Determining the temperature-dependent Flory interaction parameter for strongly immiscible polymers from block copolymer segregation measurements

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We have determined the segregation of diblock copolymers of deuterated polystyrene (dPS) and poly(2-vinylpyridine) (PVP) to a planar interface between the homopolymers using forward recoil spectrometry. The segregation isotherms, namely the interfacial excess *versus* its volume fraction in the homopolymer phase far from the interface, for the diblock copolymers were measured at several temperatures. Using a self-consistent mean field (SCMF) theory, one can fit the segregation data accurately if the Flory interaction parameter χ is treated as a fitting parameter. Using this scheme, the temperature-dependent Flory interaction parameter χ between PS and PVP was determined to be $-0.033+63/T$(K). In contrast to this evaluation of χ which depends heavily on a model, we have shown that the isosteric heat of segregation q_{seg} can be directly extracted from the experimental data. We demonstrate that the enthalpic portion of the Flory interaction parameter χ_H can be estimated directly from q_{seg}, without recourse to a model of the segregation layer, and the χ_H from this direct method is in good agreement with that determined using the SCMF theory. These two methods provide a new approach for determining χ for strongly immiscible polymers.

(Keywords: forward recoil spectrometry; interfacial excess; Flory interaction parameter)

INTRODUCTION

Segregation of diblock copolymers to the polymer–polymer interface has been used to increase the adhesion between immiscible polymers[1–4]. Moreover, the reduction in interfacial tension also can be utilized to regulate the particle size in a phase-separated polymer blend[5] and it is even possible to form a microemulsion if the interfacial tension vanishes[6]. In both of these cases, it is believed that the interfacial properties are intimately related to the amount of copolymer at the interface. Therefore, knowledge of this segregation is essential for the purpose of tailoring polymer interfaces.

A qualitative approach proposed by Leibler[7] provides a basic understanding of the copolymer segregation at polymer–polymer interfaces. In general, the enthalpic interaction between components dominates the phase behaviour in polymer blends. The mixing free energy of an A–B copolymer chain in homopolymer A mostly comes from the unfavourable interaction between B segments of the copolymer and A segments of the homopolymer as represented by the Flory interaction parameter χ. The portion of chemical potential resulting from this enthalpic interaction is what drives the copolymer to segregate to the polymer–polymer interface. Based on Leibler's scheme, this unfavourable interaction is simply minimized by confining the copolymer joints at the interface which then results in a loss of entropy due to this chain localization and an increase in elastic free energy due to the stretching of the copolymer chain at the interface. As shown by Dai *et al.*[8], this simple argument can indeed reproduce the form of the segregation isotherm if χ is treated as an adjustable fitting parameter. However, different values of χ have to be used to reproduce the observed segregation isotherms if the molecular weights of the homopolymers are varied. Recently, Semenov[9] has proposed a model which reconciles the fact that the copolymer joints are not strictly confined at the interface. Although this model shows a good agreement with the observed isotherm using an appropriate χ if the molecular weight of homopolymer is relatively high, it still fails to account for the dependence of segregation on the molecular weight of homopolymers. Therefore, a more elaborate theory, such as a self-consistent mean field (SCMF) theory, must be used to describe the segregation quantitatively.

The first SCMF theory for the homopolymer interface with no block copolymer additives was developed by Helfand and Tagami[10,11] for the strong segregation limit, i.e. when $\chi N \gg 2$. This approach was then adopted by Noolandi and Hong[12,13] to describe the case of block copolymer segregation at an immiscible homopolymer interface in the presence of a solvent and further adapted to describe the solvent-free case by Shull and Kramer[14]. As in Leibler's model, χ remains as an adjustable parameter in these SCMF theories. However, it has been shown that the segregation isotherm can be reproduced by using a SCMF theory developed by Shull

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and Kramer with a single value of χ for the cases of deuterated polystyrene–poly(2-vinylpyridine) (dPS-PVP) diblock copolymer with homopolymer of different molecular weights[8]. Furthermore, one can compare the SCMF theoretical prediction of the copolymer segment density profile near the interface with experimental measurements. Neutron reflectometry (NR) is capable of revealing such profiles with excellent depth resolution ($\sim$5–10 Å). In the case of dPS-PVP copolymers at interfaces between PS and PVP homopolymers, NR results[15] can be reasonably fitted by the segment density profile predicted by the SCMF theory using the same value of χ required to fit the segregation data. Based upon this evidence, we believe this SCMF quantitatively describes the block copolymer segregation. In turn, these results imply that measurements of segregation of the block copolymer can be analysed to accurately determine χ using the same SCMF theory. Hence, such measurements provide a new way of determining χ for highly immiscible polymers.

In this paper we demonstrate this point by measuring the segregation isotherms of a diblock copolymer of dPS and PVP to a planar interface between PS and PVP homopolymers at different temperatures and then use these isotherms to determine the temperature-dependent Flory interaction parameter χ between PS and PVP.

EXPERIMENTAL

The characteristics of the polymers used in this study are summarized in *Table 1*. The PVP homopolymer film was prepared by spin-casting onto a Si wafer and a film containing an intimate mixture of PS homopolymer and dPS-PVP block copolymer was spun cast onto this PVP layer using toluene as the solvent which does not swell PVP strongly. The detailed geometry of these film layers is shown in *Figure 1*. These bilayer specimens with various concentrations of copolymer were then annealed at four different temperatures between 156°C and 230°C for several hours to allow equilibrium to be established. The amount of copolymer segregated to the homopolymer interface is determined from the volume fraction *versus* depth profile measured by forward recoil spectrometry (FRES). A typical example of such a profile is shown in *Figure 2*. The interface excess z_i^*, shown as the hatched area in *Figure 2*, is used to determine the areal chain density Σ of copolymer at the interface as follows:

$$\Sigma=\frac{z_i^*\rho}{N_c}=\frac{\left(\int_{\text{interface}}[\phi(x)-\phi_\infty]\mathrm{d}x\right)\rho}{N_c} \tag{1}$$

where $\phi(x)$ is the block copolymer volume fraction at depth x and ϕ_∞ is its value in the PS homopolymer phase far from the interface after annealing. The parameters N_c and ρ are the (total) degree of polymerization and the segment density of the block copolymer, respectively. Since the segment densities of PS and PVP are nearly identical, ρ is approximated by its value for PS[16] of 0.0094 mol cm^{-3}.

Table 1 Characteristics of the polymers used

Polymer	N_{dPS}-N_{PVP} ^{a}	$N_{homopolymer}$ ^{a}	M_w/M_n
dPS-PVP	596–59^b		1.08
PS		2240^c	1.05
PVP		2000^c	1.2

^{a} N is the degree of polymerization
^{b} Determined by g.p.c. and ^{13}C n.m.r.
^{c} Determined by g.p.c. using PS standards

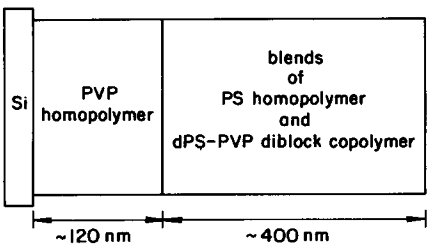

Figure 1 Schematic diagram of the bilayer specimen

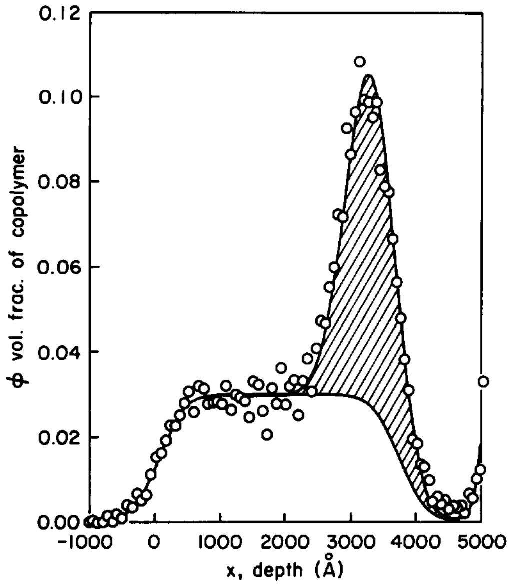

Figure 2 Volume fraction profile of copolymer from FRES measurements, where ϕ_∞ and z_i^* are 0.03 and 86 Å, respectively

RESULTS AND DISCUSSION

The segregation isotherm, namely z_i^* *versus* ϕ_∞, is plotted in *Figure 3* for different annealing temperatures. As can be seen, there is less segregation of copolymer at any given ϕ_∞ as the annealing temperature is increased mainly due to the decrease of importance of the unfavourable enthalpic interaction between PS and PVP polymers relative to entropic contribution to the free energy. The initial concentration of copolymer in the host PS homopolymer blend can be estimated by the following formula:

$$\phi_0=\phi_\infty+\frac{z_i^*}{L} \tag{2}$$

where ϕ_0 and L are the initial concentration and thickness of the host PS homopolymer layer, respectively. *Figure 4* shows z_i^* as a function of temperature at a constant ϕ_0 of 0.08 based on the information obtained from *Figure 3* and an assumed L of 4500 Å. As shown, z_i^* can be increased from $\sim$80 to $\sim$125 Å by simply varying the annealing temperature from 230 to 156°C. This result demonstrates the possibility of

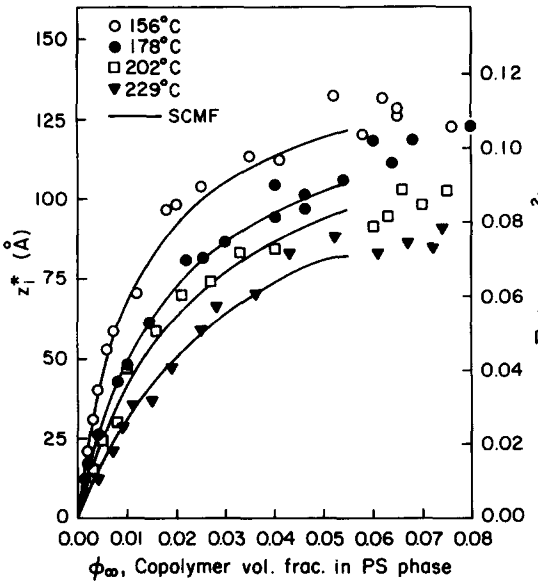

Figure 3 Segregation isotherms as a function of the annealing temperature. The solid line is the best fit to a SCMF theory with appropriate χ at different temperatures

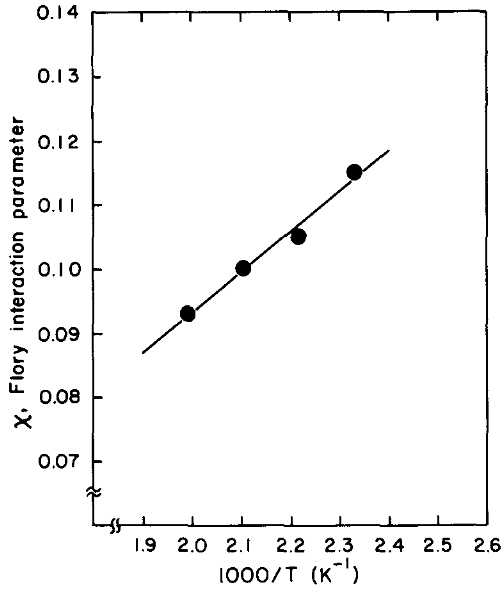

Figure 5 Flory interaction parameter obtained from the best fit to the segregation isotherm *versus* the reciprocal of the annealing temperature

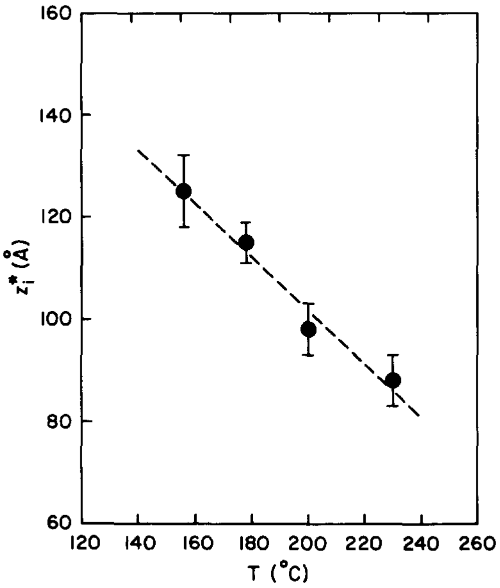

Figure 4 Interfacial excess as a function of the annealing temperature at an initial volume fraction $\phi_0=0.08$ and initial thickness $L=4500$ Å

tailoring the interfacial composition by changing the processing temperature at constant initial concentration of copolymer.

The Flory interaction parameter χ was obtained from the best fit of the segregation isotherm predicted by the SCMF theory to the experimental isotherms. The best fit isotherms at each temperature are shown by the solid lines in *Figure 3*. The Flory interaction parameter χ determined in this way is plotted *versus* the reciprocal of the annealing temperature in *Figure 5*. The data are reasonably represented by a linear relationship over the experimental range of temperatures and can be described by the following equation:

$$\chi=\chi_s+\frac{\chi_H}{T} \qquad (3)$$

where χ_H is the enthalpic contribution to χ and χ_s is the non-combinatorial entropic contribution. From the data fitting, $\chi_H=63$ K and $\chi_s=-0.033$ for PS and PVP. As originally pointed out by Leibler[17] and further developed by several workers[18,19], a microphase separation theory based on the random phase approximation (RPA) can be used to evaluate χ parameters from scattering experiments[20,21]. However, this type of experiment must be carried out in the miscible state above the order–disorder transition temperature (ODT) which may not be accessible for highly immiscible polymers, but is perfectly suitable for weakly immiscible polymers. Based on Leibler's result[17], the lowest ODT occurs at $f=0.5$ with $\chi N_c=10.45$ where f is the fraction of one block in the block copolymer. However, for highly immiscible polymers, it may still be practically difficult to access the needed temperature. For example, we predict that the ODT of a symmetric PS-PVP copolymer with $N_c=200$ is 466°C and will not be lower than 200°C unless N_c is <100. In contrast, the method of segregation experiments proposed by us is perfectly suitable for determining χ parameters for highly immiscible polymers. The combination of this proposed segregation method and a scattering technique, allows the determination of χ for polymers over the whole range of χN_c and f.

The chemical potential of the copolymer in the dilute limit, i.e. as ϕ_∞ approaches zero, can be estimated using the Flory–Huggins approximation[14].

$$\frac{\mu}{k_BT}\cong\ln\phi_\infty+\chi N_{PVP} \qquad (4)$$

Analogous to the segregation of a solute at the interface between the dilute solution and its vapour phase, the isosteric heat of segregation, q_{seg}, in this dilute limit can be defined as[22]:

$$q_{seg}=-k_BT^2\left(\frac{d\ln\phi_\infty}{dT}\right)_{z_i^*}=k_B\left(\frac{d\ln\phi_\infty}{d1/T}\right)_{z_i^*} \qquad (5)$$

where k_B is the Boltzmann constant. In essence, this q_{seg} is the enthalpy needed to compensate the entropy loss while the copolymer chains segregate from the bulk phase of the host homopolymer to the interface. By this definition q_{seg}/k_BT is negative and its magnitude approximately equals the enthalpic part of χN_{PVP}, i.e. $\chi_H N_{PVP}/T$. Therefore, q_{seg} can be used to estimate χ_H $(=|q_{seg}|/N_{PVP}k_B)$. Since the segregation for such strong immiscible polymers is driven mainly by the enthalpic interaction, χ can be approximated by its enthalpic part χ_H/T. This provides an alternative method of estimating χ in which no theoretical model of the segregation layer is needed. The values of ϕ_∞ obtained from the segregation isotherm at a constant z_i^* for different temperatures can be used to construct the segregation isosteres, namely the logarithm of ϕ_∞ *versus* the reciprocal of the annealing temperature, as shown in *Figure 6*. Open symbols represent the ϕ_∞ data obtained by interpolation between experimental data points on the segregation isotherms. The q_{seg} values are then calculated from the slope according to equation (5) and are listed in *Table 2* for different z_i^* values ranging from 40 to 70 Å. It is important to realize that the extraction of an isosteric heat from the segregation experiments is only valid if the segregation is a thermodynamically reversible process. The reversibility is verified by experiments reported in the Appendix. To carefully analyse the data, 90% confidence intervals[23] of these calculated q_{seg} values are included in the table. As seen, q_{seg} is virtually a constant at -0.3 ± 0.07 eV per molecule in the range of z_i^* between 40 Å and 70 Å. The SCMF theory was used to determine q_{seg} using χ obtained from the fitting of the segregation isotherms; the value obtained is -0.29 ± 0.02 independent of z_i^* in the range between 20 Å and 80 Å which agrees well with our experimental results. As discussed above, χ_H can be estimated directly from q_{seg} and is found to be 59 ± 14 K. This value agrees well with the χ_H determined by SCMF theory which is 63 K. It is to be emphasized that the conclusions that can be drawn from the isosteres so constructed are independent of any detailed model of the segregation. Nevertheless the good agreement of the SCMF theory with the experimental data demonstrates that it will produce isosteres as well as isotherms in good agreement with experiment.

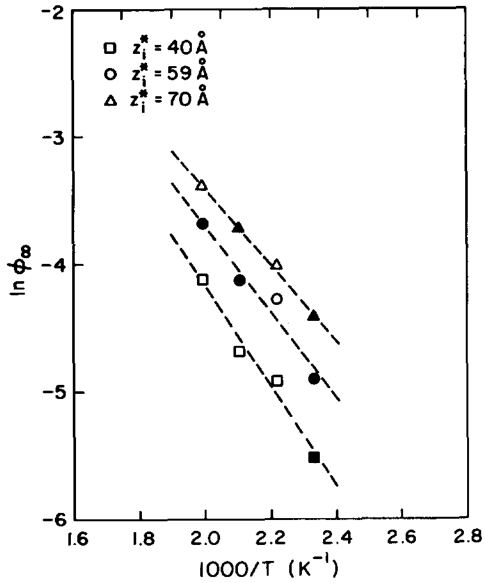

Figure 6 Isosteres for copolymer segregation for z_i^* values of 40, 59 and 70 Å. Open symbols represent the ϕ_∞ data obtained by interpolation between the experimental data of the segregation isotherm (*Figure 3*)

Table 2 Isosteric heat of segregation as a function of interfacial excess

Interfacial excess (Å)	Isosteric heat of segregation	
	($\times 10^{-20}$ J per molecule)	(eV per molecule)
40	-5.4 ± 1.2	-0.34 ± 0.08
59	-4.6 ± 1.3	-0.29 ± 0.08
70	-4.1 ± 0.6	-0.27 ± 0.04

In conclusion, we have revealed the possibility of tailoring the interfacial composition by exploiting the temperature dependence of segregation isotherms. A new approach of determining χ for highly immiscible polymers by fitting the segregation isotherm with the SCMF theory yields very reasonable values for the PS and PVP system. In addition, we have demonstrated that χ_H can be directly estimated from q_{seg}, without recourse to a model of the segregation layer, which then can be used to approximate χ for strongly immiscible polymers. This method yields the χ_H in good agreement with that determined using the SCMF theory.

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APPENDIX

It is important to realize that the extraction of an isosteric heat from the segregation experiments is only valid if the segregation is a thermodynamically reversible process. To examine the reversibility of such a segregation process, a series of segregation isotherms was measured from the specimens sequentially annealed at 156°C and 200°C. The filled circular symbols in *Figure A1* represent the segregation isotherm measured from a set of specimens annealed first at 156°C for 36 h and then subsequently at 200°C for 20 h. The open circles represent the segregation isotherm obtained from the specimens annealed at 156°C. It should be pointed out that these two sets of specimens were annealed at 156°C simultaneously and thereafter one set was subjected to a second anneal (at 200°C) and the other set was used for the measurement of the segregation isotherm. This isotherm thus indicates that the specimens for the sequential anneal achieved their equilibrium segregation (at 156°C) during the first anneal of 156°C prior to the second anneal at 200°C. As seen in *Figure A1*, the segregation isotherm obtained for the sequential anneal (156°C→200°C) is virtually the same as if it were annealed directly at 200°C. This result indicates that the equilibrium interfacial excess can be achieved by desorbing the pre-adsorbed copolymer chains from the interface.

The segregation isotherm for a corresponding two-step sequential annealing experiment, first at 200°C for 18 h and then subsequently at 156°C for 48 h, is reported in *Figure A1* (filled triangles) and shows a good agreement with the isotherm corresponding to annealing directly at a temperature of 156°C. This result indicates that the equilibrium interfacial excess can also be achieved by segregating more copolymer chains to an interface which already has some segregated copolymer chains. In addition, the segregation isotherm obtained from a set of specimens subjected to an annealing cycle, first at 200°C, then at 156°C and finally at 200°C, is represented by open squares in *Figure A1*. This set of samples shows virtually the same segregation isotherm as the one measured after direct anneal at the same final temperature.

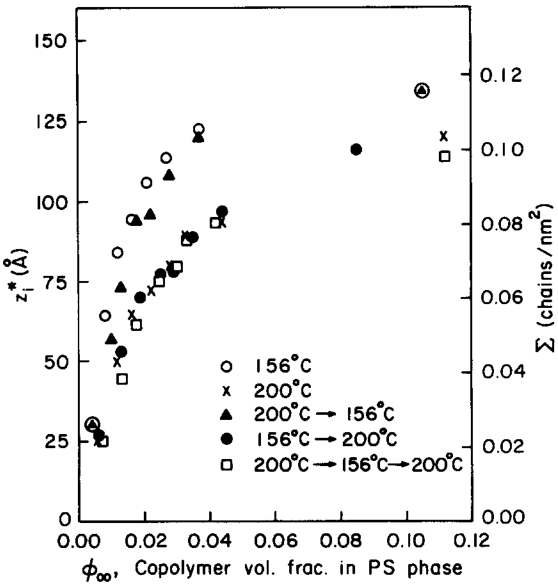

Figure A1 Segregation isotherms as a function of annealing sequences at temperatures of 156°C and 200°C: (○) 156°C for 36 h; (×) 200°C for 18 h; (▲) 200°C for 18 h, then 156°C for 48 h; (●) 156°C for 36 h, then 200°C for 20 h; (□) 200°C for 18 h, then 156°C for 36 h, then 200°C for 20 h

The results of copolymer segregation from the sequential anneals imply that the copolymer segregation will achieve the equilibrium interfacial excess of the corresponding annealing temperature provided sufficient annealing time elapses regardless of its thermal (annealing) history. This evidence demonstrates that the segregation process is indeed reversible and thus the isosteric heat of segregation can be properly constructed. In addition, this set of experiments demonstrates that one can obtain a specific interfacial excess by annealing the specimen at an appropriate temperature without the knowledge of its thermal (annealing) history.