

CO₂ Gas Sorption Properties in Single-Phase and Phase-Separated Polystyrene/Poly(vinylmethylether) Blends

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ABSTRACT: To elucidate the mechanism of gas sorption in polymer blends in glassy and rubbery states, CO₂ sorption of polystyrene [PS] ($T_g = 75^\circ\text{C}$), poly(vinylmethylether) [PVME] ($T_g = -26^\circ\text{C}$), and their blends was studied at 25°C and the influence of the single-phase or separated-phase of their blends on sorption properties was also investigated. The solubility in the rubbery polymer blends obeyed Henry's law and that in the glassy blends were described well by the dual-mode sorption model which consists of two contributions of Henry's law mode and Langmuir mode sorption applied often to glassy polymer-gas systems. The dual-mode sorption parameters were obtained by a curve fitting of experimental data to the theoretical curve. The value of Henry's law constant k_D of the single-phase polymer blends deviated negatively from semilogarithmic additivity. The k_D of the phase-separated blends was slightly higher than that of single-phase blends and was smaller than the semilogarithmic additivity, reflecting that the single-phase blends did not separate completely to the pure polymer phases of PS and PVME but to two mixed phases. The Langmuir sorption capacity term C_H' of single-phase or phase-separated blends was proportional to ($T_g - 25^\circ\text{C}$) of each phase, irrespective of the single-phase or separated-phase and the C_H' became zero at the temperature above the T_g .

KEY WORDS Polymer Blend / Single-Phase / Phase-Separation / Dual Sorption / Langmuir Sorption Capacity Term / Henry's Law Constant / CO₂ Gas Sorption / Polystyrene / Poly(vinylmethylether) /

It is expected to develop new high performance materials by physical blending of two or more existing polymers since the list of new concepts in polymer synthesis has not been exhausted. The miscibility and phase behavior of the polymer blends have fundamentally been studied and a great number of reviews and books with respect to the polymer blends have been published recently.¹⁻⁶ The gas sorption and transport properties in and through polymer blends have been also subjects of study to develop new transport membrane materials and interpret the phase behavior of polymer blends.⁷⁻¹² One can use a penetrant as a probe to investigate the phase behavior of blends.

Paul *et al.* have reported some basis associated with sorption and transport in homogeneous mixtures in relation to the characteristics of an individual component.⁷⁻¹¹ Namely, they found that gas solubility, diffusivity, and permeability in single-phase polymer blends displayed a negative deviation from their semilogarithmic additive rule and suggested characteristic parameters representing the state of a polymer blend.

Gas sorption behavior depends on whether polymers are glassy or rubbery at observation temperature. It is interesting to investigate the influence of blending of glassy and rubbery polymers on sorption properties and the con-

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tribution of a phase structure to the solubility.

In this study, we report the influence of the single-phase on CO₂ sorption properties of polymer blends which consist of polystyrene [PS] as a glassy polymer and poly(vinylmethylether) [PVME] as a rubbery one. This blend system is known to exhibit a lower critical solution temperature (LCST),^{3,13-15} and phase separation behavior by annealing above a phase separation temperature.^{3,14,15} However, a systematic study of sorption properties for polymer blends in single-phase and separated-phase has been scarcely reported. The approaches on this subjects are to discuss the various sorption parameters for CO₂ of the glassy and rubbery PS/PVME blends in single-phase and separated-phase by applying Henry's law and the dual-mode sorption model, respectively.

EXPERIMENTAL

Materials

The PS was supplied kindly from Tosoh Corporation. The weight-average molecular weight (M_w) and molecular weight dispersity (M_w/M_n) of PS are 1.02×10^5 and 1.02, and those of PVME are 6.8×10^4 and 2.2, respectively. PVME (Tokyo Kasei Industrial Co. Ltd.) was dissolved at 30 wt% in pure water and purified by removing a supernatant solution, which contains a lower molecular weight component and impurity, obtained by a phase separation due to annealing at 40°C.

PS/PVME blends with compositions of 75/25, 50/50, and 20/80 were completely dissolved at 5 wt% of total polymer in toluene and were prepared by casting on a petri dish at room temperature. The blend films obtained were transparent reflecting a single-phase. On the other hand, the phase-separated blends were prepared by the following procedure: single-phase blends having various compositions were maintained at temperature above the phase separation temperature, which is 125, 110, and 120°C for PS/PVME = 75/25,

50/50, and 20/80, respectively, for 30 min and were quenched by liquid N₂ to freeze their phase separated structures. The films obtained became turbid reflecting phase-separated states. These films obtained were dried completely under vacuum below 10^{-3} mmHg before various measurements.

CO₂ used for the sorption measurement was at least greater than 99.9% purity and used without further purification.

Methods

The glass transition temperature (T_g) was measured by a differential scanning calorimeter (DSC) [type SSC 560, Seiko Electronics Co., Ltd.] at a heating rate of 15°C min⁻¹ from -140°C to 140°C in nitrogen atmosphere. The onset temperature of the transition from the heat capacity of the glassy state to that of rubbery state was taken as T_g as indicated by the cross point shown by a dotted line in the DSC thermogram.

Sorption measurement was carried out using gravimetric sorption apparatus with an electromicrobalance 2000 (Cahn Instruments, Inc.). After sufficient drying of the films under about 10^{-4} mmHg, the net amount of gas sorbed in a film under a fixed pressure was corrected subtracting the buoyancy contribution.

RESULTS AND DISCUSSION

Phase Behavior

Various PV/PVME blend films cast from toluene solution were transparent and their DSC thermograms showed that each blend film had a single T_g located between T_g 's of homopolymers, PS and PVME as shown in Figure 1(a)–(c). Their T_g 's are tabulated in Table I. On the other hand, DSC thermograms of the phase-separated PS/PVME blends showed that each blend film had two T_g 's as a result of the phase separation as shown in Figure 1(a)–(c). The two T_g 's obtained by phase separation did not correspond to the T_g

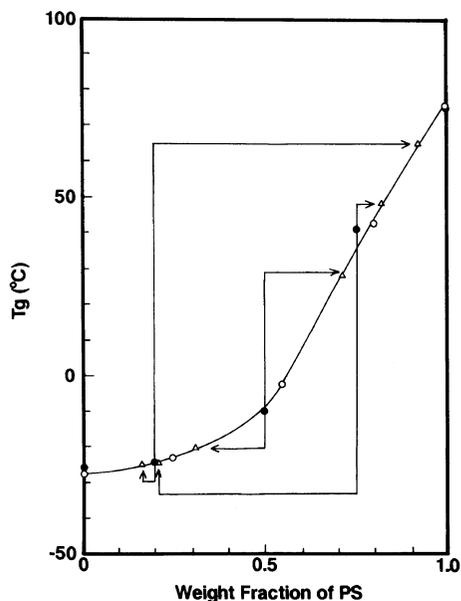
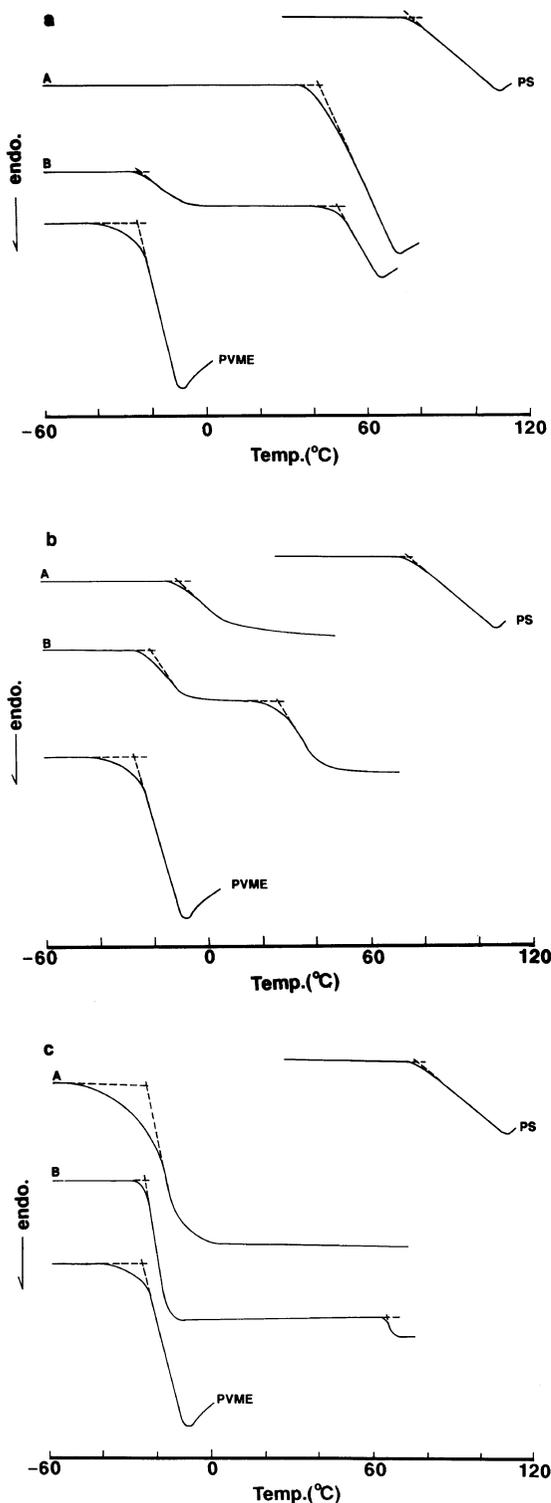


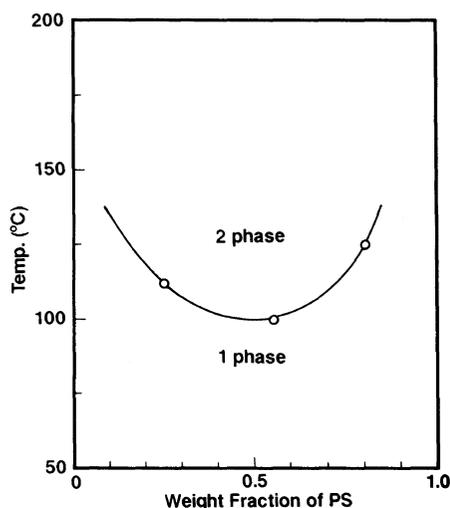
Figure 2. Glass transition temperature (T_g) of single-phase and phase-separated PS/PVME blends with various compositions as a function of weight fraction of PS: \circ , T_g with single-phase PS/PVME blends determined by dilatometry¹³; \bullet , T_g of single-phase PS/PVME blends determined by DSC measurement; Δ , two T_g 's of phase-separated PS/PVME blends determined by DSC measurements.

of an individual homopolymer and were located between T_g 's of homopolymers. This behavior suggest two mixed phases. The T_g 's measured by DSC and dilatometry¹³ are plotted against weight fraction of PS in Figure 2. The T_g 's obtained by two different methods showed good agreement. The two compositions in the phase-separated blends were determined using both T_g 's of two separated phase (Δ) obtained by DSC measurement and the experimental smoothed curve in Figure 2 and are tabulated in Table I with their T_g 's. This method is also supported by a phase diagram. Figure 3 shows the phase diagram based on the dilatometry of a PS/PVME blend system studied earlier.¹³

Figure 1. DSC thermograms of homopolymer (PS and PVME), single-phase (A) and phase-separated (B) PS/PVME blends with various compositions: (a) PS/PVME = 75/25; (b) PS/PVME = 50/50; (c) PS/PVME = 20/80.

Table I. Dual-mode sorption parameters of various single-phase and phase-separated PS/PVME blend membranes

Sample	T_g	C_H'	$b \times 10^3$	$k_D \times 10^2$
	°C	cm ³ cm ⁻³ polym.	cmHg ⁻¹	cm ³ cm ⁻³ polym. cmHg
PS	74.8	4.1	2.36	1.12
75/25 (single-phase)	41.8	1.5	1.45	1.41
75/25 ————— (phase-separated)	83/17	48.0	2.4	2.76
	21/79	-24.0	—	—
50/50 (single-phase)	-10.3	—	—	2.01
50/50 ————— (phase-separated)	73/27	28.0	0.4	4.73
	31/69	-20.0	—	—
20/80 (single-phase)	-24.6	—	—	2.62
20/80 ————— (phase-separated)	74/26	35.4	1.1	3.95
	19/81	-25.2	—	—
PVME	-26.0	—	—	4.00

**Figure 3.** Phase diagram of PS/PVME blend observed by dilatometry.¹³

This phase diagram exhibiting a typical LCST is reasonable.^{3,14,15} This diagram was also used to determine two compositions and their weight fractions of phase-separated blends and to compare the results of dilatometry. The two compositions obtained by DSC agreed very closely with those predicted by the phase

diagram.

Sorption Properties

CO₂ sorption isotherms of rubbery polymer blend films were linear against pressure, whereas the isotherms of glassy polymer blends were nonlinear. This behavior was successfully analyzed by the dual-mode sorption model¹⁶⁻¹⁸ described by

$$C = k_D p + \frac{C_H' b p}{1 + b p} \quad (1)$$

where k_D is Henry's law constant, C_H' is the Langmuir capacity term related to the unrelaxed volume in the glassy state,¹⁹⁻²¹ b is the affinity constant of Langmuir site, and p is the pressure of the penetrant. One can evaluate dual mode sorption parameters by using isotherm data and eq 1 by the non-linear least square method.

Figure 4 shows the CO₂ sorption isotherms in PS and PVME at 25°C. The sorption isotherm of PS had the characteristic shape expected for glassy polymers and was well described by the dual-mode sorption model expressed in eq 1 because PS is in the glassy state

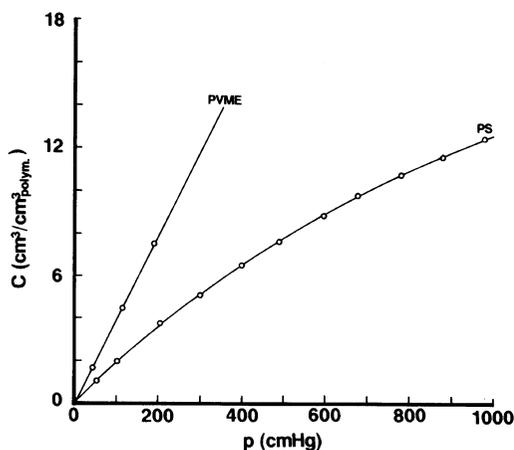


Figure 4. CO₂ sorption isotherms of PS and PVME films at 25°C.

at 25°C. On the other hand, the sorption isotherm of PVME obeyed Henry's law reflecting a rubbery state and the sorption amount increased linearly with pressure. As the k_D of PVME was larger than that of PS, it is expected that the k_D of the blends increases with increasing PVME composition.

Figure 5(a)–(c) shows the CO₂ sorption isotherms in single-phase PS/PVME blends of various compositions. A straight line obeying Henry's law was observed for the rubbery PS/PVME blend films, PS/PVME = 50/50 and 20/80, while a slightly convex curve against pressure was seen for the glassy one, PS/PVME = 75/25. The various sorption parameters obtained by applying eq 1 and Henry's law are tabulated in Table I. The k_D increased and the C_H' decreased with increasing weight fraction of PVME.

The CO₂ sorption amount was enhanced with increasing weight fraction of PVME which has higher k_D . However, in the lower pressure range, the CO₂ sorption amount of the single-phase blends, PS/PVME = 75/25 and 50/50, was smaller than that of PS in spite of the increase of PVME composition. This behavior can be attributed to the fact that the C_H' and b contribute remarkably to the sorption amount at lower pressure range as expect-

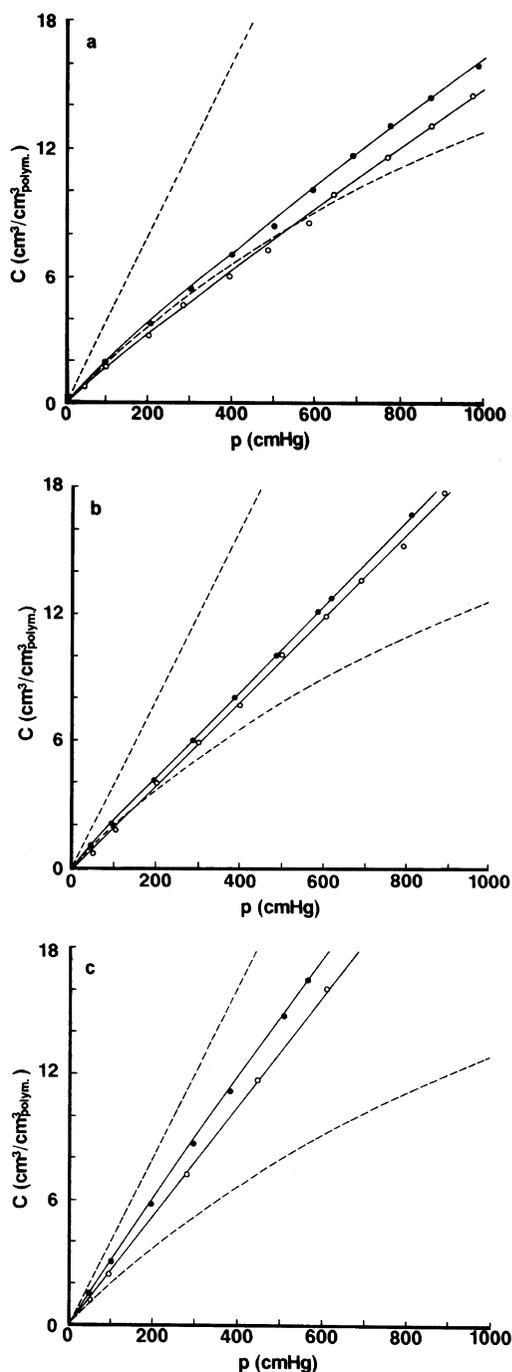


Figure 5. CO₂ sorption isotherms of single-phase (○) and phase-separated (●) PS/PVME blend films with various compositions at 25°C: (a) PS/PVME = 75/25; (b) PS/PVME = 50/50; (c) PS/PVME = 20/80. Dashed lines are the isotherms of PS (lower) and PVME (upper).

ed by the dual-mode sorption model. Namely, the sorption amount of PS at lower pressure range is larger than that of two blends (75/25 and 50/50) owing to larger $C_H'b$ of PS though the k_D of PS is lower than that of two blends as shown in Table I.

On the other hand, the sorption isotherms of the phase-separated PS/PVME blends were observed as slightly convex curves against pressure because one of two phases is in the glassy state as shown in Figure 5(a)–(b). But the C_H' in the phase-separated blends is corrected by the volume fraction in the glassy state obtained from the phase diagram in Figure 3. The sorption amounts of various phase-separated blends were larger than those of single-phase blends over the entire pressure range. This behavior can be attributed to the solubility of the PVME rich phase.

Next, the logarithm of k_D for various single-phase PS/PVME blends were plotted as a function of weight fraction of PS as shown in Figure 6. The k_D of the single-phase blends deviated negatively from the semilogarithmic additivity and that of the phase-separated blends was slightly higher than that of single-

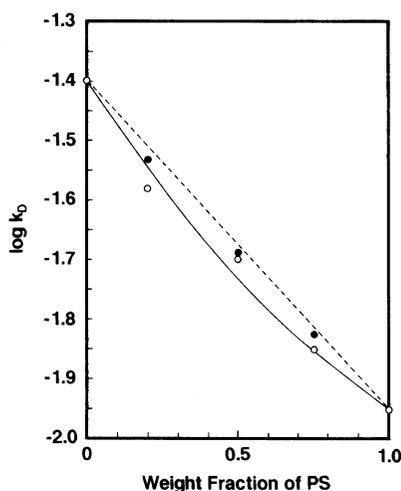


Figure 6. Henry's law constant (k_D) for CO₂ of single-phase (○) and phase-separated (●) PS/PVME blends films with various compositions as a function of weight fraction of PS at 25°C. Solid line is calculated curve fit to eq 7.

phase blends and was smaller than semilogarithmic additivity. Such behavior of a single-phase blend can be analysed according to the following rule.

A mixture rule of k_D of polymer blend system can be developed from Flory–Huggins theory for ternary system.^{3,7} Flory–Huggins theory gives the following expression for the activity of component 1, penetrant probe molecule (CO₂), in polymer p

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) + \chi_{1p}(1 - \phi_1)^2 \quad (2)$$

where a_1 is the activity of penetrant probe, ϕ_1 is the volume fraction of component 1, and χ_{1p} is the interaction parameter between component 1 and polymer p . An analogous expression for the activity of penetrant probe 1 in the blend of polymers 2 and 3 is expressed by following equation.

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(1 - \phi_1) - \chi'_{23}\phi_2\phi_3 \quad (3)$$

where

$$\chi'_{23} = (V_1/V_2)\chi_{23} = (V_1/V_3)\chi_{32} \quad (4)$$

V_i is the molar volume of component i , ϕ_i is the volume fraction of component i , and χ_{ij} is the interaction parameter between components i and j . By treating the blend as a pseudo-single component, the interaction parameter between component 1 and the blend b is

$$\chi_{1b} = \chi_{12}\phi_{20} + \chi_{13}\phi_{30} - \chi'_{23}\phi_{20}\phi_{30} \quad (5)$$

where $\phi_{20} + \phi_{30} = 1$. In the limit of $\phi_1 \rightarrow 0$, ϕ_1/a_1 becomes proportional to the k_{D1} defined by Henry's law ($\phi_1 = k_{D1}a_1$) and eq 5 is reduced to

$$\ln k_{D1b} = \phi_{20} \ln k_{D12} + \phi_{30} \ln k_{D13} + \phi_{20}\phi_{30}\chi'_{23} \quad (6)$$

This equation expressed the mixing rule of k_D . Equation 6 is rewritten to following equation as polymer components 1 and 2

$$\ln k_{D12} = \phi_1 \ln k_{D1} + \phi_2 \ln k_{D2} + \phi_1\phi_2\chi'_{12} \quad (7)$$

A negative deviation of k_D of various single-phase blends from the semilogarithmic additive rule shown by the dashed line in Figure 6 is predicted from eq 7 since χ'_{12} is negative for a single-phase blend. The solid line drawn in Figure 6 is the theoretical line calculated using eq 7 and $\chi'_{12} = -0.575$. The χ value obtained appears reasonable and sorption probe techniques may prove valuable for quantifying the thermodynamics of polymer blend system.

On the other hand, the k_D of the various phase-separated PS/PVME blends formed by phase separation are also indicated by closed circles in Figure 6. The values are located between k_D of the single-phase blends and the dashed line indicating the semilogarithmic additive rule. This behavior can be attributed to the fact that the various single-phase PS/PVME blends do not separate completely to each homopolymer, PS and PVME, as mentioned above on the variation of T_g . This suggests that k_D can be varied between k_D 's of two homopolymers by composition and the phase-separated state formed by heating above LCST.

Figure 7 shows the variation of C_H' as a function of $(T_g - 25^\circ\text{C})$ of the polymer blends. The C_H' of phase-separated polymer blends are the corrected values as mentioned above. It

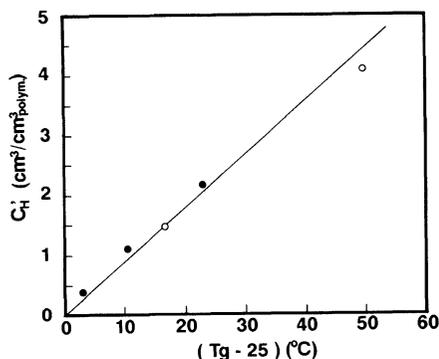


Figure 7. Langmuir sorption capacity term (C_H') for CO_2 in single-phase and phase-separated PS/PVME glassy blend films with various compositions at 25°C as a function of $(T_g - 25^\circ\text{C})$; \circ , single-phase; \bullet , phase-separated.

has been reported that C_H' varies linearly as a function of $(T_g - T)$.^{7,19-21} This was also observed with respect to the temperature dependence of C_H' for this PS/PVME blend system. A good linear relationship of the C_H' and $(T_g - 25^\circ\text{C})$ was obtained irrespective of single- and separated-phases both in glassy states. This suggests the possibility that C_H' can be varied by composition and the phase-separated state formed by heating above LCST.

In conclusion, k_D of the single-phase polymer blends deviated negatively from its semilogarithmic additivity. The deviation is interpreted by the χ interaction parameter, and *vice versa* k_D of polymer blend systems could provide information on interactions between each polymer. k_D of the phase-separated blends was slightly higher than that of single-phase blends and smaller than semilogarithmic additivity, reflecting that the single-phase blends did not separate completely to the pure polymer phases of PS and PVME but did to two mixed phases. C_H' of single- or phase-separated blends was proportional to $(T_g - 25^\circ\text{C})$ of each phase and became zero at a temperature above T_g . It is suggested that the sorption properties of PS/PVME blend may be changed by composition and phase separation.

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