1H NMR spectra were recorded using a Varian Unity Inova 500 FT NMR spectrometer operated at 500 MHz, with CDCl_3 or DMSO-*d*₆ as the solvent. Molecular weights and molecular weight distributions were determined at 80 °C through gel permeation chromatography (GPC) using a Waters 510 HPLC equipped with a 410 differential refractometer, a UV detector, and three Ultrastaygel columns (100, 500, and 103 Å) connected in series; DMF was the eluent (flow rate: 0.6 mL min⁻¹). The molecular weight calibration curve was obtained using polystyrene (PS) standards. FTIR spectra were recorded using a Bruker Tensor 27 FTIR spectrophotometer; 32 scans were collected at a spectral resolution of 1 cm⁻¹. The conventional KBr disk method was employed: the sample was dissolved, then cast onto a KBr disk, and dried under vacuum at 120 °C. Because polymers containing amino and C=O groups are hygroscopic, pure N₂ gas was used to purge the spectrometer's optical box to maintain dry sample films. The glass transition (*T_g*) and melting (*T_m*) temperatures of the copolymers and their complex films were determined through DSC using a TA Q-20 instrument (scan rate: 20 °C min⁻¹; temperature range: 30–250 °C). The value of *T_g* was measured in the DSC sample cell after the sample (5–10 mg) had been cooled rapidly to -90 °C of the first scan. The *T_g* was defined at the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines. Viscoelastic measurements were performed using an Anton Paar (Physica) MCR 301 rheometer with parallel plate geometry. The measurements were undertaken within the temperature range 160–260 °C, depending upon the blend composition. During measurement, the sample was enclosed in a convection oven and the temperature was controlled by N₂ gas. At each temperature, the samples, which were always kept within ±0.3 °C of the set temperature, were equilibrated for 20 min prior to measurement. All measurements were performed in dynamic mode. Prior to loading the sample, the gap was zeroed at a certain reference temperature. Sufficient sample was loaded on the plates to maintain a gap close to 1 mm. During data analysis, the gap was adjusted to account for thermal expansion of the tools.

3. Results and Discussion

3.1. Synthesis of PS-co-PVBC and PS-co-PVBN₃

Figure 1 presents the ^1H NMR spectra (with peaks assignments) of VBC, PS-co-PVBC, and PS-co-PVBN₃ in CDCl_3 . For



■ Figure 1. ^1H NMR spectra of (a) VBC, (b) PS-co-PVBC, and (c) PS-co-PVBN₃ in CDCl₃.

VBC, signals for the vinyl groups appear at $\delta = 5.34$, 5.89, and 6.78 with a relative ratio of 1:1:1, corresponding to the *cis*, *trans*, and substituted vinyl protons, respectively, (Figure 1a). These peaks disappeared after copolymerization with styrene, providing evidence for the complete reaction leading to PS-co-PVBC (Figure 1b). We estimated the mole percentage of VBC moieties from the ratio of the integrals of the benzylic (H_a) protons of the VBC units and the aromatic (H_b , H_c , H_d) protons of both the styrene and VBC units. Table 1 lists the monomer feed ratios and resultant copolymer compositions, from which we calculated reactivity ratios ($r_{\text{PS}} = 0.76$; $r_{\text{PVBC}} = 1.04$) using the

■ Table 1. Properties of the PS, PVBC, and PS-co-PVBC copolymers used in this study.

Sample	Feed styrene/ VBC	Copolymer ^{a)} PS/PVBC	\bar{M}_w ^{b)}	\bar{M}_n ^{b)}	PDI ^{b)}
pure PS	100/0	100/0	342 00	21 200	1.61
PS83-PVBC17	85/15	83/17	54 900	24 400	2.24
PS70-PVBC30	75/25	70/30	26 300	16 300	1.61
PS45-PVBC55	50/50	45/55	32 100	21 600	1.48
PS38-PVBC62	40/60	38/62	39 300	24 500	1.60
PS26-PVBC74	25/75	26/74	34 300	22 300	1.54
PS13-PVBC87	15/85	13/87	34 600	17 800	1.94
pure PVBC	0/100	0/100	41 700	29 100	1.43

^{a)}Estimated from ^1H NMR data; ^{b)}Relative molecular weights against polystyrene standard calculated from GPC in DMF.

methodology of Kelen and Tudos, as discussed previously.^[43,44] The apparent linear relationship suggests that the copolymerization of these two monomers followed a simple two-parameter (terminal) model.^[45] The products of the reactivity ratios were close to 1, indicating that these two monomers were introduced into the polymer chain in an essentially random manner, with only a slight tendency toward alternating copolymers. Hence, the copolymers we synthesized through free-radical polymerization were essentially random copolymers. Figure 1c displays the ^1H NMR spectrum of PS-co-PVBN₃ in CDCl₃. The resonance of benzylic CH_2N_3 units of PS-co-PVBN₃ at $\delta = 4.23$ was shifted upfield significantly from that of the benzylic CH_2Cl units of PS-co-PVBC at $\delta = 4.54$. The absence of any remnant resonance at $\delta = 4.54$ suggested that the substitution reaction had occurred to completion. This conclusion was confirmed from the ^{13}C NMR spectra, where

the signal of the benzylic CH_2N_3 units shifted downfield to $\delta = 54.3$ from 46.3 for the benzylic CH_2Cl units (cf. Figure 3c and d), and from the presence of the characteristic signal for the azido groups at 2105 cm^{-1} in the Fourier-transform infrared (FTIR) spectrum of PS-co-PVBN₃ (cf. Figure 4d).

3.2. Synthesis of PT

We prepared PT through a substitution reaction of propargyl bromide with T. The complete substitution of PT was confirmed in the ^1H NMR spectrum in Figure 2b, where the signal of the propargylic CH_2 group of propargyl bromide ($\delta = 4.60$) shifted downfield (to $\delta = 4.56$) for PT. The lack of any remnant signal at $\delta = 4.60$ suggested that the substitution reaction had reached completion. Figure 4d displays the FTIR spectrum of PT at room temperature. The substitution of the bromine atom by T led to the appearance of a stretching vibration band for the $\text{C}\equiv\text{C}$ group at 2120 cm^{-1} and the $\equiv\text{C}-\text{H}$ group at 3254 cm^{-1} ; meanwhile, the $\text{C}=\text{O}$ group of the T unit appears at 1690 cm^{-1} , confirming the successful synthesis of PT.

3.3. Synthesis of PS-co-PVBT

We performed the click reaction by first introducing PT as a concentrated solution

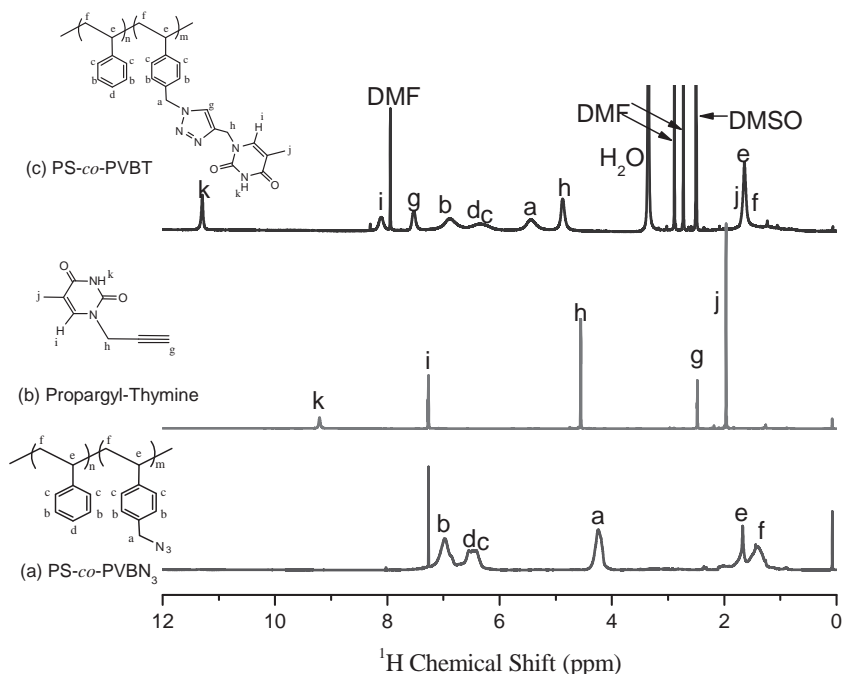


Figure 2. ^1H NMR spectra of (a) PS-co-PVBN₃ in CDCl₃, (b) PT in CDCl₃, and (c) PS-co-PVBT in deuterated dimethyl sulfoxide (DMSO-*d*₆).

in DMF to a vigorously stirred solution of PS-co-PVBN₃ at room temperature, followed by the addition of CuBr and PMDETA. Figure 2 displays the ^1H NMR spectra (with peak assignments) of PS-co-PVBN₃, PT, and PS-co-PVBT. The signal of the benzylic CH₂N₃ units of PS-co-PVBN₃ at $\delta = 4.23$ (in CDCl₃) shifted downfield significantly to $\delta = 5.45$ for the benzylic CH₂-triazole groups of PS-co-PVBT (in DMSO-*d*₆). The signal of the propargylic CH₂ unit of PT also shifted downfield from $\delta = 4.56$ (in CDCl₃) to 4.88 ppm for PS-co-PVBT (in DMSO-*d*₆); the signal of the CH proton of the triazole appeared at $\delta = 7.53$. Together, these signals confirmed the successful synthesis of PS-co-PVBT.

We also characterized the click reaction in terms of ^{13}C NMR spectra (Figure 3). The signal of the benzylic CH₂ groups of PS-co-PVBN₃ at $\delta = 54.6$ (Figure 3b) shifted to $\delta = 52.67$ for PS-co-PVBT (Figure 3d). The signals of the alkyne carbon atoms of PT (at $\delta = 74.8$ and 76.0) were absent in the spectrum of PS-co-PVBT (Figure 3c), but two new peaks appeared at $\delta = 124.0$ and 142.6 (Figure 3d), representing the carbon atoms of the triazole units, confirming the successful synthesis of PS-co-PVBT. In addition, the signal for the CH₂ group

of PT at $\delta = 36.3$ shifted to $\delta = 35.5$ in the spectrum of PS-co-PVBT; meanwhile, the signals of the carbon atoms of the phenyl ring of PT appeared near $\delta = 133$, whereas the other phenyl ring carbon atoms resonated near $\delta = 123.6$. The C=O groups of the T moiety (NCONH, NHCOCCH₃) appeared at $\delta = 162.25$ and 164.54, again confirming the successful synthesis of PS-co-PVBT.

FTIR spectroscopic analysis (Figure 4) also confirmed the complete disappearance of the characteristic signals for the azido and acetylene groups. The signal at 2105 cm⁻¹, corresponding to the absorbance of the azido groups of PS-co-PVBN₃, was absent in the spectra of PS-co-PVBT; the absorption band of the C=O group of PT appeared at 1690 cm⁻¹ in the spectra of the PS-co-PVBT copolymers, indicating that the azido and acetylene functionalities had participated in the click reactions. Taken together, the ^1H NMR, ^{13}C NMR, and FTIR spectra all confirmed the successful

synthesis of PS-co-PVBT. Table 1 characterizes the copolymers synthesized in this study. In terms of nomenclature, the descriptor PS13-co-PVBT87, for example, represents a copolymer containing 87 mol% of VBT. Clearly, highly T-functionalized PS copolymers—the first examples, to

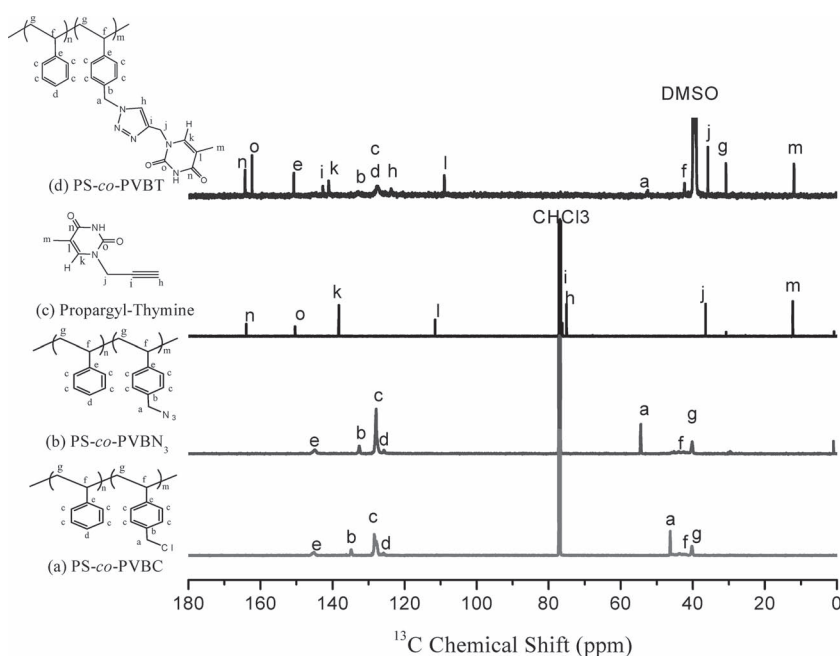


Figure 3. ^{13}C NMR spectra of (a) PS-co-PVBC in CDCl₃, (b) PS-co-PVBN₃ in CDCl₃, (c) PT in CDCl₃, and (d) PS-co-PVBT in DMSO-*d*₆.

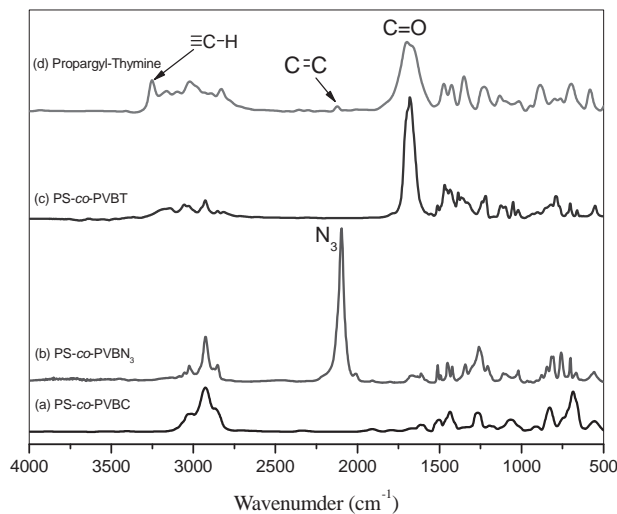


Figure 4. FTIR spectra of (a) PS-co-PVBC, (b) PS-co-PVBN₃, (c) PS-co-PVBT, and (d) PT.

the best of our knowledge—can be obtained through a combination of free-radical copolymerization and click chemistry.

3.4. Thermal Analyses of PS-co-PVBT Copolymers

Figure 5 displays DSC curves, recorded from 70 to 210 °C, of pure PS, pure PVBT, and various PS-co-PVBT copolymers. During the second heating run of each of these systems, we observed only one T_g for these copolymers; their values increased upon increasing the content of T units. We also observed single T_g s for the PS-co-PVBT copolymers, suggesting that these copolymers were homogeneous. Figure 6 plots the dependence of T_g on the various VBT contents of the PS-co-PVBT copolymers. The Kwei equation^[46] is usually employed for systems displaying specific interactions:

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + qW_1 W_2 \quad (1)$$

where W_1 and W_2 are the weight fractions of the components, T_{g1} and T_{g2} are the corresponding glass transition temperatures, and k and q are fitting constants. The parameter q represents the strength of the specific interactions in the system, reflecting a balance between the breaking of self-association interactions and the forming of inter-association interactions. For the PS-co-PVBT copolymers, we obtained values of k and q of 1 and -60 , respectively, from non-linear least-squares “best fits” of the plots. This negative value of q suggests that the intermolecular interactions between the PS-co-PVBT polymer chains were weaker than the self-association of PVBT.

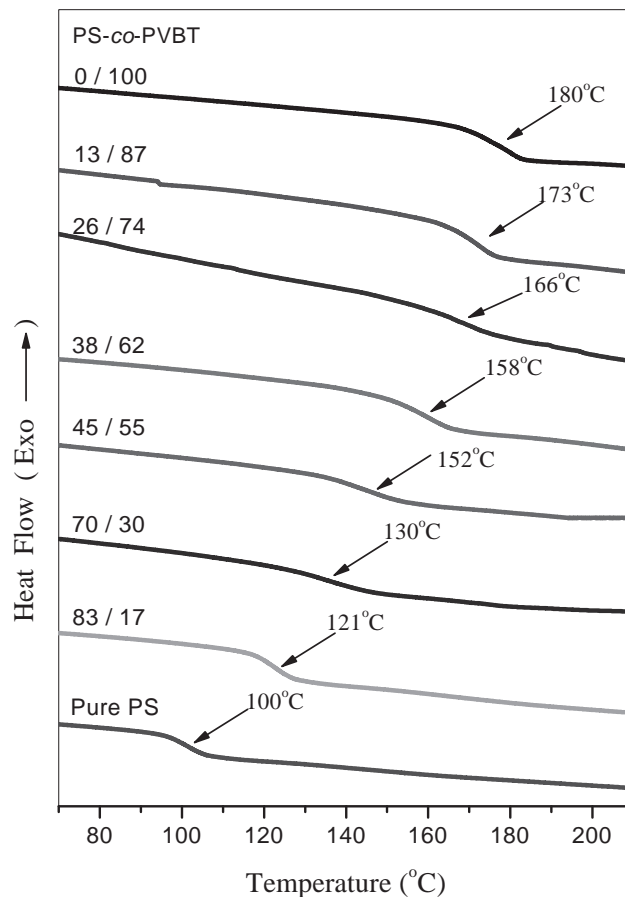


Figure 5. DSC thermograms of PS-co-PVBT copolymers featuring various T ratios.

Thus, the self-association of pure PVBT decreased significantly after incorporation of the inert diluent PS segment in PS-co-PVBT copolymers, because the spacing between the T groups along the copolymer chains and their

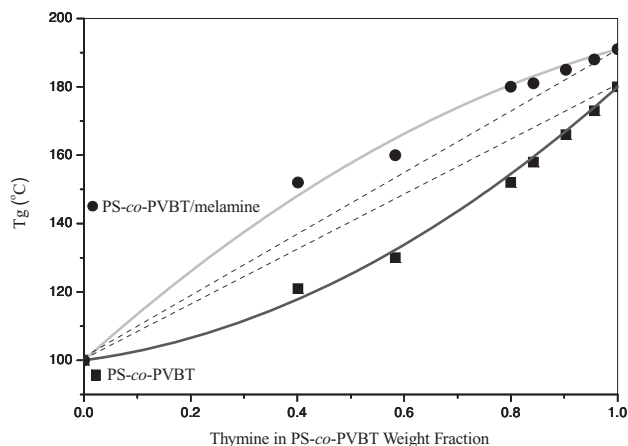


Figure 6. Glass transition behavior of PS-co-PVBT and the PS-co-PVBT/M complexes.

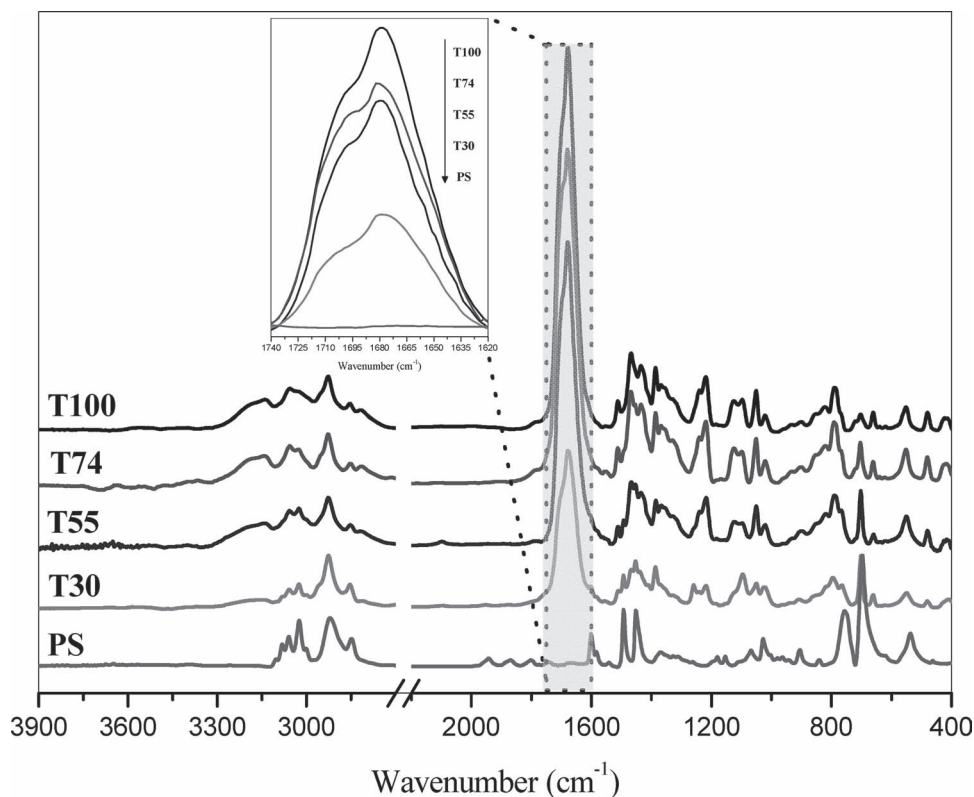


Figure 7. FTIR spectra of PS-co-PVBT copolymers featuring various T ratios.

bulk also significantly decreased the inter-association hydrogen bonding per unit volume through a so-called functional group accessibility effect, which also reflected the steric crowding and shielding.^[47–49]

Figure 7 displays FTIR spectra of PS-co-PVBT copolymers incorporating various T contents. The C=O stretching of VBT appeared as signals located at 1680 (hydrogen-bonded C=O) and 1705 (free C=O) cm^{-1} ; additional signals appeared at 3140 (NH stretching) and 2850–3100 (ArCH stretching) cm^{-1} . The intensities of the absorptions of the T moieties at 1600–1750 cm^{-1} increased upon increasing the fraction of VBT in the copolymers. In addition, the fraction of hydrogen-bonded C=O groups of VBT decreased accordingly with the increase of PS contents, due to the functional group accessibility effect.

Figure 8 displays ^1H NMR spectra of PS-co-PVBT copolymers (in $\text{DMSO-}d_6$) featuring various VBT contents. The downfield shift of the signal of the NH units from $\delta = 11.295$ for pure PVBT to $\delta = 11.317$ for PS-co-PVBT reveals that the

functional group accessibility effect could also influence the chemical shifts in these ^1H NMR spectra. Increasing the PS content in the PS-co-PVBT copolymer system disrupted the

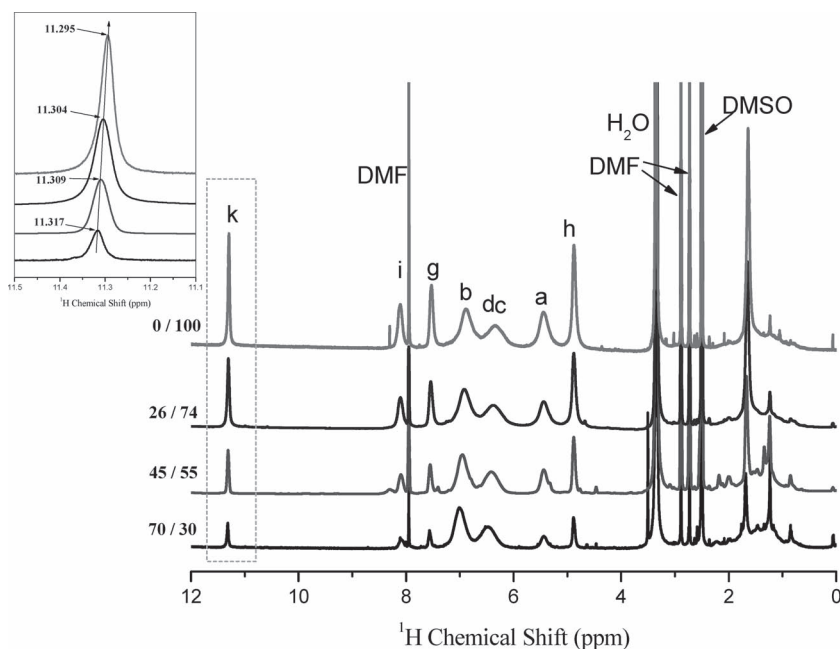


Figure 8. ^1H NMR spectra ($\text{DMSO-}d_6$, room temperature) of PS-co-PVBT copolymers featuring various T ratios.

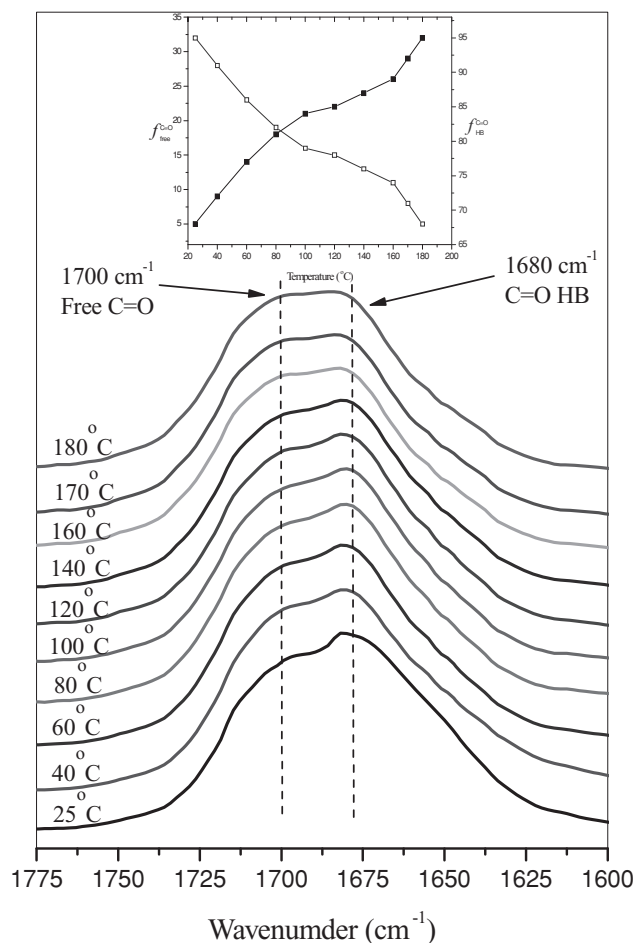


Figure 9. FTIR spectra of the PS26-co-PVBT74 copolymer recorded after different temperature stages.

the self-association hydrogen-bonding interactions of the T-T units and resulted in a negative deviation of the thermal properties determined from the Kwei equation. The decreased self-association through T-T interactions after incorporating the inert diluent moieties (styrene units) led to increased inter-association with DMSO- d_6 solvent molecules, leading to the downfield shift in the signal of the NH units upon increasing the contents of PS in the PS-co-PVBT copolymers.

3.5. Variable-Temperature FTIR Spectroscopic Analyses

Variable-temperature infrared spectroscopy is a highly effective means of investigating the specific interactions between polymers. It can be used as a tool to study, both qualitatively and quantitatively, the mechanism of inter-polymer miscibility through the formation of hydrogen bonds. Figure 9 displays FTIR spectra ($1600\text{--}1775\text{ cm}^{-1}$) recorded at various temperatures for the PS26-co-PVBT74 copolymer. As mentioned above, the signal of the free C=O groups of VBT appeared at 1700 cm^{-1} , with the absorption

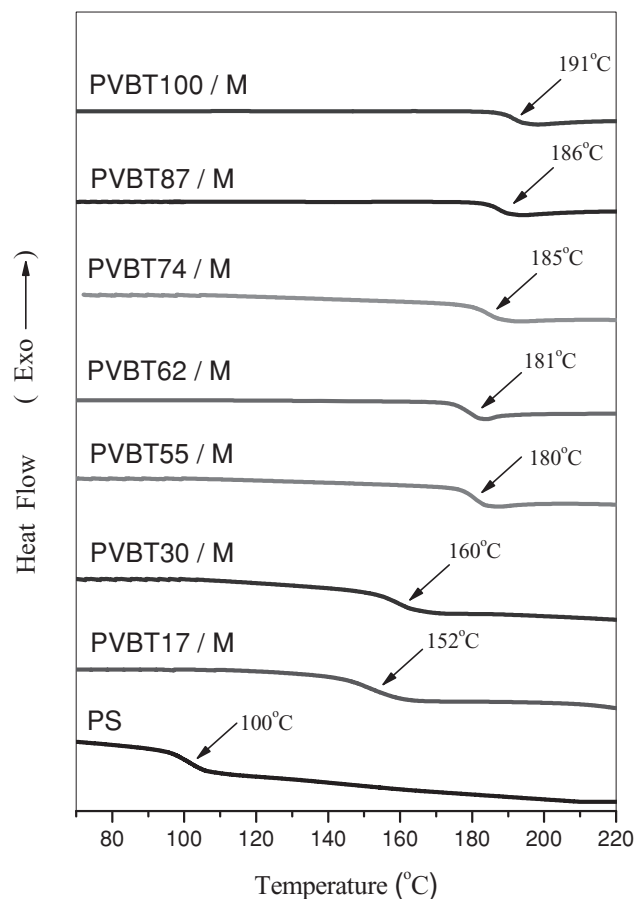


Figure 10. DSC thermograms of PS-co-PVBT copolymers featuring various T ratios, in the presence and absence of M.

near 1680 cm^{-1} being due to the hydrogen-bonded T groups.^[50] The position of the signal for the free C=O groups of VBT changed upon increasing the temperature; the intensity of this peak decreased accordingly because heat disrupts hydrogen-bonding interactions.

3.6. Supramolecular Complexes Formed Between PS-co-PVBT and M

Figure 10 displays DSC thermograms recorded at a PS-co-PVBT:M molar ratio of 3:1, but with the PVBT components containing various contents of T. Each of these binary mixtures exhibited a single T_g , with the value of T_g increasing upon increasing the PVBT content. In general, blending with low-molecular-weight compound (such as plasticizer) would decrease the T_g value due to increase the free volume of polymer chains. Notably, but for the supramolecular complex formed between PS-co-PVBT copolymers and the low-molecular-weight M, the values of T_g increased by $10\text{--}30\text{ }^\circ\text{C}$ relative to those of the PS-co-PVBT copolymers, which is similar with previous study of alternating copolymer of styrene and maleimide blending with M.^[51] Table 2

Table 2. DSC analysis of PS-*co*-PVBT copolymers and PS-*co*-PVBT/melamine complex.

Sample	Weight fraction of VBAT	T_g^a [°C]	Blend melamine T_g^a [°C]
pure PS	0	100	–
PS83-PVBT17	0.40105	121	152
PS70-PVBT30	0.58352	130	160
PS45-PVBT55	0.79983	152	180
PS38-PVBT62	0.84212	158	181
PS26-PVBT74	0.90296	166	185
PS13-PVBT87	0.95629	173	186
pure PVBT	1	180	191

^a)Determined by DSC at 20 °C min⁻¹.

summarizes the data from the DSC analyses of the PS-*co*-PVBT copolymers and PS-*co*-PVBT/M complexes; Figure 6 also reveals the dependence of T_g on the compositions of the PS-*co*-PVBT/M complexes featuring various VBT contents. For the PS-*co*-PVBT/M complex system, we obtained the positive value of q (+50) based on the Kwei equation, implying that the complex system featured stronger complementary multiple hydrogen bonds as a result of the

presence of a larger number of nucleic acid base units.^[19] The self-association equilibrium constant (K_b) of T was approximately 3 L mol⁻¹, as determined for 2-ethylthymine as a model compound.^[50] We used the inter-association constant (K_a) of the low-molecular-weight model compounds 2,4-diamino-6-dodecyltriazine and *N*-1-propylthymine to determine the inter-association equilibrium constant ($K_a = 890$ L mol⁻¹), based on an approach described previously by Beijer et al.^[52] The value of the inter-association constant was two orders of magnitude higher than the value of the self-association constant ($K_a/K_b = \text{ca. } 300$), implying that the tendency for hydrogen bonding of the PVBT and M units dominated over self-association of the pure PVBT. Furthermore, this result is also in good agreement with the relationship between the values of T_g and the composition, as determined based on the Kwei equation. In addition, the values of T_g increase of the PS-*co*-PVBT/M complexes, relative to those of the PS-*co*-PVBT copolymers, increased upon increasing the PS content in the copolymers, presumably because the inert diluent PS segments decreased the self-association constant of PVBT; thus, the relative values of K_a/K_b and differences in the values of T_g both increased.

Figure 11a presents FTIR spectra (from 2600 to 3800 cm⁻¹) of PS-*co*-PVBT and the PS-*co*-PVBT/M complexes at room temperature. The characteristic peak of the free amide NH

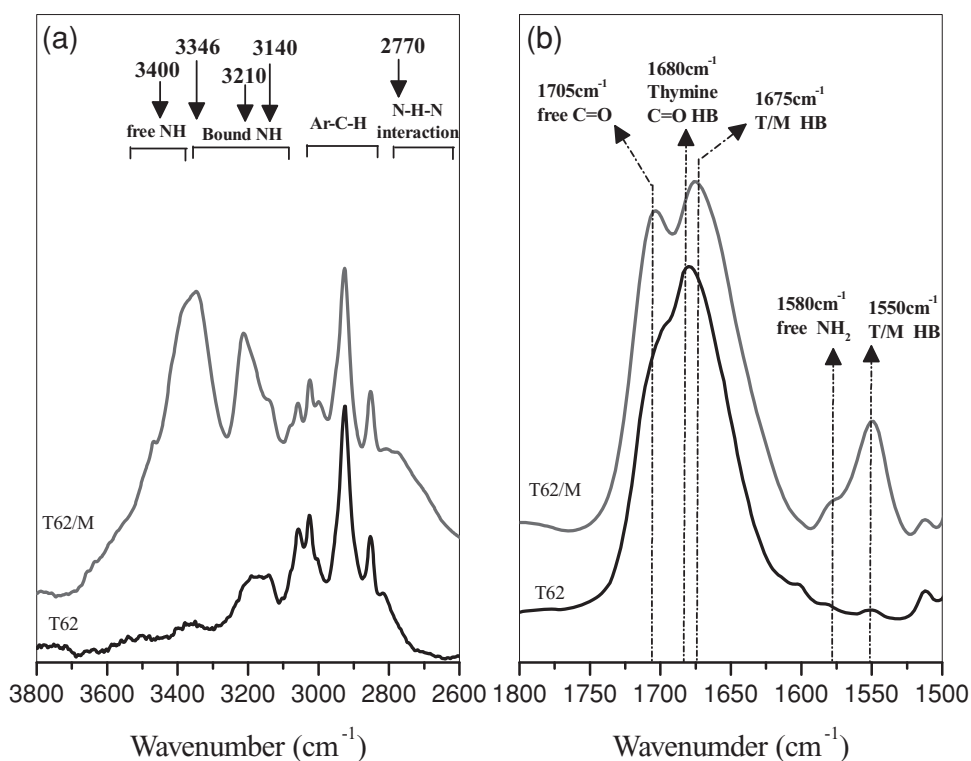


Figure 11. Room-temperature FTIR spectra in the ranges (a) 2500–3800 and (b) 1500–1800 cm⁻¹ for the PS-*co*-PVBT62/M complex in the bulk state.

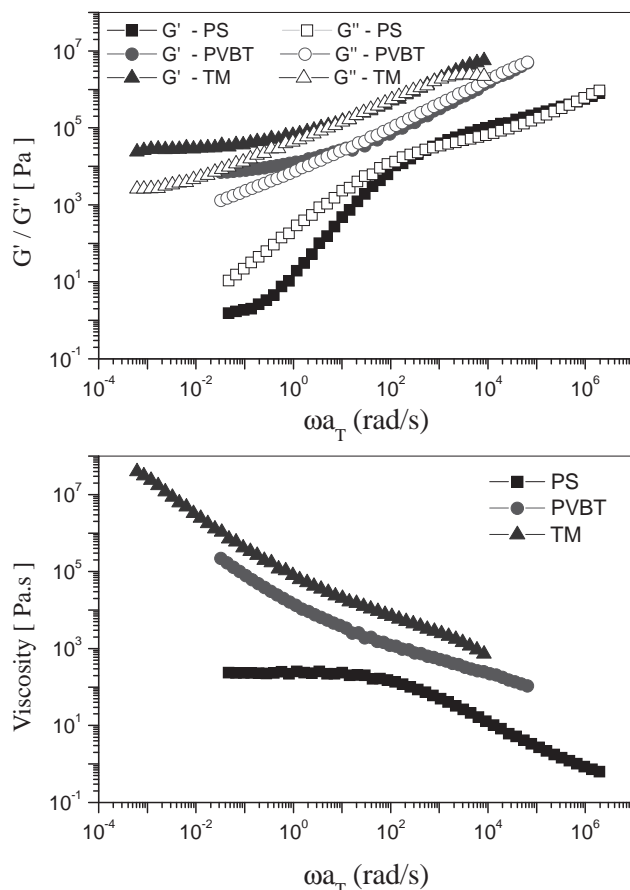


Figure 12. Master curves of storage (G') and loss (G'') moduli and viscosity (η^*) for PS, PVBT, and PVBT/M plotted with respect to the angular frequency; reference temperature for each curve: 230 °C.

group of PVBT appeared at 3400 cm^{-1} ; we attribute the signals at 3210 and 3140 cm^{-1} to the NH units involved in T–M and T–T interactions, respectively. In addition, a peak appeared at 3346 cm^{-1} that corresponded to the NH groups of self-associated M units. An absorption peak in the range 2600–2800 cm^{-1} is indicative of N–H···N inter-association,^[53] implying that PVBT and M instantly formed hydrogen-bonded complexes in the bulk state. Figure 11b displays FTIR spectra (1500–1800 cm^{-1}) of PS-co-PVBT and the PS-co-PVBT/M complexes at room temperature. The signal of the free C=O groups of PVBT appeared at 1705 cm^{-1} ; the absorption near 1680 cm^{-1} was due to the hydrogen bonded C=O groups of the T units. We did, however, observe a new peak near 1675 cm^{-1} , representing the C=O groups involved in the multiple hydrogen-bonded interactions between the T and M groups. Two new peaks appeared near 1580 cm^{-1} (free primary amino group of M) and 1550 cm^{-1} (primary amino group of M interacting with the C=O group of T). The changes were caused by multiple hydrogen bond formation between the M units and the imide groups of the T units.^[54]

3.7. Association of Supramolecular Complex Studied by Rheology

The time-temperature superposition (TTS) principle is based on the concept that all polymer relaxations are derived from the same underlying segmental motions and, thus, exhibit the same temperature dependence. Under TTS, the frequency (ω) dependence of the complex modulus at two different temperatures is given by the simple scaling

$$G^*(\omega, T) = b_T G^*(a_T \omega, T_0) \quad (2)$$

where T_0 is the chosen reference temperature and a_T and b_T are the shift factors. The horizontal shift factors a_T are determined by shifting the $\tan(\delta)$ data until optimal superposition is observed. Subsequently, an independent vertical shift b_T , accounting for density variations, is applied to the modulus data to obtain good master curves. Figure 12 displays the storage modulus (G'), loss modulus (G''), and viscosity (η^*) curves for PS, PVBT, and the PVBT/M complex. A single reference temperature of 230 °C was adopted for all samples. In Figure 12a, the master curves of the storage and loss moduli, the values of G' at a high-angle frequency (1700 rad s^{-1}) for PS, PVBT, and TM, were 6.0×10^3 , 4.3×10^4 , and 3.1×10^5 Pa, respectively. The non-hydrogen-bonded reference compound PS ($\bar{M}_n = 21\,200$ g mol^{-1}) exhibited viscoelastic behavior for the covalent bonded polymers. Compared with the values for pure PVBT, the PVBT/M complex had higher storage and loss moduli because the addition of the low-molecular-weight M, which underwent strong complementary multiple hydrogen bonding with PVBT to create physical crosslinking. Figure 12b plots the complex melt viscosities of PS, PVBT, and the PVBT/M complex as a function of the angle frequency. The viscosity of pure PS at low-angle frequency ($\omega a_T = 1$ rad s^{-1}) reached as low as 2.0×10^2 Pa s, whereas those of PVBT and the PVBT/M complex reached up to 1.6×10^4 and 1.1×10^5 Pa s, respectively. Thus, the introduction of multiple hydrogen-bonding sites caused the mechanical strength of the materials to increase by more than 500 times.

4. Conclusion

We have synthesized PS copolymers featuring a high content of T units through a combination of free-radical copolymerization and click chemistry. Incorporating these multiple-hydrogen-bonding units into PS enhanced its thermal properties and dramatically increased its viscosity as a result of the formation of supramolecular polymers. We observed a positive deviation in the dependence of the value of T_g on PS-co-PVBT/M complexes as a result of the strong, complementary, multiple hydrogen bonds that formed between the T and M units, as characterized through FTIR spectroscopic analysis.

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