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Evaluation of the styrene/*n*-butyl methacrylate binary interaction energy density

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Abstract

The phase behavior of blends of S–nBMA copolymers with monodisperse PS homopolymers was studied at three temperatures: 120, 150 and 180 °C. Quantitative evaluation of the binary interaction energy density between styrene (S) and *n*-butyl methacrylate (nBMA), $B_{\mathrm{S/nBMA}}$, was made at each temperature by analyzing the miscibility data using the copolymer/critical molecular weight method. The temperature dependence of $B_{\mathrm{S/nBMA}}$ is interpreted by the Sanchez–Lacombe lattice fluid theory using a constant bare interaction energy $\Delta P^*_{\mathrm{S/nBMA}}$. The $B_{\mathrm{S/nBMA}}$ values determined in this study were much larger than those reported by others. Deuteration effects may be the reason for this difference.

Keywords: S–nBMA copolymer; Copolymer/critical molecular weight method; Deuteration effects

1. Introduction

Accurately quantifying polymer–polymer interactions is an important issue since these thermodynamic interactions are the key to rational design and selection of blends with useful properties [1,2].

The interaction between styrene (S) and *n*-butyl methacrylate (nBMA) repeat units has recently become of interest because of technological applications of S/nBMA block copolymers in the areas of high temperature adhesives and new thermal sensors, etc. [3]. Consequently, the phase behavior of S/nBMA block copolymers or blends containing S and nBMA repeat units and the responsible interaction between S and nBMA have been explored by various approaches in recent years [3–14]. For example, Russell and coworkers investigated the morphologies for S/nBMA block copolymers by using small angle neutron scattering (SANS) and dynamic rheological measurements [3,6–8]. They reported that the S/nBMA block copolymers may exhibit both an upper critical order transition (UCOT) and a lower critical order transition (LCOT) depending upon their compositions and molecular weights [3]. Russell et al. also studied the lower critical solution temperature (LCST) phase behavior for blends of PS homopolymers with PnBMA homopolymers using SANS [5]. More recently, Winey and coworkers evaluated the interaction between S and nBMA by a technique they called cross-sectional microscopy [14]. Stamm et al. reported the temperature and molecular weight dependence of the Flory–Huggins (FH) based interaction between S and nBMA and the morphologies for compositionally symmetric S/nBMA block copolymers by using various techniques such as SANS, neutron reflectivity (NR), small angle X-ray scattering (SAXS), and rheology, etc. [9–13]. For all these studies, information about the binary interaction energy density between S and nBMA, or $B_{\mathrm{S/nBMA}}$, is essential to understand the phase behavior of the block copolymers or blends containing S and nBMA repeat units. Unfortunately, the values of $B_{\mathrm{S/nBMA}}$ reported by these different research groups vary greatly (ranging from 0.01 to 0.27 cal/cm^3) [3–15]. It should also be noted that in all these prior reports, except the work from Winey et al., deuteration was required to achieve contrast in SANS and NR measurements; deuteration is well-known to perturb the interaction energy [16–18] and its effect is likely to be much greater on a relative basis for weakly interacting systems like the S/nBMA pair.

The main objective of this study is to provide a more exact value of $B_{\mathrm{S/nBMA}}$ by using the copolymer/critical

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molecular weight approach [19–23], i.e. to observe the phase boundaries (molecular weight, copolymer composition, temperature) that separate miscible from immiscible regions for blends of S–nBMA copolymers with monodisperse PS homopolymers and interpret the results within the framework of an appropriate thermodynamic theory. Another goal of this paper is to measure the temperature dependence of $B_{\mathrm{S/nBMA}}$ and to compare with that predicted by modern theories [24–26].

2. Background and theory

The phase behavior of polymer blends is governed by the Gibbs free energy of mixing per unit volume (Δg_{mix}) which, for a blend of monodisperse homopolymers A and B, can be simply modeled by the FH theory [27,28]

$$\Delta g_{\mathrm{mix}} = B\phi_{\mathrm{A}}\phi_{\mathrm{B}} + RT\left[\frac{\rho_{\mathrm{A}}\phi_{\mathrm{A}}\ln\phi_{\mathrm{A}}}{M_{\mathrm{A}}} + \frac{\rho_{\mathrm{B}}\phi_{\mathrm{B}}\ln\phi_{\mathrm{B}}}{M_{\mathrm{B}}}\right] \tag{1}$$

where R is the universal gas constant, T is the absolute temperature, and ϕ_i, ρ_i and M_i are the volume fraction, density, and molecular weight of component i, respectively, and B is the desired binary interaction energy density. Stone and Sanchez recently gave new insights about why the FH model is so enduring even though far more sophisticated theories are rapidly evolving [29]. The critical interaction energy at the boundary between miscibility and immiscibility, where the energy and entropy terms in Eq. (1) are balanced, is given by the following expression

$$B_{\mathrm{critical}} = \frac{RT}{2}\left(\sqrt{\frac{\rho_{\mathrm{A}}}{(\bar{M}_{\mathrm{W}})_{\mathrm{A}}}} + \sqrt{\frac{\rho_{\mathrm{B}}}{(\bar{M}_{\mathrm{W}})_{\mathrm{B}}}}\right)^2 \tag{2}$$

where $(\bar{M}_{\mathrm{w}})_i$ is the weight average molecular weight of polymer i. This form adequately accounts for polydispersity effects for polymers with molecular weight distributions of the type considered here [30–35]. For a given interaction energy, B, Eq. (2) also defines critical molecular weights that divide miscible and immiscible behavior.

The copolymer/critical molecular weight method [19–22] combines the copolymer composition mapping method and the so-called critical molecular weight method [30,36–38]. Due to its advantages of simplicity and accuracy, it has been the focus of our recent interest [19–22]. However, it should be noted that only positive binary interaction energies can be determined by this method, and for very low molecular weight homopolymers end groups can become an issue [30]. In this paper, blends of monodisperse homopolymers of PS with S–nBMA copolymers of different compositions are investigated by this approach. For the blend systems of interest here, the binary interaction model can be simplified to

$$B = B_{\mathrm{S/MMA}}\phi_{\mathrm{nBMA}}^2 \tag{3}$$

where B represents the net interaction energy density for each blend system, $B_{\mathrm{S/nBMA}}$ is the interaction energy density for the S/nBMA pair, and ϕ_{nBMA} is the volume fraction of nBMA in the S–nBMA copolymer. The equations that describe the boundary between miscibility and immiscibility at a given temperature are obtained by combining Eqs. (2) and (3), i.e.

$$\phi_{\mathrm{nBMA}} = \sqrt{\frac{B_{\mathrm{critical}}}{B_{\mathrm{S/nBMA}}}} \tag{4}$$

Thus, a plot of ϕ_{nBMA} versus $\sqrt{B_{\mathrm{critical}}}$ leads to a diagram where miscible blends are separated from the immiscible blends by a straight line passing through the origin with a slope of $1/\sqrt{B_{\mathrm{S/nBMA}}}$.

The net interaction energy density B in Eq. (1) is an excess free energy term that includes the contributions of the heat of mixing plus any other non-combinatorial effects and, in general, is temperature dependent. An alternative way to study the temperature dependence of the FH based interaction energy B is to use equation-of-state (EOS) theories since they include the effects of compressibility and, thus, account for the temperature dependence of B arising from volumetric contributions. It should be noted that other factors may contribute to the temperature dependence of the observed FH based interaction energy as well. In this study, we explore whether the lattice fluid (LF) theory developed by Sanchez and Lacombe can account for the temperature dependence of the FH based interaction energy, $B_{\mathrm{S/nBMA}}$. The LF theory is a particularly useful EOS theory due to its versatility and simplicity [24–26,29].

The interaction parameter, B, in the FH framework can be translated into the bare interaction energy, ΔP^*, of the Sanchez–Lacombe LF framework and vice versa via the following relationship [30]

$$\begin{aligned} B = \tilde{\rho}\Delta P^* + \Bigg\{ & [P_2^* - P_1^* + (\phi_2 - \phi_1)\Delta P^*] \\ & + \frac{RT}{\tilde{\rho}}\left(\frac{1}{r_1^0 v_1^*} - \frac{1}{r_2^0 v_2^*}\right) - RT\left(\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\right) \\ & \times \left(\frac{1}{v_1^*} - \frac{1}{v_2^*}\right)\Bigg\}^2 \\ & \times / \left\{\frac{2RT}{v^*}\left[\frac{2\ln(1-\tilde{\rho})}{\tilde{\rho}^3} + \frac{1}{\tilde{\rho}^2(1-\tilde{\rho})} + \frac{(1-1/r)}{\tilde{\rho}^2}\right]\right\} \end{aligned} \tag{5}$$

3. Experimental

3.1. Materials

The monomers nBMA and S were purchased from Scientific Polymers and Aldrich, respectively; they were purified and then polymerized by the methods described in

Table 1
S–nBMA copolymers synthesized for this study

Abbreviation	Wt% nBMA[a]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[b]	T_g (°C)[c]
SnBMA43	43.1	2,62,000	1.97	61.6
SnBMA56	55.9	3,34,500	1.74	50.9
SnBMA66	66.2	3,26,800	1.77	44.0
SnBMA75	75.0	4,07,000	1.71	36.2
SnBMA84	83.7	5,11,600	1.67	31.7
SnBMA93	92.6	6,07,900	2.09	28.2

[a] Determined by NMR.
[b] Determined by GPC.
[c] Determined by DSC.

prior publications [22]. The characteristics of the S–nBMA copolymers synthesized in this study are listed in Table 1. The comonomer compositions, weight average molecular weights and polydispersities of these copolymers were determined by ^{1}H NMR and gel permeation chromatography (GPC) calibrated with polystyrene standards, respectively. Fig. 1 shows the copolymerization diagram of the S/nBMA comonomer pair. The solid curve was calculated from the reactivity ratios $r_S = 0.43$ and $r_{nBMA} = 0.71$. These values are consistent with those reported from the literature [39]. The various S–nBMA copolymers of different compositions were blended with monodisperse PS homopolymers. The PS homopolymer standards are described elsewhere [19–22,40]. Fig. 2 shows the onset T_g for the synthesized S–nBMA copolymers with the solid lines representing the prediction of the Fox equation.

3.2. Blend preparation and assessment

Blend preparation and the assessment of miscibility were discussed in detail elsewhere [23]. Visual determination of phase behavior was made before and after the annealing treatment for each blend. Since the differences of both the refractive indices and glass transition temperatures between the constituent materials in this study are large enough to make quite reliable evaluations, both differential scanning calorimetry (DSC) and static light scattering experiments were performed to determine the state of blend miscibility. The light scattering apparatus used for this study was described in detail elsewhere [41]. The methodology on how to justify the optical assessment of blend miscibility is also reported previously [23]. The results obtained from these two independent techniques agree well. The three annealing temperatures used in this study are 120, 150 and 180 °C, respectively.

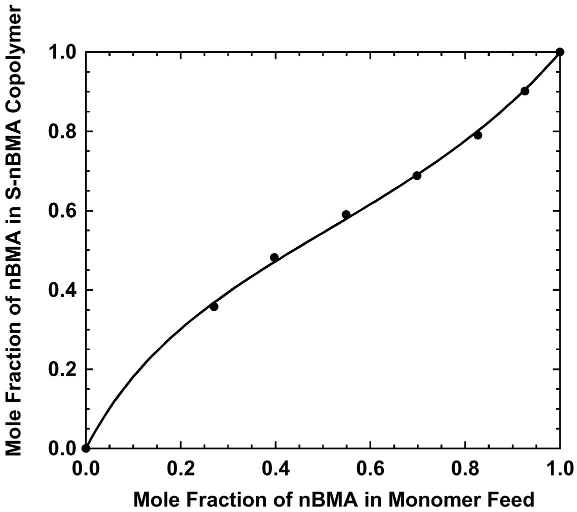

Fig. 1. Copolymer diagram for the S/nBMA system; the curve was calculated using the reactivity ratios $r_S = 0.43$ and $r_{nBMA} = 0.71$.

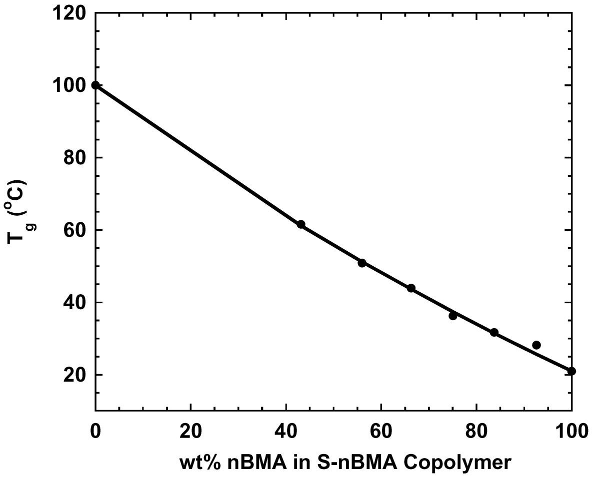

Fig. 2. Glass transition temperature (T_g) of synthesized S–nBMA copolymers versus copolymer composition. The solid line represents the prediction of the Fox equation.

4. Results and discussion

4.1. Evaluation of $B_{S/nBMA}$ by the copolymer/critical molecular weight method

The copolymer/critical molecular weight method has proven to be quite powerful to determine positive interaction energies between unlike unit pairs due to its potentially greater accuracy and more direct error limit analysis compared to the copolymer composition mapping method [21–23]. In this study, the value of $B_{S/nBMA}$ was determined by this approach using experimentally observed phase behavior of blends of S–nBMA copolymers with monodisperse PS standards.

Miscibility data for PS/S–nBMA copolymer blends are plotted, in the manner suggested by Eq. (4), in Fig. 3 for 120, 150 and 180 °C where the open circles represent miscible blends and the closed circles represent immiscible blends. For all the S–nBMA copolymers, blends are miscible only when the molecular weight of the monodiperse PS is low enough so that the entropic contribution overcomes the energetic counterpart in Eq. (1). The blends containing PS with $\bar{M}_W = 17,500$ g/mol are immiscible with S–nBMA copolymers containing 43.1 and more wt%

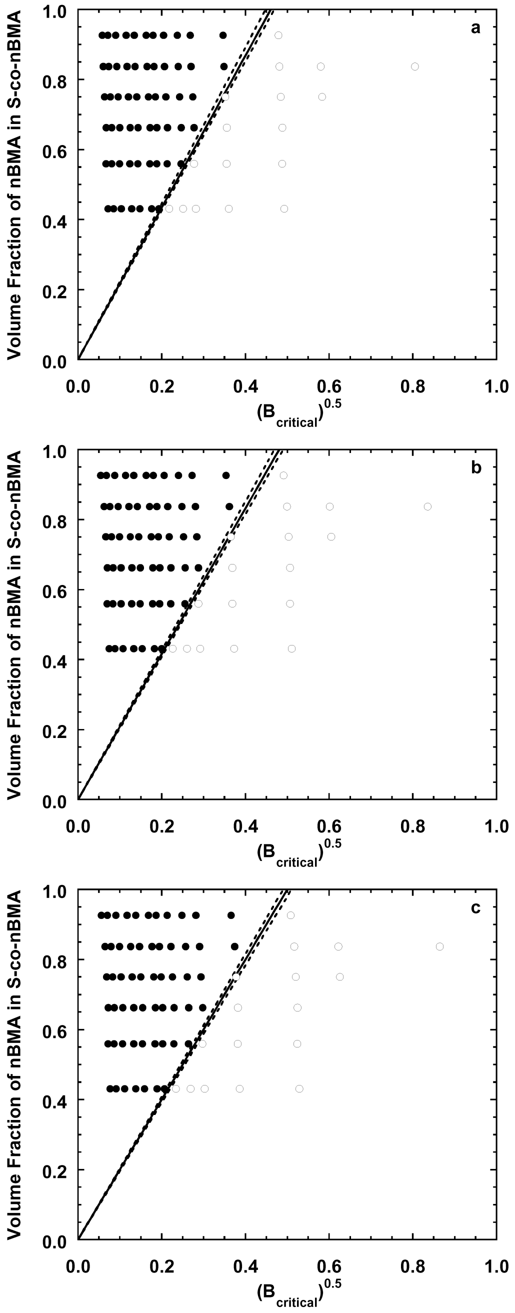

Fig. 3. Isothermal miscibility maps at (a) 120 °C; (b) 150 °C; (c) 180 °C for 50/50 blends of S–nBMA copolymers with PS homopolymers of varying molecular weights plotted according to Eq. (4): (○) miscible; (●) immiscible. From the slopes of the lines separating the miscible and immiscible blends, the following were calculated: $B_{\mathrm{S/nBMA}} = 0.21 \pm 0.01$ cal/cm^3 at 120 °C, $B_{\mathrm{S/nBMA}} = 0.23 \pm 0.01$ cal/cm^3 at 150 °C, $B_{\mathrm{S/nBMA}} = 0.25 \pm 0.01$ cal/cm^3 at 180 °C.

nBMA. The blends of the PS with $\bar{M}_{\mathrm{W}} = 4000$ g/mol did not become immiscible until the nBMA content was 83.7 wt%.

In these plots of ϕ_{nBMA} versus $\sqrt{B_{\mathrm{critical}}}$, straight lines passing through the origin can be drawn that well separate the miscible from the immiscible blends, see the solid lines in Fig. 3. The error limits associated with data analysis can be estimated by constructing the dashed lines shown. The values of $B_{\mathrm{S/nBMA}}$ determined at a given temperature from the slopes of the lines drawn are 0.21 ± 0.01 cal/cm^3 at 120 °C, 0.23 ± 0.01 cal/cm^3 at 150 °C and 0.25 ± 0.01 cal/cm^3 at 180 °C. These values are much larger than those reported previously from Russell and Stamm research groups [3,5–13]. Comparisons between $B_{\mathrm{S/nBMA}}$ values reported in the literature and those determined in the current study are given in Section 4.2.

4.2. Temperature dependence of $B_{\mathrm{S/nBMA}}$

The $B_{\mathrm{S/nBMA}}$ values determined from the copolymer/critical molecular weight method, are plotted versus temperature in Fig. 4 along with other values from the literature [4,5, 11,42]. The results from Russell and Stamm research groups [3,5–13], however, are substantially smaller; a possible explanation is presented later in this section. The results in Fig. 4 suggest that $B_{\mathrm{S/nBMA}}$ increases with temperature. As demonstrated previously [21–23,43], in many cases, the EOS effects account for most of the temperature dependence of the FH value of binary interaction energy, at least when there are no strong specific interactions. This proposal is tested in Fig. 4 to see if Eq. (5) adequately describes how $B_{\mathrm{S/nBMA}}$ varies with temperature by assuming that the bare interaction energy, $\Delta P^*_{\mathrm{S/nBMA}}$, in the Sanchez–Lacombe theory is independent of temperature. The Sanchez–Lacombe characteristic parameters, P^*, T^*, and ρ^*, used in the calculations and the corresponding standard deviations in terms of specific volume for PS and PnBMA are listed in Table 2. The three constant PS characteristic parameters reported previously [29] for the temperature range of 115–195 °C were used in the calculation since all the three experimental annealing temperatures in this study fall into this temperature range. However, our results are not dramatically altered if temperature dependent characteristic

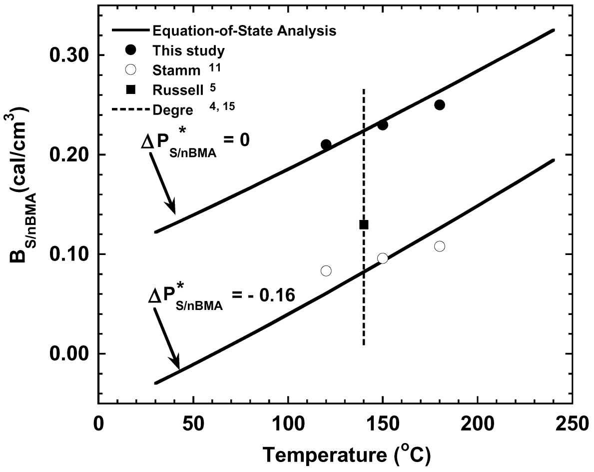

Fig. 4. Summary of $B_{\mathrm{S/nBMA}}$ values obtained from various sources (see Refs. [4,5,11,15]) including this study. The solid curves were calculated according to Eq. (5) for the values of $\Delta P^*_{\mathrm{S/nBMA}}$ shown using the Sanchez–Lacombe characteristic parameters from Table 2.

Table 2
Sanchez–Lacombe characteristic parameters used in this study

Polymer	T^* (K)	P^* (MPa)	ρ^* (g/cm^3)	Temperature range (°C)	Standard deviation of specific volume (cm^3/g)	Reference
PS	735	357	1.1050	115–195	9.80×10^{-4}	[29]
PnBMA	641	436	1.1184	34–200	9.62×10^{-4}	This study

parameters for PS are used in the calculation. On the other hand, the constant characteristic parameters for PnBMA were recomputed from PVT data published previously [44]. It should be noted that the parameters for PnBMA obtained here lead to a lower standard deviation than those reported previously [25]. This can be clearly seen from Fig. 5 in which the resulting calculated specific volume data for PnBMA are plotted against the experimental specific volume; the standard deviation of 9.62×10^{-4} cm^3/g, is smaller than that previously reported [25]. As seen in Fig. 4, the temperature dependence of $B_{\mathrm{S/nBMA}}$ in this study (see the upper curve in Fig. 4) is well described by the Sanchez–Lacombe LF theory with a constant value of $\Delta P^*_{\mathrm{S/nBMA}} = 0\ \mathrm{cal/cm^3}$; while the lower curve in Fig. 4 predicted by Eq. (5) with a constant value of $\Delta P^*_{\mathrm{S/nBMA}} = -0.16\ \mathrm{cal/cm^3}$ is roughly consistent with Stamm's data [11]. Fig. 4 suggests that EOS effects are primarily responsible for the temperature dependence of the FH based interaction energy for the current system. Hence, to a good approximation, the bare interaction energy between S and nBMA, $\Delta P^*_{\mathrm{S/nBMA}}$, is independent of temperature.

The discrepancy between the $B_{\mathrm{S/nBMA}}$ data from Russell and Stamm [5,11] and that reported here may be the result of a deuteration effect as described in prior publications [23, 30]. A number of experiments have shown that the interaction energy, and the resultant phase behavior determined by labeling techniques such as SANS and NR may differ from the values for the unlabeled components. For example, isotopic blends of polybutadiene (PB) (i.e. PB(D)/PB(H)) [17] and of poly(dimethylsiloxane) (PDMS) (i.e. PDMS(D)/PDMS(H)) [45] were observed to have finite interaction energies. These studies, together with subsequent investigations of other isotopic blends [46,47], suggested that the unfavorable interactions originate from the difference in polarizability between C–H and C–D bonds. Lin et al. [18] demonstrated that blends of PS and poly (vinyl methyl ether) showed an appreciable deuterium isotope effect on the cloud points of the mixture. Callaghan et al. also reported large differences of the interaction energy $B_{\mathrm{S/MMA}}$ between the values determined from blends of PS with PMMA without deuteration and those from deuterated polymers [30]. Another possible explanation could be due to the fact that the Stamm data were obtained from S/nBMA block copolymers while the current data is from physical blends. In their studies, Stamm and coworkers employed the random phase approximation (RPA) [48] introduced by de Gennes to determine the interaction parameters from their SANS data for S/nBMA block copolymers; RPA provides a relationship for the structure factor in SANS measurement of homogeneous binary polymer blends [49]. However, the RPA method assumes that the polymer chains are nearly ideal. As pointed out by Leibler [49], RPA is a good approximation for homopolymer mixtures; whereas, when segregation effects in block copolymers become important, RPA may not be accurate enough. As can be seen from Fig. 4, the above explanation is further supported by the fact that $B_{\mathrm{S/nBMA}}$ determined from the SANS study on blends of PS(D) homopolymers with PnBMA homopolymers from Russell et al. work [5] is significantly larger than that obtained from the SANS study on S(D)/nBMA block copolymers reported by Stamm and coworkers [11]. The fact that the FH based interaction energies $B_{\mathrm{S/nBMA}}$ determined in the current study are much larger than those from prior reports is further supported by reports from Vavasour et al. and Winnik et al. [50,51]. In their direct non-radiative energy transfer (DET) study of homopolymer (PS) localization in block copolymers (PS-b-PnBMA) [51], they suggested that their experimental measurements of the penetration level of PS would be more consistent with the predictions of numerical self-consistent field (NSCF) theory if much larger $B_{\mathrm{S/nBMA}}$ values than those reported previously are used in their calculations [50,51]. Our current $B_{\mathrm{S/nBMA}}$ value is consistent with their recommendations.

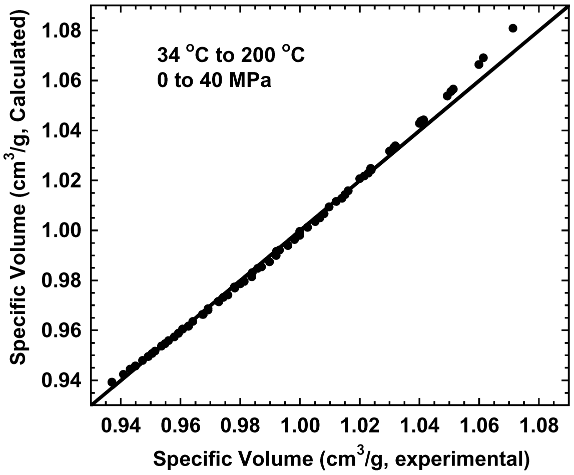

Fig. 5. Calculated specific volume as a function of experimental specific volume for PnBMA. The characteristic parameters for PnBMA listed in Table 2 were used in the calculation.

5. Conclusions

The state of miscibility for blends of S/nBMA copolymers with monodisperse PS homopolymers was determined at three different temperatures 120, 150 and 180 °C. Binary interaction energies, $B_{\mathrm{S/nBMA}}$, at each temperature were accurately determined by the copolymer/critical molecular weight approach, see Fig. 3. An EOS analysis was used to interpret the temperature dependence of $B_{\mathrm{S/nBMA}}$, see Fig. 4. The current values were much larger than the results from the prior literature. A deuteration effect was thought to be the main contributing factor for the absolute difference between the current values and those reported previously.

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