

# Effects of Copolymer Composition and Free Volume Change on the Miscibility of Poly(styrene-*co*-vinylphenol) with Poly( $\epsilon$ -caprolactone)

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**ABSTRACT:** A series of poly(styrene-*co*-vinylphenol) (PSOH) copolymers were prepared and characterized. The miscibility and hydrogen bonding between the partially hydroxylated polystyrene with poly( $\epsilon$ -caprolactone) (PCL) blend were investigated by differential scanning calorimetry and Fourier transform infrared spectroscopy. The copolymers containing higher than 13 mol % vinylphenol were found to be fully miscible with PCL according to differential scanning calorimetry studies. Quantitative analyses on the fraction of hydrogen-bonded carbonyl groups in the solid state were made by FTIR spectroscopy, and good correlations between thermal behaviors and infrared results were observed. The critical vinylphenol content of 0.1 mol % in PSOH copolymer for the blend to be miscible was predicted from the Painter–Coleman association model and binary interaction model. The discrepancy between the experimental result and theoretical prediction is probably caused by significant free volume increase in this blend system, which is analyzed by the Kovacs' free volume theory. The free volume of the PSOH/PCL is increased which give a positive contribution in the Gibbs free energy. As a result, the polystyrene needs to incorporate more poly(vinylphenol) in PSOH copolymer in order to overcome the free energy increased caused by the free volume increase predicted by the Painter–Coleman association model and the binary interaction model.

## Introduction

There has been much interest in miscible polymer blends where one or both polymers are random copolymers.<sup>1–4</sup> Many studies have shown that several copolymer–homopolymer and copolymer–copolymer blends may be miscible in a certain range of compositions and temperatures even though the respective constituent homopolymers are pairwise immiscible, and no specific interaction exists between these blend systems due to the so-called “copolymer repulsion effect”.<sup>5,6</sup> The overall interaction energy in these blend systems can be obtained by the binary interaction model based on Flory–Huggins lattice theory which can predict the effect of the copolymer composition on these miscible blends.<sup>7</sup>

It is well-known that the polystyrene is immiscible with many polymers due to lack of functional group capable of interacting with other polymers. In general, the miscibility of an immiscible blend can be enhanced by introducing a functional group to one polymer capable of forming intermolecular association with other polymer.<sup>8</sup> In our previous study,<sup>9</sup> we have found that the incorporation of a small amount of hydrogen bond acceptor (such as acetoxystyrene) into the polystyrene main chain renders the modified polymer to be miscible with phenolic resin, a well-known hydrogen bond donor. The Painter–Coleman association model<sup>10</sup> is able to predict the miscibility of this blend system successfully.

In this study, we deal with blends of PCL and styrene/vinylphenol copolymers (PSOH) containing various vinylphenol contents. The specific interaction was investigated by using Fourier transform infrared spectroscopy. A minimum vinylphenol content in PSOH copoly-

mer required to make a blend miscible is predicted from the Painter–Coleman association model or the binary interaction model. The observed difference between the experimental result and the theoretical prediction is probably caused by the significant free volume change in this blend system, which is analyzed by Kovacs' free volume theory.<sup>11</sup>

## Experimental Section

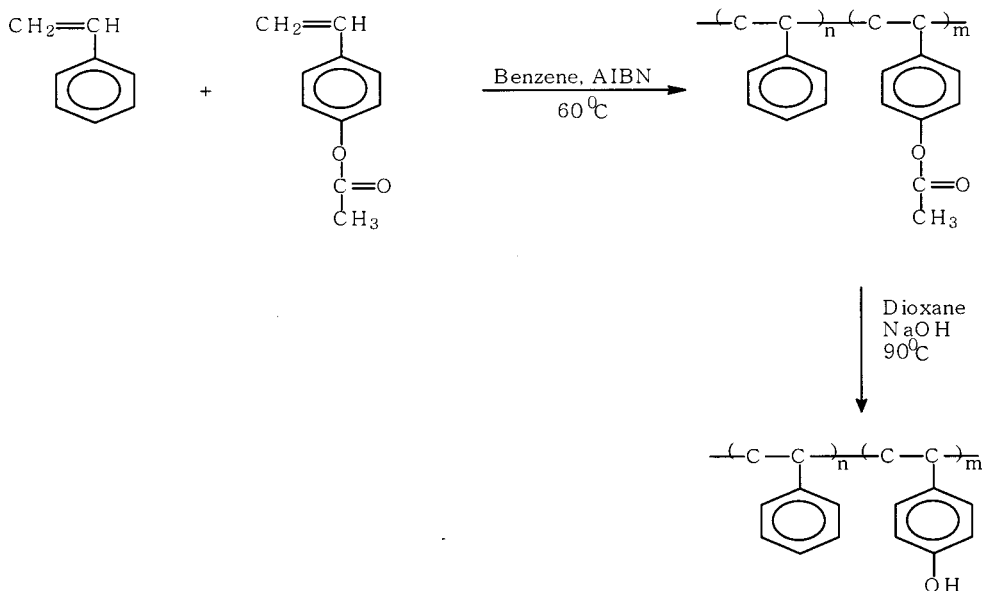
**A. Samples.** PCL used in this study is the TONE Polymer P-787 purchased from Union Carbide Corporation with  $M_n = 80\,000$ . It is difficult to synthesize poly(vinylphenol) by direct polymerization of vinylphenol due to the occurrence of side reactions involving the hydroxyl group during polymerization.<sup>12</sup> As a result, the poly(styrene-*co*-vinylphenol) copolymers were synthesized by copolymerization of styrene and acetoxystyrene. The monomer reactivity ratios of  $r_1$ (styrene) = 0.72 and  $r_2$ (acetoxystyrene) = 2.36 and various copolymers containing different contents of acetoxystyrene were obtained in our previous study.<sup>9</sup> The poly(styrene-*co*-acetoxystyrene) was dispersed in aqueous 1 N sodium hydroxide–dioxane mixture (10/100 wt %) and stirred for 4 h at 90 °C under a nitrogen atmosphere. The product was then poured into an excess hydrochloric acid solution under vigorously agitation to precipitate the PSOH copolymer, then filtered, and rinsed with water. The PSOH copolymer was dissolved in methanol and then precipitated from water. The same procedures were repeated twice to obtain the pure PSOH copolymer. The chemistry and structures are summarized in Scheme 1. The purified PSOH copolymers containing various vinylphenol contents were characterized by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC).

**B. Blend Preparation.** Polymer blend of PSOH/PCL = 50/50 was cast from the THF solution blending. The THF containing 5 wt % polymer mixture was stirred for 6–8 h, and the solution was allowed to evaporate slowly at room temperature for 1 day. The obtained film was then dried in a vacuum oven at 50 °C for 2 days.

**C. Characterizations. Differential Scanning Calorimetry.** Thermal analysis was carried out on a DSC instrument

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Scheme 1



from DuPont (model 910 DSC-9000 controller) with a scan rate of 20 °C/min and temperature range of 30–150 °C. Approximately 5–10 mg of each blend was weighted and sealed in an aluminum pan. This sample was quickly cooled to –100 °C from the melt for the first scan and then scanned between –100 and 180 °C at 20 °C/min. The glass transition temperature is taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines.

**Infrared Spectroscopy.** FTIR measurement was made using a Nicolet Avatar 320 FT-IR spectrophotometer, and 32 scans at a resolution of 1 cm<sup>-1</sup> were collected with a NaCl disk. The THF solution containing the blend was cast onto a NaCl disk and dried under condition similar to that used in the bulk preparation. The film used in this study was thin enough to obey the Beer–Lambert law. The sample chamber was purged with nitrogen in order to maintain the sample film dryness.

**Excess Volume.** The specific volume were determined at 298.15 K using a pycnometer calibrated with *n*-heptane. The excess volume is defined as

$$V_E = V - (w_a V_a^0 + w_b V_b^0) \quad (1)$$

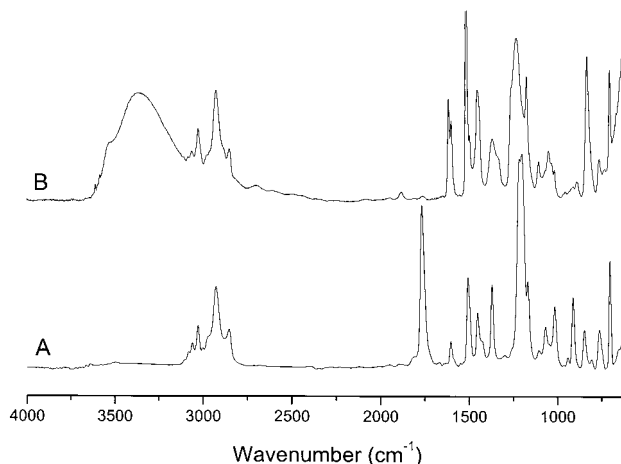
where  $w_i$  is the weight fraction of  $i$  component,  $V_i^0$  is the specific volume of the  $i$ th pure component, and  $V$  is the specific volume of the blend.

## Results and Discussion

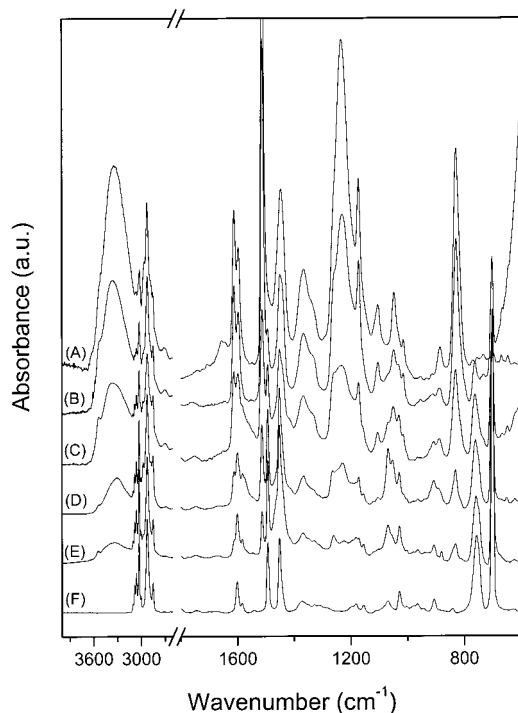
**Copolymer Analyses.** Figure 1 shows infrared spectra recorded at room temperature in the region from 600 to 4000 cm<sup>-1</sup> of the PSOH copolymer containing 29 mol % styrene before and after deacetylation. The carbonyl group absorption is at 1763 cm<sup>-1</sup>, which totally disappeared after deacetylation. The corresponding hydroxyl group of a broad absorbance between 3100 and 3700 cm<sup>-1</sup> can be clearly observed following the deacetylation. Figure 2 shows scale expanded infrared spectra at 2700–3800 and 600–1800 cm<sup>-1</sup> of polystyrene, PVPh, and four PSOH copolymers at room temperature. The band intensity of the hydroxyl stretching between 3100 and 3700 cm<sup>-1</sup> increases with the increase of the vinylphenol content in the PSOH copolymer as would be expected. We assume that the backbone structure and the vinylphenol content in the prepared PSOH copolymer are identical to the original poly(styrene-*co*-acetoxystyrene).<sup>9</sup> Figure 3 shows the

DSC curves of these PSOH copolymers from 70 to 180 °C. The glass transition temperature of the copolymer increases with the increase of the vinylphenol content in the PSOH copolymer, which obeys the simple Fox equation.<sup>13</sup>  $T_g$  and molecular weight of synthesized poly(styrene-*co*-vinylphenol) copolymers and PCL are summarized in Table 1. The numerical expression in brackets and in the symbols, i.e., 4PSOH, represents 4 mol % vinylphenol in the copolymers.

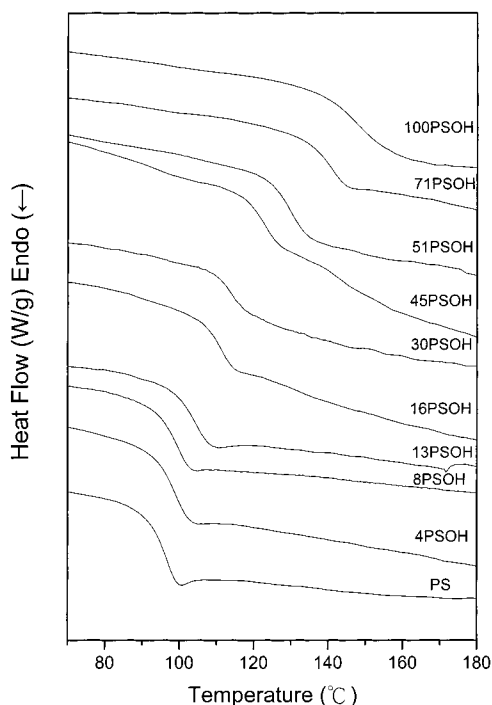
**Thermal Analyses.** A single  $T_g$  detected by DSC is the most conventionally employed criterion for the miscibility of a polymer blend. A single compositionally dependent glass transition implies full miscibility of the blend with a dimension on the order of 20–40 nm. Figure 4 shows DSC thermograms of PSOH/PCL = 50/50 blends where the PSOHs contain different vinylphenol contents, and data are summarized in Table 2. Blends of the PCL with PSOH containing 13 mol % and higher of the vinylphenol exhibit a single glass transition, an indication of complete miscibility. Table 2 also indicates that the blend containing 45 mol % of vinylphenol in the copolymer has the greatest ability to form a miscible blend because the melting temperature of PCL is absent. According to the Painter–Coleman association model,<sup>10</sup> two major factors are responsible



**Figure 1.** Comparison of FTIR spectra before (A) and after (B) deacetylation reaction.

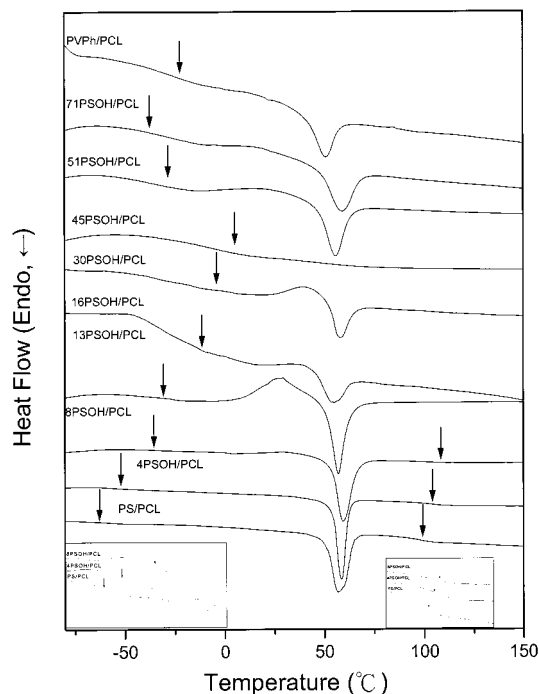


**Figure 2.** IR spectra at 3100–370 000 and 600–1800  $\text{cm}^{-1}$  regions for PSOH copolymers containing (A) 100, (B) 71, (C) 51, (D) 30, (E) 8, and (F) 0 mol % vinylphenol at room temperature.



**Figure 3.** DSC thermograms of pure PS, pure PVPh, and PSOH copolymers with different vinylphenol contents in mol %.

for the increase in the miscibility window. First, when the difference in the solubility parameters of the two blend components is lower, the corresponding  $\chi$  will also be low as well. However, the incorporation of poly(vinylphenol) ( $\delta = 10.6 \text{ cal/cm}^3$ ) into the polystyrene ( $\delta = 9.48 \text{ cal/cm}^3$ ) is expected to increase its solubility parameter difference with PCL ( $\delta = 9.21 \text{ cal/cm}^3$ ). Second, the strength of interassociation over self-as-



**Figure 4.** DSC curves of PSOH/PCL = 50/50 blends containing different vinylphenol contents in mol %.

**Table 1.**  $T_g$  and  $M_n$  of Polymers and Blend

polymer	aberration	$T_g$	$M_n$
poly( $\epsilon$ -caprolactone)	PCL	-60	80 000
poly(styrene)	PS	96.9	24 500
poly(styrene- <i>co</i> -vinylphenol [4])	4PSOH	99.2	21 600
poly(styrene- <i>co</i> -vinylphenol [8])	8PSOH	102.3	22 600
poly(styrene- <i>co</i> -vinylphenol [13])	13PSOH	104.3	28 760
poly(styrene- <i>co</i> -vinylphenol [16])	16PSOH	111.8	19 850
poly(styrene- <i>co</i> -vinylphenol [30])	30PSOH	113.8	26 000
poly(styrene- <i>co</i> -vinylphenol [45])	45PSOH	123.2	26 400
poly(styrene- <i>co</i> -vinylphenol [51])	51PSOH	129.9	25 400
poly(styrene- <i>co</i> -vinylphenol [71])	71PSOH	141.3	23 200
poly(vinylphenol)	PVPh	146.1	11 000

**Table 2.** Thermal Properties of PS-*co*-PVPh/PCL = 50/50 Blends

component	$T_g$ (°C)	$T_m$ (°C)	$\Delta H_f$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)
PCL	-62.3	60.9	77.7		
PS/PCL	-61.7, 100.1	57.5	26.2		
4PSOH/PCL	-56.4, 104.1	58.5	27.9		
8PSOH/PCL	-32.4, 107.1	59.4	25.9	27.8	3.2
13PSOH/PCL	-25.4	57.0	23.2	29.2	23.1
16PSOH/PCL	-9.7	54.4	2.2	37.1	0.3
30PSOH/PCL	-3.8	54.8	2.1		
45PSOH/PCL	0.3				
51PSOH/PCL	-18.9	55.7	15.1	18.3	4.7
71PSOH/PCL	-38.9	58.9	10.9	16.0	2.2
PVPh/PCL	-25.4	50.7	8.8		

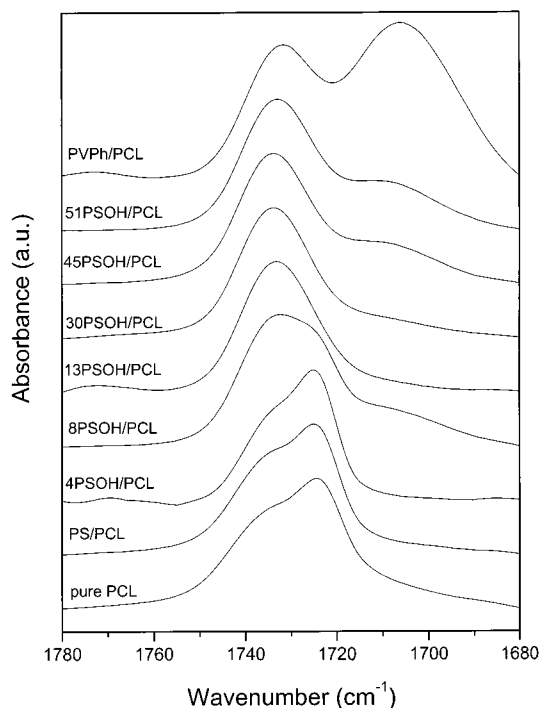
sociation will increase with the increase of the vinylphenol content in the PSOH copolymer that tends to enhance the favorable contribution from the  $\Delta G_H/RT$  term in the Painter–Coleman association model (see eq 3) and results in a favorable trend for miscibility. Therefore, an optimum vinylphenol content in the PSOH copolymer is expected to have the most favorable trend to form miscible blend due to the competition between these two adverse effects.

**FTIR Analyses.** FTIR spectroscopy has been successfully applied in polymer blends possessing intermolecular interaction through hydrogen bonding.<sup>14–17</sup> Figure 5 shows the infrared spectra measured at 25 °C

**Table 3. Curve-Fitting Results of PS-co-PVPh/PCL = 50/50 Blends at Room Temperature**

	free C=O			H-bonded C=O			
	$\nu$ , $\text{cm}^{-1}$	$W_{1/2}$ , $\text{cm}^{-1}$	$A_f$ , %	$\nu$ , $\text{cm}^{-1}$	$W_{1/2}$ , $\text{cm}^{-1}$	$A_b$ , %	fb, % <sup>a</sup>
13PSOH/PCL	1733.3	15.2	80.8	1711.6	26.0	19.2	13.62
30PSOH/PCL	1734.0	15.5	80.0	1712.4	24.5	20.0	14.24
45PSOH/PCL	1734.1	15.6	69.0	1710.0	21.9	31.0	23.02
51PSOH/PCL	1733.3	15.3	65.3	1709.4	21.7	34.7	26.15
PVPh/PCL	1732.6	14.5	34.7	1705.8	21.8	65.3	55.63

<sup>a</sup> fb: fraction of hydrogen bonding.

**Figure 5.** IR spectra at 1680–1780  $\text{cm}^{-1}$  of PSOH/PCL = 50/50 blends containing different vinylphenol contents.

ranging from 1680 to 1780  $\text{cm}^{-1}$  for various PSOH/PCL = 50/50 blends containing different vinylphenol contents in PSOH copolymers. The carbonyl stretching for the pure PCL is split into two bands: absorptions by the amorphous and the crystalline conformations at 1734 and 1724  $\text{cm}^{-1}$ , respectively. Another band appearing at approximately 1708  $\text{cm}^{-1}$  is assigned to the PCL carbonyl group that is hydrogen bonded to the vinylphenol hydroxyl group. The crystalline conformation at 1724  $\text{cm}^{-1}$  is disappeared from the 13PSOH/PCL = 50/50 composition, showing the same miscibility trend as the DSC analyses. In general, the polymer crystallinity measured by FTIR is from the in-situ measurement because no thermal history is involved for the prepared sample. On the contrary, the polymer crystallinity detected by DSC depends on the thermal history because the recrystallization may occur during cooling or heating scan. As a result, we confirm that the copolymer containing higher than 13 mol % vinylphenol are miscible with PCL on the basis of DSC and FTIR studies. The carbonyl stretching frequency splits into only two bands at 1734 and 1708  $\text{cm}^{-1}$ , corresponding to the free and the hydrogen-bonded carbonyl groups, which can be fitted well to the Gaussian function. The fraction of the hydrogen-bonded carbonyl group can be calculated by eq 2:<sup>10</sup>

$$f_b^{\text{C=O}} = \frac{A_b/1.5}{A_b/1.5 + A_f} \quad (2)$$

**Table 4. Parameters for Estimating the Critical Composition of Homopolymer–Copolymer Blend by Using the Painter–Coleman Equation**

	$K$ (25 °C)	$\Delta H$ (kcal/mol)
self-association <sup>a</sup>		
dimer formation $K_2$	21.0	-5.6
multimer formation $K_B$	66.8	-5.2
interassociation between PVPh and PCL <sup>a</sup>	66.2	-4.3

polymer	mol vol (mL/mol)	mol wt (g/mol)	solubility (cal/mL) <sup>0.5</sup>	DP
PVPh <sup>b</sup>	100	120.1	10.6	100
PS <sup>b</sup>	93.9	104.1	9.48	100
PCL <sup>b</sup>	102.1	114.1	9.21	714

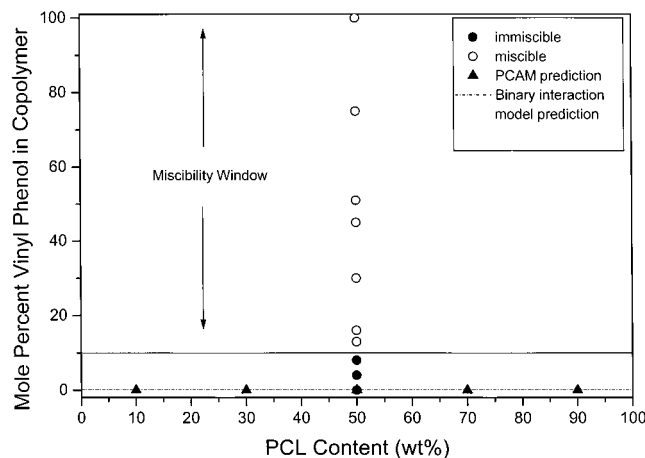
<sup>a</sup> Reference 10. <sup>b</sup> Estimated by using a group contribution method proposed by Coleman et al.<sup>10</sup>

$A_b$  and  $A_f$  denote peak areas corresponding to the free and the hydrogen-bonded carbonyl groups, respectively. The conversion coefficient 1.5 is the ratio of these two bands according to previous infrared studies in a similar system.<sup>10</sup> The results from curve fitting are summarized in Table 3, indicating that the hydrogen-bonded fraction of the carbonyl group increases with the increase of the vinylphenol content in PSOH copolymers. For blends containing lower vinylphenol contents (8% and less) at room temperature, the absorption of the hydrogen-bonded carbonyl (1708  $\text{cm}^{-1}$ ) is interfered by absorption of the PCL crystalline phase (1724  $\text{cm}^{-1}$ ) and is difficult to be estimated precisely.

**Painter–Coleman Association Model (PCAM) and Binary Interaction Model Analyses.** Painter and Coleman<sup>10</sup> suggested adding an additional term accounting for the free energy of the hydrogen-bonding formation into a simple Flory–Huggins expression for the free energy of mixing of two polymers as eq 3:

$$\frac{\Delta G_N}{RT} = \frac{\Phi_1}{N_1} \ln \Phi_1 + \frac{\Phi_2}{N_2} \ln \Phi_2 + \Phi_1 \Phi_2 \chi_{12} + \frac{\Delta G_H}{RT} \quad (3)$$

where  $\Phi$  is the volume fraction,  $N$  is the degree of polymerization,  $\chi$  is the “physical” interaction parameter, and subscripts 1 and 2 refer to the blend components.  $\Delta G_H$  is the free energy change contributed by the hydrogen bonding between two components, which can be estimated by FTIR.<sup>18</sup> This equation ignores the free volume change and other complications.<sup>19–21</sup> All parameters required to estimate the miscibility window for a homopolymer–copolymer blend by the Painter–Coleman association model are listed in Table 4. The calculation has been made using the Miscibility Guide & Phase Calculator (MG&PC) software package. Figure 6 shows the theoretical predicted and experimental miscibility window for PSOH/PCL = 50/50 blends at



**Figure 6.** Theoretical miscibility window of PSOH/PCL blends from the Painter–Coleman association model (▲) binodal curve, binary interaction model (---), and experimental data (●) two-phase system, (○) one-phase system.

room temperature by the PCAM where blends of PS/PCL are immiscible at all compositions.

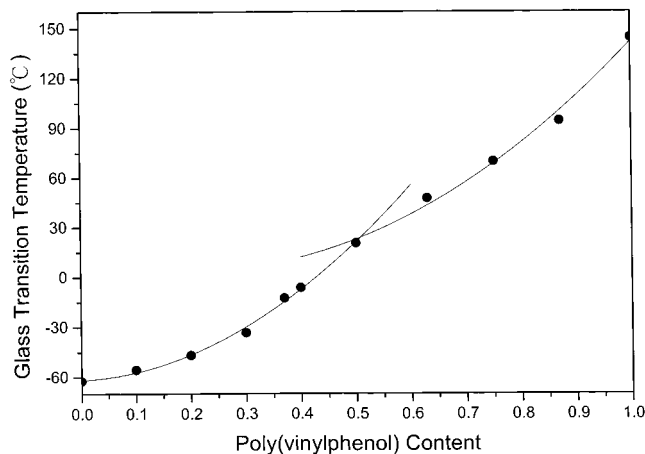
Now, we turn our attention to the application of the binary interaction model. The miscibility of copolymer/homopolymer system has been analyzed by several research groups by the binary interaction model. The enthalpy of mixing is usually responsible for the miscibility because the contribution from the entropy changes for a polymer blend is usually insignificant. For a binary mixture of homopolymer A with a  $C_yD_{1-y}$  copolymer, the expression for the enthalpy of mixing is given by eq 4:

$$\frac{\Delta H_M}{V} = B\Phi_1\Phi_2 \quad (4)$$

$V$  is the total volume of mixture,  $\Phi_1$  and  $\Phi_2$  are their respective volume fractions, and  $y$  is the molar fraction of component C in copolymer. The  $B$  value in eq 4 can be expressed as

$$B = yB_{AC} + (1 - y)B_{AD} - y(1 - y)B_{CD} \quad (5)$$

The interaction parameter  $B$  has to be negative for a polymer blend to be miscible. Therefore, the miscibility of a blend containing a copolymer depends on the segmental  $B_{ij}$  values and the copolymer compositions as shown in eq 5. According to the binary interaction model, we designate A, C, and D as PCL, poly(vinylphenol), and polystyrene units, respectively. It has been recognized that  $B_{AC}$  is negative while  $B_{AD}$  and  $B_{CD}$  are both positive. The value of  $B_{AC} = -9.82 \text{ cal/cm}^3$  was determined by our previous study,<sup>22</sup> while values of  $B_{AD}$  and  $B_{CD}$  are estimated from the solubility parameter of these two polymers using group contribution method<sup>10</sup> to be 0.07 and 1.25  $\text{cal/cm}^3$ , respectively. The poly(vinylphenol) is miscible with PCL due to the formation of interassociation hydrogen bonding between the hydroxyl group of PVPh and the carbonyl group of PCL. Positive values of  $B_{AD}$  and  $B_{CD}$  indicate that blends of PCL/PS and PVPh/PS are both immiscible. A critical vinylphenol content in the PSOH copolymer can be estimated from the binary interaction model by assuming zero enthalpy of mixing of the blend. The  $y$  in eq 5 can be solved by assuming  $B = 0$ , and the obtained  $y$



**Figure 7.** Composition dependence of the glass transition temperature for the PVPh/PCL blends.

value is approximately 0.1 mol %. This result is very close to the Painter–Coleman association model prediction. However, the experimental data show that the blend of PCL with PSOH containing 13 mol % of vinylphenol and higher exhibit a single glass transition, an indication of total miscibility. While blends containing 8 mol % and less of vinylphenol in PSOH copolymer give two  $T_g$ 's (Table 2), implying immiscibility of these blends.

The difference between the experimental results and the theoretical prediction by either the Painter–Coleman association model or the binary interaction model is probably caused by the significant free volume change in this blend system. It is well-known that the free energy of mixing of two polymers consist of three contributions: the combinatorial of mixing, the intermolecular interaction, and free volume effect.<sup>23</sup> However, the Painter–Coleman association model and the binary interaction model ignore the contribution by the free volume change mentioned above.

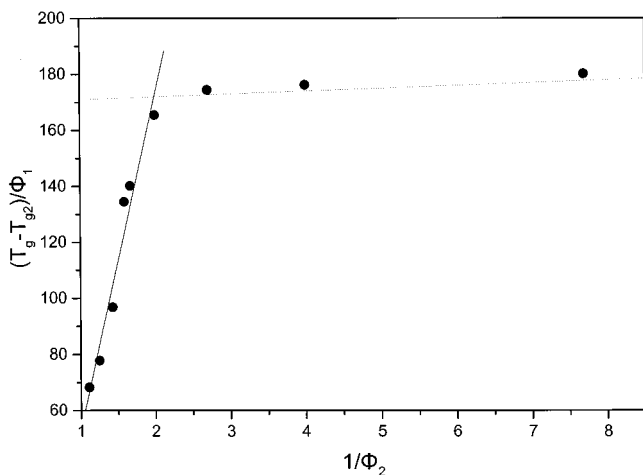
**Kovacs' Free Volume Theory Analyses.** In this study, we simplify the qualitative analysis the free volume change in this blend system by following Kovacs' free volume theory.<sup>11</sup> We take the poly(vinylphenol)/PCL blend system to calculate the free volume change between the hydroxyl group of PVPh and the carbonyl group of PCL. Figure 7 shows the  $T_g$ –composition curve as a function of the volume fraction of the PVPh. According to the free volume theory of Kovacs, the free volume term can be expressed by the following equation

$$f = \Phi_1 f_1 + \Phi_2 f_2 - V_e/V \quad (6)$$

where  $f$  is the free volume of the blend and  $f_i$  and  $\Phi_i$  are the free volume and the volume fraction of component  $i$ .  $V$  is the total volume of the blend,  $V_e$  is the excess volume (eq 1), and the  $V_e/V$  term is usually related to an interaction term  $g$  by means of

$$\frac{V_e}{V} = g\Phi_1\Phi_2 \quad (7)$$

According to Kovacs' free volume theory,<sup>11</sup> if the  $T_g$  difference ( $T_{g1} - T_{g2}$ ) between blend components 1 and 2 is higher than 50 °C, there is a critical temperature ( $T_c$ ) at which the free volume of the polymer with higher glass transition temperature becomes zero, and the



**Figure 8.** Analysis of the experimental data for PVPh/PCL blends according to Kovacs' free volume theory.

corresponding critical volume fraction ( $\Phi_c$ ) calculated by Kovacs is

$$T_{\text{crit}} = T_{g1} - \frac{f_{g1}}{\Delta\alpha_1} \quad (8)$$

$$\Phi_c = f_{g1} \left[ \Delta\alpha_2 (T_{g1} - T_{g2}) + f_{g1} \left( 1 - \frac{\Delta\alpha_1}{\Delta\alpha_2} \right) \right] \quad (9)$$

Below  $T_c$ , Kovacs has shown that the  $T_g$  of the blend is given by

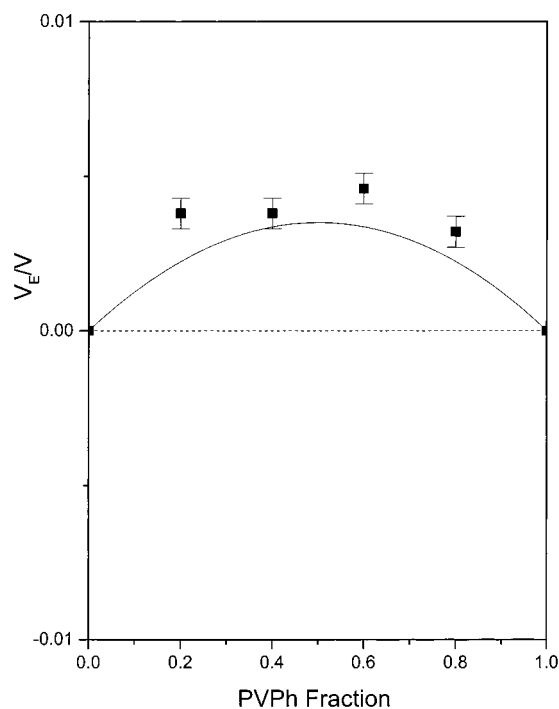
$$T_g = T_{g2} + \frac{\Phi_1 f_{g1} + g \Phi_1 \Phi_2}{\Phi_2 \Delta\alpha_2} \quad (10)$$

where  $f_{g1}$  is the fractional free volume of component 1 at  $T_{g1}$  and  $\Delta\alpha_i$  is the difference between the volume expansion coefficients in the liquid and glassy state. To analyze the experimental data in terms of eq 10, it can be rearranged to

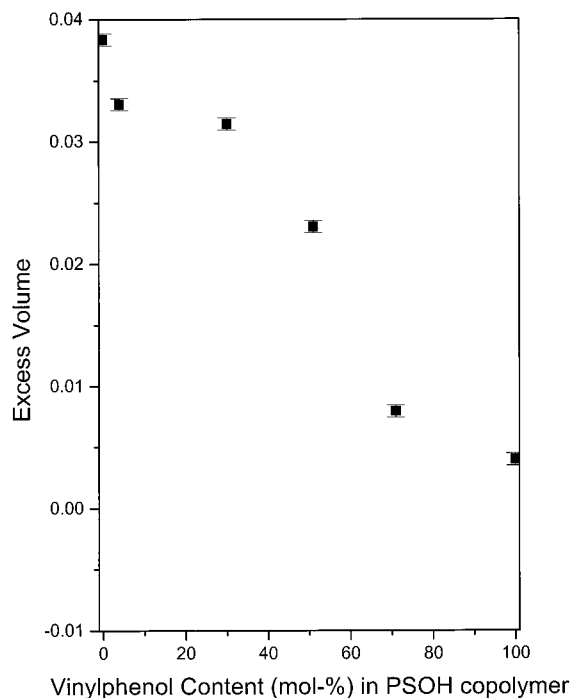
$$\frac{T_g - T_{g2}}{\Phi_1} = \frac{g}{\Delta\alpha_2} + \frac{f_{g1}}{\Delta\alpha_2} \frac{1}{\Phi_2} \quad (11)$$

Therefore, the  $f_{g1}/\Delta\alpha_2$  can be calculated by a plot of  $(T_g - T_{g2})/\Phi_1$  vs  $1/\Phi_2$  from its slope and the  $g/\Delta\alpha_2$  from its intercept. Analysis of the experimental data for  $T < T_c$  can be made following this theory by using eq 11 as shown in Figure 8.  $\Delta\alpha_2$  and  $g$  can be obtained by using the classical value of 0.025 for  $f_{g1}$ , so that  $\Delta\alpha_2$  and  $g$  are obtained as  $2.1 \times 10^{-4}$  and  $-0.014$ , respectively.

The  $T_c$  and  $\Phi_c$  given by eqs 8 and 9 are 22 °C and 0.50 (PVPh), respectively. As a result, the negative value of Kovacs  $g$  parameter ( $-0.014$ ) is obtained which tends to increase the free volume of the blend from eq 6. The experimental and predicted excess volumes are shown in Figure 9, indicating that the average distance of intermolecular hydrogen-bonding distance increases. This result reveals that the increase of free volume contributes a positive value in Gibbs free energy. Figure 10 shows the excess volume vs vinylphenol content in PSOH copolymer, indicating that the lower vinylphenol content has a larger excess volume due to relative weaker hydrogen-bonding strength in this blend system. Iriarte et al.<sup>24</sup> have also proposed that the effect of the free volume term for weaker hydrogen bonding play an important role in the Gibbs free energy. Therefore, the



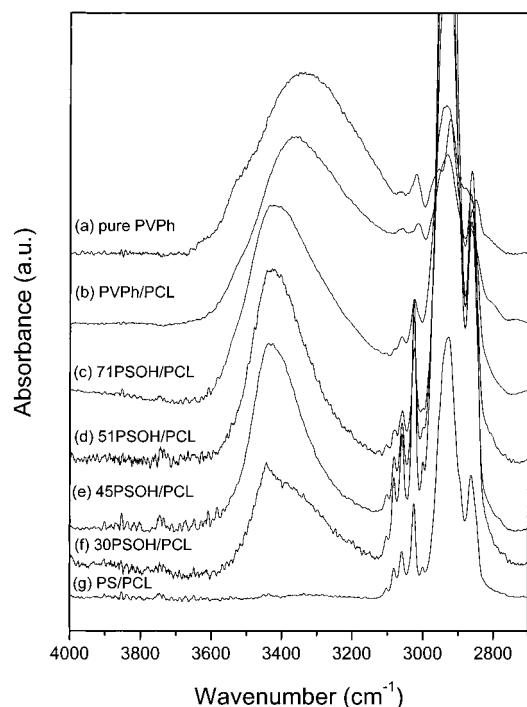
**Figure 9.** Excess volume of mixing for PVPh/PCL at 298.15 K: (■) experimental result and (—) predicted by Kovacs' free volume theory.



**Figure 10.** Excess volume vs the different vinylphenol content in PSOH copolymer.

polystyrene needs to incorporate more poly(vinylphenol) in PSOH copolymer to increase the  $\Delta G_{\text{H}}$  term (eq 3) to offset the free energy increase caused by the free volume increase.

IR spectra for these blends were measured at room temperature, and the results support this claim. A comprehensive understanding of the change occurring in the hydroxy stretching region is important to the phase behavior of polymer blends. Therefore, we now turn our attention to the hydroxy stretching region in IR spectra. Figure 11 shows the absorption region



**Figure 11.** IR spectra at 2700–4000  $\text{cm}^{-1}$  of pure PVPh and PSOH/PCL = 50/50 blends containing different vinylphenol contents: (a) pure PVPh, (b) PVPh/PCL, (c) 71PSOH/PCL, (d) 51PSOH/PCL, (e) 45PSOH/PCL, (f) 30PSOH/PCL, and (g) PS/PCL.

between 2700 and 4000  $\text{cm}^{-1}$  of the pure PVPh and various PSOH/PCL = 50/50 blends. As shown in Figure 11a, the pure PVPh polymer exhibits two bands in the hydroxy stretching region of the infrared spectrum. The free hydroxyl group absorption is located at 3525  $\text{cm}^{-1}$ , while the hydrogen-bonded hydroxyl gives a broad absorption at 3350  $\text{cm}^{-1}$  due to wide distribution of hydrogen-bonded hydroxyl groups. As also shown in Figure 11, the intensity of the free hydroxyl group (3525  $\text{cm}^{-1}$ ) decreases with increase of PCL in this blend system. In addition, the self-association band of the hydroxyl group of the PSOH copolymer shifts into higher frequency with the decrease of the vinylphenol content. The average strength of the intermolecular interaction can be estimated on the basis of the extent of frequency difference ( $\Delta\nu$ ) between the hydrogen-bonded hydroxyl absorption and free hydroxyl absorption.<sup>25</sup> Consequently, the average strength of interassociation decreases with the decrease of the vinylphenol content in PSOH copolymers, resulting in the free volume increase in this blend system.

### Conclusions

Blends of PCL with a series of PSOH copolymers containing various vinylphenol contents were prepared and studied. The incorporation of vinylphenol monomer into the polystyrene main chain is able to enhance its miscibility with PCL due to the increase of interassociation between the hydroxyl group in PSOH copolymers and the carbonyl group in PCL. However, the incorporation of poly(vinylphenol) into polystyrene tends to increase the solubility parameter difference with PCL

and thus decrease its miscibility. Compromising these two adverse effects, an optimum vinylphenol content in PSOH copolymer (45PSOH) exists to give the maximum miscibility of the blend.

Experimental results show that the vinylphenol content of 13 mol % or higher in the PSOH is required to make the PSOH/PCL blend miscible. The minimum vinylphenol content in PSOH copolymer for the blend to be miscible predicted by the Painter–Coleman association model and the binary interaction model is significantly lower at 0.1 mol %. The discrepancy between the experimental result and theoretical prediction is probably caused by significant free volume increase in this blend system. On the basis of Kovacs' free volume theory, the free volume of the PVPh/PCL is increased, which gives a positive contribution in the Gibbs free energy. Therefore, the polystyrene needs to incorporate more poly(vinylphenol) in PSOH copolymer in order to overcome the free energy increase caused by the free volume increase predicted by the Painter–Coleman association model and the binary interaction model.

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