

# Miscibility enhancement of supramolecular polymer blends through complementary multiple hydrogen bonding interactions

Shiao-Wei Kuo\* and Cheng-Huo Hsu

## Abstract

We have investigated the miscibility behavior and specific interactions of supramolecular poly[vinylbenzylthymine-co-(butyl methacrylate)] (T-PBMA) and poly[(2-vinyl-4,6-diamino-1,3,5-triazine)-co-styrene] (VDAT-PS) blends with respect to their vinylbenzylthymine (VBT) and 2-vinyl-4,6-diamino-1,3,5-triazine (VDAT) contents. Fourier transform infrared spectroscopy revealed that multiple hydrogen bonding interactions occurred exclusively between the VDAT and VBT units, which were stronger than adenine and thymine interactions. A miscibility window occurred in the VDAT-PS/T-PBMA blend system when the VBT and VDAT fractions in the copolymers were greater than 7 mol%, as predicted using the Painter–Coleman association model.

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**Keywords:** hydrogen bonding; miscibility; supramolecule; nucleobase

## INTRODUCTION

Polymer blends are combinations of two or more different polymer components which can exhibit mechanical, optical or thermal properties superior to those of the individual polymers. From a practical and economic point of view, polymer blending from existing polymers is the most effective and convenient route to create new and useful materials with greater versatility and flexibility, rather than the development of new polymers.<sup>1</sup> Three different types of blends can be distinguished: completely miscible blends, partially miscible blends and immiscible blends. Unfortunately, most polymer blends are immiscible because of the high degrees of polymerization; as a result, the entropic term becomes small and the miscibility becomes increasingly dependent on the contribution of the enthalpic term. To enhance the formation of miscible one-phase polymer blend systems, it is necessary for favorable specific intermolecular interactions to occur between the two (or more) base components of the blend: for example, hydrogen bonding,<sup>2–9</sup> dipole–dipole<sup>10</sup> and  $\pi$ – $\pi$  interactions.<sup>11</sup> The miscibility of an immiscible blend can be enhanced by introducing a functional group to one component to enable the formation of intermolecular interactions with another.<sup>12</sup>

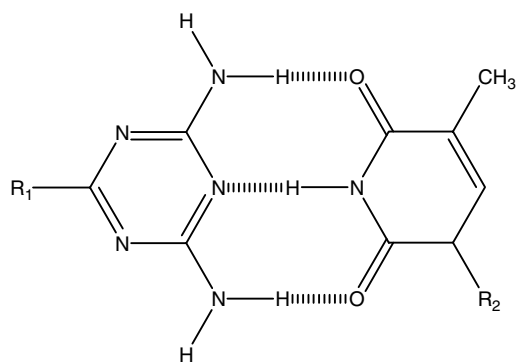
In previous studies of the roles of intermolecular association in miscibility enhancement, we found that the incorporation of a large number of hydrogen bond acceptors (*ca* 45 mol% of polyacetoxystyrene) or donors (*ca* 13 mol% of poly(vinyl phenol)) into a polystyrene (PS) chain renders the modified polymer miscible with phenolic resin<sup>13</sup> or poly( $\epsilon$ -caprolactone),<sup>14</sup> respectively. If the monomers possess relatively weak hydrogen bonding moieties (e.g. hydroxyl, carboxyl, pyridyl or ether groups), then the corresponding weak intermolecular interactions require a relatively high mole percentage of the copolymer to induce miscibility, resulting in properties of the polymer blend that differ

substantially from those of the unmodified polymer.<sup>15–18</sup> Ideally, adding low mole percentages of the recognition units into the two immiscible phases would result in a miscible phase.<sup>19–28</sup>

It is well known that molecular recognition is an essential phenomenon in living systems, as observed in the formation of complementary hydrogen bonds in DNA. The self-assembly of pairs of DNA strands is mediated by intermolecular hydrogen bonding between complementary purine (adenine (A) and guanine (G)) and pyrimidine (thymine (T) and cytosine (C)) bases attached to a phosphate sugar backbone: G binds selectively to C and A binds selectively to T.<sup>29</sup> Mimicking the molecular recognition of biological systems is one of the most attractive themes in contemporary science.<sup>30–35</sup> As a result, in our recent study,<sup>36–37</sup> we used mimic DNA-like interactions such as A and T interactions for synthesizing DNA base-containing random copolymers using conventional free radical polymerization to enhance the miscibility of immiscible PS/poly(butyl methacrylate) (PBMA) binary blends. The miscible phase of PS and PBMA was obtained when 9-(4-vinylbenzyl)adenine (VBA) and 1-(4-vinylbenzyl)thymine (VBT) units were incorporated at contents of 8 and 11 mol%, respectively, into the PS and PBMA main chains, respectively. The motivation of the study reported in the present paper was to further decrease the mole percentages of the recognition units to enhance the miscibility behavior by using stronger multiple hydrogen bonding interactions than the A–T interaction in the PS and PBMA main chains.

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**Scheme 1.** Formation of strong multiple hydrogen bonding interactions between adenine and thymine units (inter-association equilibrium constant  $K_a = 890 \text{ L mol}^{-1}$ ).

Komiyama and co-workers used free radical polymerization to prepare a series of copolymers based on 2-vinyl-4,6-diamino-1,3,5-triazine (VDAT),<sup>38–40</sup> which can form triply hydrogen bonded complexes with T adducts in non-polar solvents. A  $^1\text{H}$  NMR spectroscopic titration experiment suggested that the inter-association equilibrium constant between diamino-1,3,5-triazine (DAT) and thymine  $\text{T}^{41}$  is *ca*  $890 \text{ L mol}^{-1}$ , i.e. it is stronger than the inter-association equilibrium constant between A and T (*ca*  $530 \text{ L mol}^{-1}$ ).<sup>40</sup> As a result, we chose VDAT and VBT as monomers for independent copolymerization with styrene and butyl methacrylate monomers, noting that VDAT and T have low self-association equilibrium constants ( $K_{\text{dim}} \approx 2\text{--}3 \text{ L mol}^{-1}$ )<sup>41,42</sup> but form very strong complexes together ( $K_a \approx 890 \text{ L mol}^{-1}$ ; Scheme 1). The aims of the study reported here were: (1) to investigate the miscibility of blends of the copolymers poly[vinylbenzylthymine-*co*-(butyl methacrylate)] (T-PBMA) and poly[(2-vinyl-4,6-diamino-1,3,5-triazine)-*co*-styrene] (VDAT-PS); (2) to use spectroscopic methods to provide evidence for specific intermolecular association of the VDAT and T units; and (3) to use the Painter–Coleman association model (PCAM) to predict whether a miscibility window exists for blends of T-PBMA and VDAT-PS.<sup>43,44</sup>

## EXPERIMENTAL

### Materials

Styrene and *n*-butyl methacrylate (Aldrich, USA) were passed through an alumina column and then vacuum distilled from calcium hydride under reduced pressure prior to use. Vinylbenzyl chloride was purchased from Acros Organics (Germany) and distilled prior to use. VDAT was purchased from Tokyo Kasei Kogyo Company. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were distilled from  $\text{CaH}_2$  under vacuum prior to use. All other chemicals were of reagent grade and used as received without further purification. VBT was prepared from thymine and vinylbenzyl chloride using a procedure described previously.<sup>36</sup>

### Preparation of T-PBMA and VDAT-PS

The solution copolymerizations of butyl methacrylate and VBT<sup>36</sup> and of styrene and VDAT were performed in DMF at  $70^\circ\text{C}$  under an argon atmosphere within glass reaction flasks equipped with condensers. AIBN was employed as the initiator; the mixtures were stirred for *ca* 24 h. The products were dissolved

in DMF and then poured into excess methanol under vigorous agitation to precipitate the copolymers. T-PBMA and VDAT-PS were characterized using  $^1\text{H}$  NMR spectroscopy, elementary analysis, Fourier transform infrared (FTIR) spectroscopy, DSC, TGA and gel permeation chromatography (GPC). To determine the reactivity ratios, samples of the copolymers were taken from the reaction flasks during the early stages of copolymerization, i.e. when the degrees of conversion were low (4–9%). Scheme 2 outlines the synthetic procedures and the structures of the various components.

### Blend preparation

Blends of VDAT-PS and T-PBMA were prepared through solution blending. Tetrahydrofuran (THF) solutions containing 5 wt% of the polymer mixture were stirred for 6–8 h; the solvent was then left to evaporate slowly at room temperature for 24 h. The resulting blend films were then dried at  $50^\circ\text{C}$  for 2 days.

### Characterization

Molecular weights and molecular weight distributions were determined at  $40^\circ\text{C}$  through GPC using a Waters 510 HPLC equipped with a 410 differential refractometer, a UV detector and three Ultrastaygel columns (100, 500 and  $10^3 \text{ \AA}$ ) connected in series. DMF was the eluent and the flow rate was  $0.6 \text{ mL min}^{-1}$ . The molecular weight calibration curve was obtained using PS standards.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained using an INOVA 500 instrument, with acetone- $d_6$  as the solvent. The spectra were measured with a  $3.9 \mu\text{s}$   $90^\circ$  pulse, with 3 s pulse delay time, acquisition time of 30 ms and 2048 scans were accumulated.

Elemental analysis of N, C and H in the polymers was carried out using an auto-elemental analyzer with helium gas as the carrier.

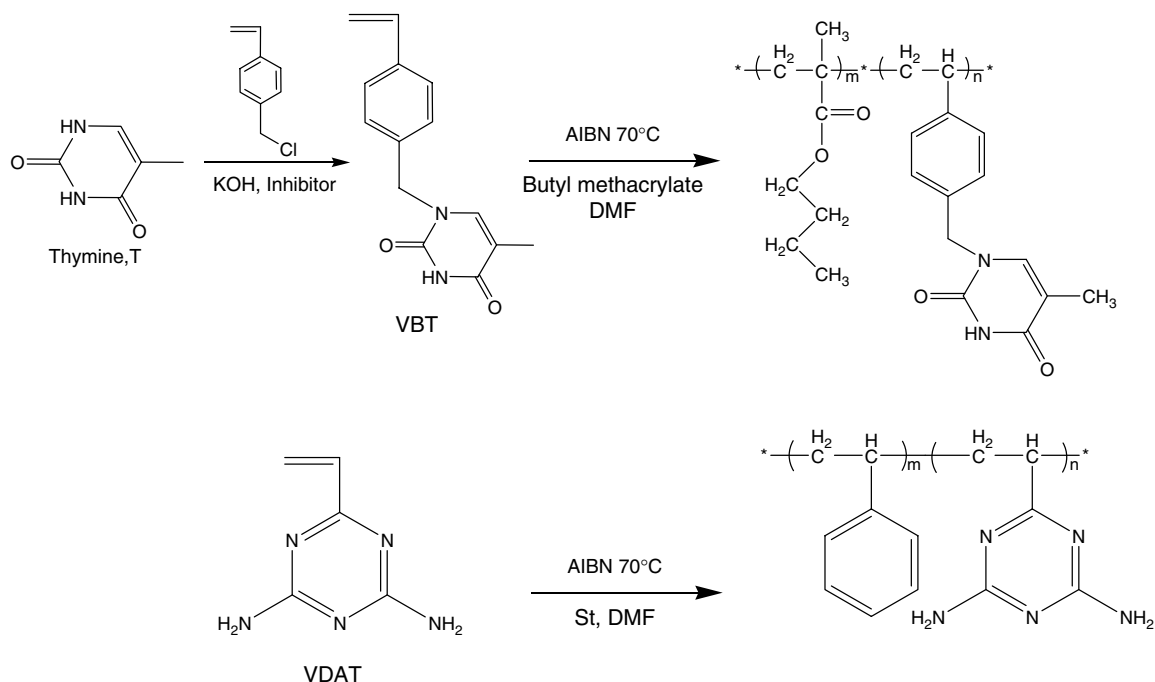
The glass transition temperatures ( $T_g$ ) of the polymer blend films were determined through DSC using a TA Q-20 instrument. The scan rate was  $20^\circ\text{C min}^{-1}$  in the temperature range  $30\text{--}200^\circ\text{C}$ ; the temperature was then held at  $200^\circ\text{C}$  for 3 min to ensure complete remove of residual solvent. Measurements of  $T_g$  were performed in the DSC sample cell after the sample (5–10 mg) had been cooled rapidly to  $-50^\circ\text{C}$  from the melt of the first scan.  $T_g$  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. TGA was performed under nitrogen or air using a TA Q50 thermogravimetric analyzer operated at a heating rate of  $20^\circ\text{C min}^{-1}$  over the temperature range from room temperature to  $800^\circ\text{C}$ . The rate of nitrogen or air flow was  $60 \text{ mL min}^{-1}$ .

FTIR spectra of the polymer blend films were recorded using the conventional KBr disc method. A THF solution containing the blend was cast onto a KBr disc and dried under conditions similar to those used for the bulk preparation. The film used in this study was sufficiently thin to obey the Beer–Lambert law. FTIR spectra were recorded using a Bruker Tensor 27 FTIR spectrophotometer; 32 scans were collected at a spectral resolution  $1 \text{ cm}^{-1}$ . Because polymers containing VDAT and T groups are hygroscopic, pure nitrogen gas was used to purge the spectrometer's optical box to ensure the sample films remained dry.

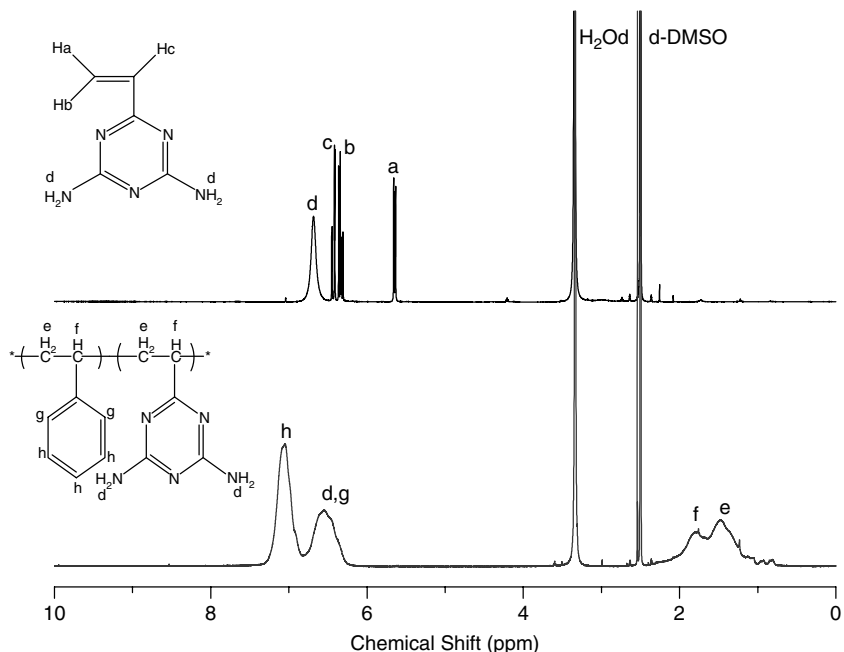
## RESULTS AND DISCUSSION

### Analyses of monomers and copolymers

VDAT is soluble in most common solvents. Figure 1 shows the  $^1\text{H}$  NMR spectra of VDAT and the copolymer VDAT-PS in DMSO- $d_6$ . For VDAT, we observe the two doublets and quartet typical



**Scheme 2.** Syntheses of PVBT-co-PBMA and PVDAT-co-PS random copolymers prepared through free radical polymerization.



**Figure 1.** <sup>1</sup>H NMR spectra of VDAT (top) and VDAT-PS (bottom) copolymers in DMSO-*d*<sub>6</sub> at room temperature.

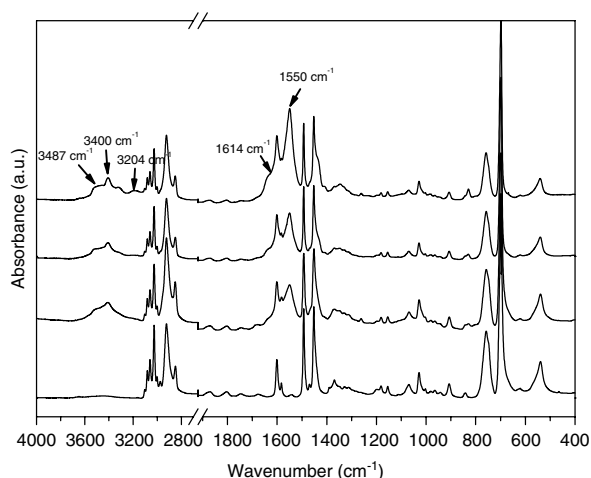
of a vinyl group (1H<sub>b</sub>, 1H<sub>a</sub> and 2H<sub>c</sub>) at 5.66, 6.32 and 6.41 ppm with a relative mole ratio of 1:1:1, corresponding to the iso, trans and substituted vinyl protons, respectively. The amino (NH<sub>2</sub>) group appears as a signal located at 6.68 ppm. The signals of the vinylic hydrogen atoms of VDAT are absent in the spectrum of VDAT12-PS (i.e. VDAT-PS copolymer containing 12 mol% of VDAT), indicating that the starting monomers had been removed completely. However, the mole percentage of VDAT cannot be estimated from the <sup>1</sup>H NMR spectrum due to the amino group signal overlapping the styrene group signal. Here, the chemical

composition of the copolymer was measured using elemental analysis. Good correlations are found between experimental and theoretical predictions of pure PVDAT and pure PS. Table 1 lists the monomer feed ratios and resultant copolymer compositions from which we calculated the reactivity ratios (*r*<sub>VBT</sub> = 3.92 and *r*<sub>BMA</sub> = 0.60; *r*<sub>VDAT</sub> = 1.23 and *r*<sub>St</sub> = 0.89) using the methodology of Kelen and Tudos, as discussed previously.<sup>13,45</sup> The apparent linear relationship suggests that the copolymerization of these two comonomers follows a simple two-parameter (terminal) model.<sup>46</sup> The products of the reactivity ratios are within the range 1.09–2.35

**Table 1.** Properties of the VDAT-PS and T-PBMA copolymers

Sample	Feed (VBT/BMA)	Copolymer <sup>a</sup> (PVBT/PBMA)	$M_w^b$	$M_n^b$	PDI <sup>b</sup>	$T_g^c$ (°C)	$T_d^d$ (°C)
Pure PBMA	0:100	0	42 000	25 000	1.68	31.4	325.9
T07-PBMA93	4:96	7:93	41 000	24 700	1.65	40.4	336.8
T11-PBMA89	6:94	11:89	45 200	28 700	1.57	49.0	346.6
T24-PBMA76	13:87	24:76	49 600	32 900	1.50	61.0	381.6
	VDAT/styrene	PVDAT/PS					
Pure PS	0:100	0	25 400	17 000	1.50	90.2	401.2
VDAT03-PS95	2.3:97.7	3.4:96.6	23 500	14 600	1.60	92.0	407.9
VDAT07-PS92	3.8:96.2	6.7:93.3	19 500	12 200	1.59	99.0	409.7
VDAT12-PS89	6.2:93.8	12.4:87.6	18 600	11 400	1.63	106.0	409.8

<sup>a</sup> Estimated from <sup>1</sup>H NMR analysis.  
<sup>b</sup> Relative molecular weights against PS standard calculated from GPC (THF eluent).  
<sup>c</sup> Determined from DSC at 20 °C min<sup>-1</sup>.  
<sup>d</sup> Determined from TGA at 20 °C min<sup>-1</sup>.

**Figure 2.** FTIR spectra of VDAT-PS copolymers recorded at room temperature.

which indicates that these two monomers are introduced into the polymer chain in an essentially random manner with only a slight tendency towards block formation. Hence, these copolymers synthesized by free radical polymerization are essentially random copolymers.

Figure 2 shows the FTIR spectra of VDAT-PS copolymers at room temperature. The NH stretching of DAT appears as signals located at 3487, 3400 and 3204 cm<sup>-1</sup> (symmetric and asymmetric stretching vibrations); additional signals appear at 1614 and 1574 cm<sup>-1</sup> (phenyl breathing) and 1550 cm<sup>-1</sup> (C=N stretching).<sup>47</sup> Clearly, the intensities of the absorptions of this DAT group at 1510–1670 and 3100–3600 cm<sup>-1</sup> increase upon increasing the VDAT fraction in the copolymers.

Figure 3 shows DSC curves, recorded from 10 to 160 °C, of the VDAT-PS and T-PBMA copolymers.  $T_g$  of these two copolymers increases upon increasing the contents of VDAT and T units, with the Fox equation revealing a positive deviation. In addition, the thermal decomposition temperatures ( $T_d$ ) also increase significantly upon increasing the contents of these nucleobases. Table 1 summarizes the monomer feed ratios and

**Table 2.** Summary of data from DSC analyses of VDAT-PS/T-PBMA binary blends

Sample (corresponding $T_g$ , °C)	$T_g$ (°C)	Fox rule predicted (°C)	Deviation compared with Fox rule (°C)
PS/PBMA (90/31)	87 31		
VDAT03PS/T7PBMA (92/40)	108 43		
VDAT03PS/T11PBMA (92/49)	66	64	+2
VDAT03PS/T24PBMA (92/61)	83	73	+10
VDAT07PS/T7PBMA (99/40)	64	57	+7
VDAT07PS/T11PBMA (99/49)	80	65	+15
VDAT07PS/T24PBMA (99/61)	88	76	+21
VDAT12PS/T07PBMA (106/40)	65	58	+7
VDAT12PS/T11PBMA (106/49)	87	67	+20
VDAT12PS/T24PBMA (106/61)	90	77	+13

the compositions, molecular weights,  $T_g$  and  $T_d$  of the synthesized copolymers. In terms of nomenclature, the descriptor T7-PBMA93, for example, represents a copolymer containing 7 mol% of VBT.

### Analyses of VDAT-PS/T-PBMA binary blends

#### DSC analyses

A single value of  $T_g$  detected by DSC is conventionally employed as a criterion reflecting the miscibility of a polymer blend. A single compositionally dependent glass transition implies full miscibility of the blend at dimensions of the order of 20–40 nm. Figure 4 shows DSC thermograms of VDAT-PS/T-PBMA = 50/50 blends, where the VDAT-PS and T-PBMA components contain various contents of VDAT and VBT, respectively; Table 2 summarizes the data. The binary blend of PS and PBMA exhibits two values of  $T_g$  located at the same temperatures as those of their respective pure polymers, revealing that they are completely immiscible. We found, however, that the value of  $T_g$  shifts upon increasing the VDAT and VBT contents in the copolymers; when 3 mol% or more of VBA and 7 mol% or more of VBT are incorporated into the PS and PBMA main chains, respectively, the PS/PBMA binary blends form miscible pairs exhibiting a single value of  $T_g$  through strong

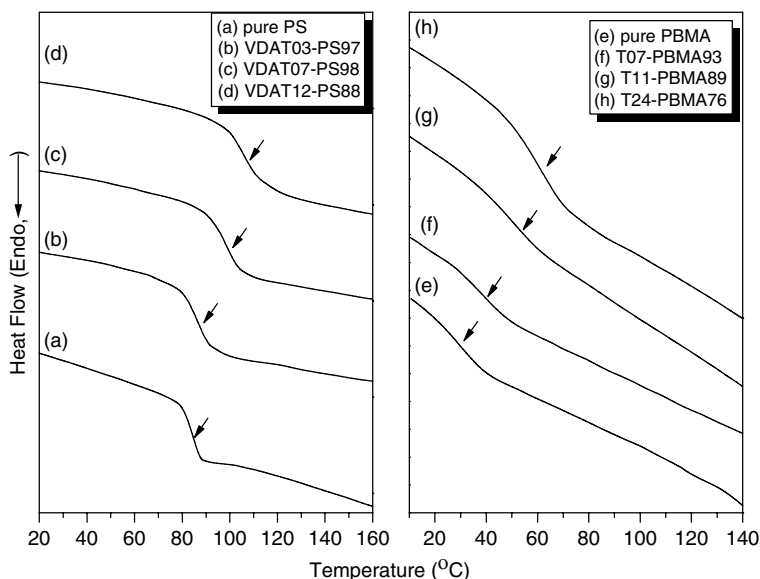


Figure 3. DSC thermograms of VDAT-PS and T-PBMA copolymers.

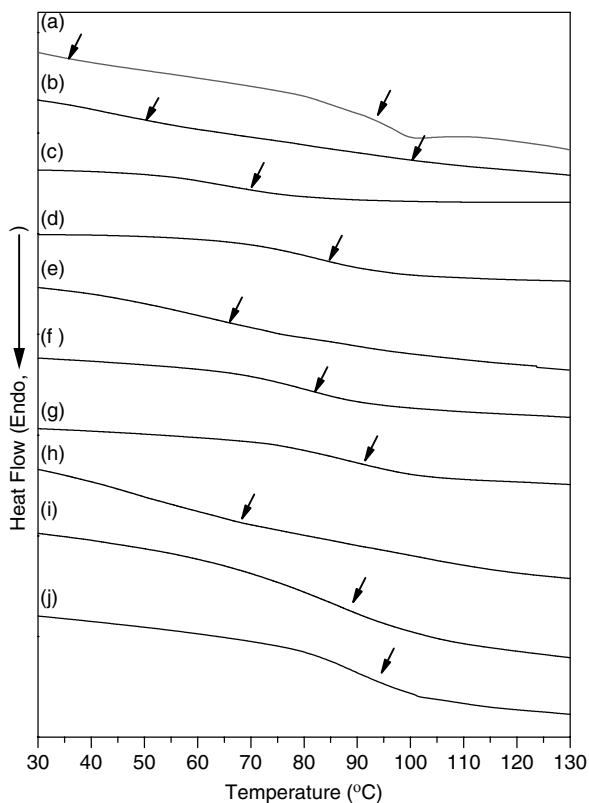


Figure 4. DSC curves of binary blends: (a) PS/PBMA; (b) VDAT3-PS/T07-PBMA; (c) VDAT3-PS/T11-PBMA; (d) VDAT3-PS/T24-PBMA; (e) VDAT7-PS/T7-PBMA; (f) VDAT7-PS/T11-PBMA; (g) VDAT7-PS/T24-PBMA; (h) VDAT12-PS/T7-PBMA; (i) VDAT12-PS/T11-PBMA; (j) VDAT12-PS/T24-PBMA.

multiple hydrogen bonding interactions between the VDAT and T units. Meanwhile, the single values of  $T_g$  of the copolymer blends fall between those of the two parent polymers (PS and PBMA), but they are significantly higher than the values predicted by the Fox equation as shown in Table 2, again indicating the presence

of strong multiple hydrogen bonding interactions between the VDAT and T segments in the copolymers.

According to the PCAM,<sup>43,44</sup> two major factors are responsible for an increase in the miscibility window. First, when the difference in the solubility parameters of the two blend components is low, the corresponding value of  $\chi$  will also be low. Second, the strength of inter-association over self-association will increase upon increasing the VDAT and VBT contents in the copolymers; this phenomenon tends to enhance the favorable contribution from the  $\Delta G_H/RT$  term in the PCAM and, therefore, improves the miscibility. We discuss in a later section the optimal values of the VDAT and VBT contents in the PS and PBMA copolymers that provide the most favorable miscible blends.

#### FTIR spectroscopic analyses

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 5 shows FTIR spectra recorded at room temperature for the PVDAT-PS/T-PBMA copolymer blends containing various mole percentages of VDAT and VBT units. The NH vibration of DAT appears as signals located at 3404 and 3540  $\text{cm}^{-1}$ , corresponding to symmetric and asymmetric stretch vibrations, respectively.<sup>50</sup> For VDAT units incorporated into the PS main chain, the absorption shifts because the DAT groups are distributed randomly in the PS and, therefore, the probability of self-associative hydrogen bonding of the VDAT groups is low because of the diluent effect in the hydrogen bonding system.<sup>48,49</sup> From Fig. 5 it is clear that the DAT groups interact with the T group – the absorptions shift to 3338 and 3462  $\text{cm}^{-1}$ . In addition, a peak appears at 3216  $\text{cm}^{-1}$  that corresponds to the NH group in T interacting with a DAT group.<sup>50</sup>

From Fig. 6(a) it is clear that the DAT groups interact with the T group – the absorptions shift to 3338 and 3462  $\text{cm}^{-1}$ . In addition, a peak appears at 3216  $\text{cm}^{-1}$  that corresponds to the NH group in T interacting with a DAT group.<sup>32</sup> Fig. 6(b) shows FTIR spectra (1500–1800  $\text{cm}^{-1}$ ) recorded at room temperature for VDAT12-PS blended with the T24-PBMA copolymer. The position of the signal for the free C=O groups of PBMA (1725  $\text{cm}^{-1}$ ) does not



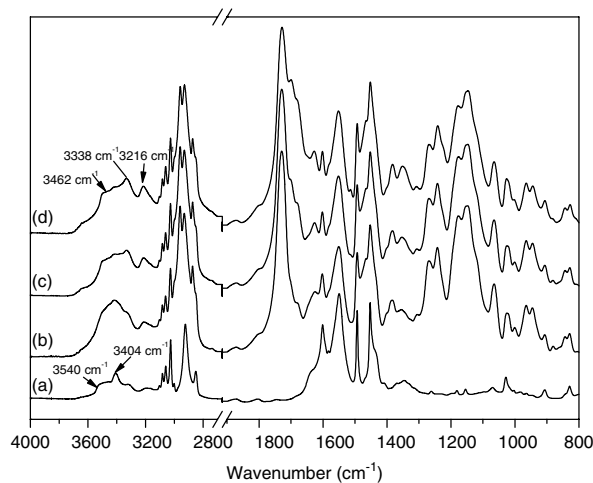
change after blending, implying the PBMA units do not form any hydrogen bonds with the VDAT and VBT units. As mentioned above, the absorptions at *ca* 1688 and 1638  $\text{cm}^{-1}$  are due to the T and DAT groups, respectively (Fig. 6(b)). We also observe two new peaks at *ca* 1677  $\text{cm}^{-1}$  (C=O group of T interacting with DAT) and 1627  $\text{cm}^{-1}$  (DAT group interacting with NH group of T). The changes are caused by multiple hydrogen bond formation between the DAT units and the imide groups of the T units.<sup>50</sup>

#### PCAM analysis of miscibility window

Painter and Coleman suggested adding an additional term – accounting for the free energy of hydrogen bond formation – to a simple Flory–Huggins expression for the free energy of mixing of two polymers:

$$\frac{\Delta G_N}{RT} = \frac{\Phi_1}{N_1} \ln \Phi_1 + \frac{\Phi_2}{N_2} \ln \Phi_2 + \Phi_1 \Phi_2 \chi_{12} + \frac{\Delta G_H}{RT} \quad (1)$$

where  $\Phi$  and  $N$  are the volume fraction and the degree of polymerization, respectively,  $\chi$  is the 'physical' interaction parameter, the subscripts 1 and 2 define the two blend components and  $\Delta G_H$  is the free energy change contributed by hydrogen bonding between two components. According to the Painter–Coleman equation, the relative magnitude of the inter- and self-association equilibrium constants, rather than their individual absolute values, is the most important factor when determining the dominant contributions to the free energy of mixing. In general, the inter-association equilibrium constant  $K_A$  is calculated using one of two methods: either from the polymer blend system or from a low-molecular-weight model compound. In our system, pure PVDAT and PVBT dissolve only in high-polarity solvents, such as DMF and DMSO, which interfere with self- and inter-association hydrogen bonding and would, therefore, provide incorrect equilibrium constants. Thus, we use the inter-association equilibrium constants of low-molecular-weight model compounds – 2,4-diamino-6-dodecyltriazine and *N*-1-propylthymine – to determine the inter-association equilibrium constant ( $K_a = 890 \text{ L mol}^{-1}$ ), based on an approach described previously by Beijer *et al.*<sup>50</sup> We transformed the value of  $K_a$  for the model compound into  $K_A$  by dividing by the molar volume of the VDAT repeat unit ( $0.121 \text{ L mol}^{-1}$  at  $25^\circ\text{C}$ ),<sup>43</sup> providing a value for the inter-association equilibrium constant  $K_A$  of 7300. Likewise, by dividing the value of  $K_b$  of  $2.2 \text{ L mol}^{-1}$  for the model compound 2,4-diamino-6-dodecyltriazine by the molar volume of the VDAT repeat unit, we determined that the self-association equilibrium constant ( $K_B$ ) of VDAT is 18. To minimize errors, we ignored the self-association of T groups because the T–T interaction is almost the same strength



**Figure 5.** FTIR spectra of VDAT12-PS/T-PBMA blends with various thymine contents recorded at room temperature (a) pure VDAT12-PS, (b) VDAT12PS/T07PBMA, (c) VDAT12PS/T11PBMA, (d) VDAT12/PS/T24PBMA.

as the DAT–DAT interaction; furthermore, two self-associating, hydrogen-bonded donor polymer blend systems would make analysis of the binary blend system too complicated.<sup>51,52</sup>

Although we did not obtain these inter-association equilibrium constants from polymer mixtures, the standard inter-association equilibrium constant of the polymer blend could be calculated from the low-molecular-weight model compound mixtures based on considering the intramolecular screening effect and functional group accessibility.<sup>53</sup> The intramolecular screening effect is a consequence of chain connectivity. The covalent linkage between polymer segments causes an increase in the number of same-polymer-chain contacts as a result of the polymer chains bending back on themselves; thus, the number of inter-association hydrogen bonds per unit volume in the polymer blend will be smaller than that for the model compound. For an infinite chain,  $\gamma$  is surprisingly large, approaching 0.38 in the melt state; for real chains, however, the value is closer to 0.3.<sup>48</sup> Moreover, the spacing between the functional groups along a polymer chain and the presence of bulky side groups can also significantly reduce the inter-association hydrogen bonding per unit volume, as a result of a so-called functional group accessibility effect. This effect is also considered to be the origin of steric crowding and shielding.<sup>55</sup> Table 3 lists all the parameters required by the PCAM to estimate the thermodynamic properties for these polymer blends.

Figures 7(a) and (b) show the miscibility window for the VDAT-PS/T-PBMA and A-PS/T-PBMA blends as predicted theoretically

**Table 3.** Summary of self- and inter-association equilibrium constants, and thermodynamic parameters of A-PS/T-PBMA blends at  $25^\circ\text{C}$

Polymer	Molar volume ( $\text{mL mol}^{-1}$ )	Molecular weight ( $\text{g mol}^{-1}$ )	$\delta^a$ ( $\text{cal mL}^{-1}$ ) <sup>1/2</sup>	Equilibrium constant <sup>b</sup>	
				$K_B$	$K_A$
PS	93.9	104.1	9.5		
PBMA	134.4	142.0	8.7		
PVDAT	122.1	133.1	12.0	18.0	
PVBT	161.7	242.1	12.1		7300

<sup>a</sup> Solubility parameter.

<sup>b</sup>  $K_B$ , self-association equilibrium constant;  $K_A$ , inter-association equilibrium constant.

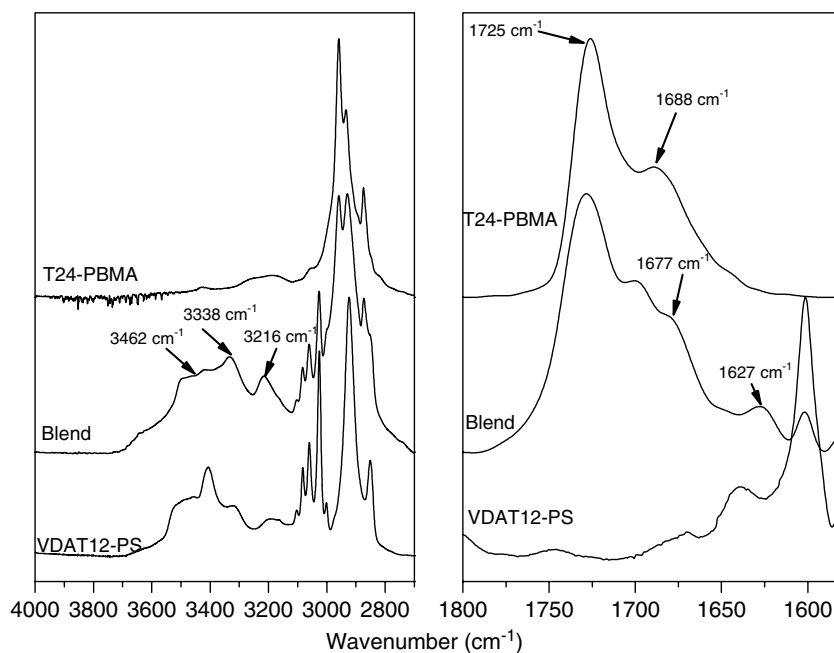


Figure 6. FTIR spectra of VDAT12-PS and T24-PBMA, and their corresponding blend, recorded at room temperature.

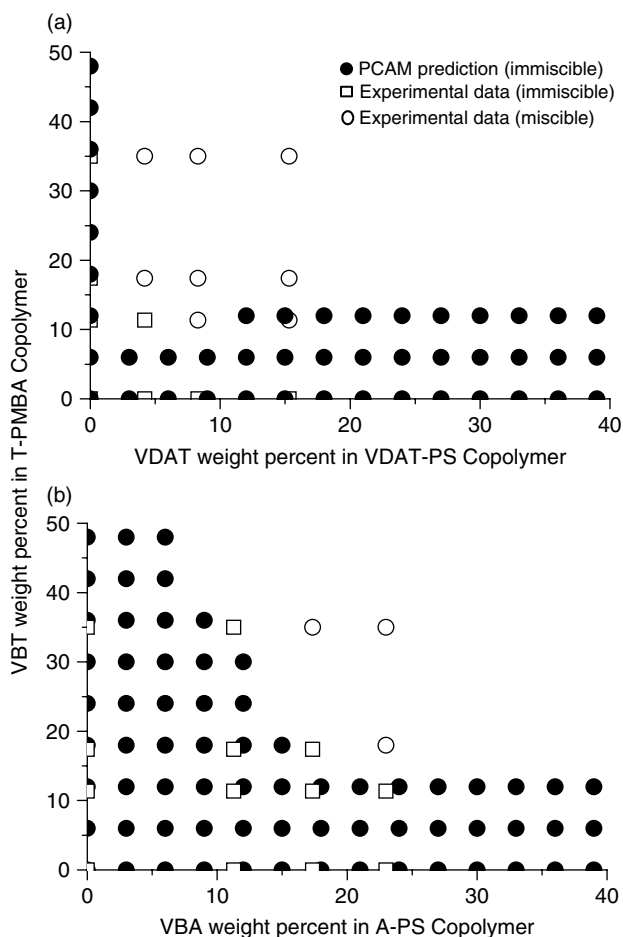


Figure 7. Theoretical miscibility windows for (a) VDAT-PS/T-PBMA and (b) A-PS/T-PBMA blends obtained from the PCAM: ●, spinodal curve and experimental data; □, two-phase system; ○, one-phase system.

using the PCAM,<sup>24</sup> respectively. The x-axes represent the weight percentage of VDAT and VBA in the PS copolymer, respectively; the y-axis represents the weight percentage of VBT in the T-PBMA copolymer. Figure 7(a) shows that the binary blends of copolymers would be completely miscible if the VDAT and VBT content were greater than 8 and 12 wt% (*ca* 7 and 11 mol%, respectively). Clearly, the miscibility window of Fig. 7(a) is larger than that of VBA-PS/T-PBMA binary blend in Fig. 7(b). In addition, the model's predicted miscibility window compares favorably with our experimental results derived from DSC analyses. The reason is that the inter-association equilibrium constant between DAT and T is *ca* 890 L mol<sup>-1</sup>, i.e. it is greater than the inter-association equilibrium constant between A and T (*ca* 530 L mol<sup>-1</sup>). In other words, the triple hydrogen bonding of DAT-T interactions is stronger than the double hydrogen bonding of A-T interactions. The stronger hydrogen bonding in the PS and PBMA main chains means a decrease of the mole percentages of the recognition units required to enhance the miscibility behavior.

## CONCLUSIONS

We have used free radical polymerization to synthesize nucleobase (VDAT and T)-functionalized random copolymers. Incorporating these multiple hydrogen bonding units into previously immiscible binary blends of PS and PBMA enhanced the miscibility as a result of the formation of supramolecular polymers. The miscibility of PS and PBMA was enhanced when the VDAT and VBT units were incorporated at quite low contents of 7 and 11 mol%, respectively, into the PS and PBMA main chains, respectively, because of the high degree of inter-association resulting from the formation of an associated VDAT-T phase. In addition, the triple hydrogen bonding of DAT-T interactions is stronger than the double hydrogen bonding of A-T interactions; thus stronger hydrogen bonding in the PS and PBMA main chains means a decrease of the mole percentages of the recognition units required to enhance the miscibility behavior. The PCAM predicted the miscibility behavior of this blend system quite well.

## ACKNOWLEDGEMENT

This work was supported financially by the National Science Council, Taiwan, Republic of China, under contract nos. NSC 97-2221-E-110-013-MY3 and NSC 97-2120-M-009-003.

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