Determination of the Flory−Huggins Interaction Parameter of Styrene and 4-Vinylpyridine Using Copolymer Blends of Poly(styrene-*co*-4-vinylpyridine) and Polystyrene

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ABSTRACT: On the basis of the experimentally determined phase behavior in blends of polystyrene and random copolymers of styrene and 4-vinylpyridine, i.e., P(S_x-*co*-$4VP_{1-x}$)/PS, the Flory−Huggins interaction parameter is demonstrated to satisfy $0.30 < \chi_{S,4VP} \leq 0.35$. This value is substantially smaller than reported before. To corroborate our results, a similar study was performed using 2-vinylpyridine leading to $0.09 < \chi_{S,2VP} \leq 0.11$, in excellent agreement with the well-established value of $\chi_{S,2VP} = 0.1$.

Introduction

One of the most active areas of research in the polymer field involves nanostructure formation in block copolymer systems.[1] Among the block copolymer systems investigated, block copolymers involving styrene and 2-vinylpyridine or 4-vinylpyridine play a prominent role.[2−6] The large contrast between the two components favors small-angle X-ray scattering studies, whereas a simple staining procedure using iodine vapor allows straightforward transmission electron microscopy studies. The theoretical description of phase behavior in polymer systems in its most simple form involves only a single system-dependent parameter, the Flory−Huggins χ parameter. In the case of blends of polystyrene and poly(2-vinylpyridine) or block copolymers thereof, the well-established value is given by $\chi_{S,2VP} \cong 0.1$, based on polymer segments corresponding to a styrene (or 2-vinylpyridine) monomer.[2] Since the molar mass of both components (homopolymers or blocks) is usually in the range of 100 000, the incompatibility parameter $N\chi$, where N represents the total number of segments in the two homopolymers or the block copolymer, satisfies $N\chi_{S,2VP} \gg 10$, which classifies these systems as being in the strong segregation limit (SSL).[1]

In the case of 4-vinylpyridine and styrene the value of the interaction parameter was addressed for the first time very recently.[6] Three different types of experiments were carried out, all of which relate a characteristic system property to the value of the interaction parameter using expressions available from the SSL description of polymer systems. The lamellar, cylindrical, or spherical micelle spacing of four different microphase-separated P(S-*block*-4VP) diblock copolymers were measured and compared to the theoretical expressions. Surprisingly large values for $\chi_{S,4VP}$ varying from 1.4 to 7.5 were required to reach agreement. On the other hand, contact angle measurements of a PS droplet on a layer of P4VP gave a value of “only” $\chi_{S,4VP} = 0.38$. However, the authors argue this to be a lower bound only because the evaluation required the surface tension of P4VP, which was assumed to be equal to that of P2VP. Finally, the interaction parameter value was also determined from the interfacial width of a PS−P4VP bilayer leading to a lower bound of $\chi_{S,4VP} = 1.0$. According to this work, the interaction parameter between PS and P4VP is an order of magnitude greater than between PS and P2VP, which seems to make these systems good candidates for the so-called super strong segregation limit.[7,8]

The extremely large value of $\chi_{S,4VP}$ predicted as well as the large variation in this value prompted us to start the present investigation using the well-established method of phase behavior in random copolymer blends to determine the χ parameter value directly from the phase behavior observed. To corroborate the results concerning 4VP, the corresponding random copolymer blends involving 2VP have been investigated as well.

Experimental Details

Materials. Copolymers of styrene and 4-vinylpyridine (4VP) (2-vinylpyridine (2VP)) were synthesized radically in toluene using 2,2-azobis(isobutyronitrile) (AIBN) as initiator. Styrene, 2-vinylpyridine, and 4-vinylpyridine monomers were distilled under reduced N_2 pressure and stored at −18 °C. Toluene was distilled from Na. AIBN was recrystallized from ethanol. Two different polystyrene homopolymer samples were used. A high molar mass polystyrene (HMPS), DOW STYRON 666, precipitated from chloroform into methanol; $M_w = 240\,000$ and $M_n = 105\,000$ (gel permeation chromatography at 25 °C in chloroform). The low molar mass polystyrene (LMPS) was obtained from Polymer Laboratories with $M_w \cong M_n = 9800$.

Copolymers. Two different series of copolymerization reactions were carried out to receive random copolymers of styrene and 4-vinylpyridine with different molar masses and low 4-vinylpyridine contents. One series of copolymerization reactions with styrene and 2-vinylpyridine was executed to receive random copolymers of styrene and 2-vinylpyridine.

Reaction mixtures with different ratios of styrene/4-vinylpyridine or styrene/2-vinylpyridine monomers in 55 mL of toluene in a three-necked round-bottom flask (total weight of monomers ca. 16 g) and 40 mg of AIBN in 5 mL of toluene in a separate two-necked round-bottom flask, both equipped with

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Table 1. Composition, Molecular Weight, and Glass Transition Temperature of the Polystyrene Samples and the P(S-*co*-4VP) Copolymers

code	% 4VP	M_V (g/mol) × 10^{-3}	T_g (°C)[a]
HMPS		240	103.9
LMPS		9.8	96.4
RMO1	5.7	30.9	106.2
RMO2	8.6	33.8	108.0
RMO3	11.8	32.0	108.9
RMO4	15.6	32.7	106.5
RMO5	16.9	26.0	105.2
RMO6	21.4	28.0	104.9
RMO7	7.1	70.6	108.2
RMO8	10.7	63.3	110.4
RMO9	13.9	55.4	110.7
RMO10	18.8	62.8	113.0
RMO11	19.6	45.2	112.2
RMO12	18.9	82.5	111.7

[a] Inflection point, heating rate 10 °C/min.

Table 2. Composition, Molecular Weight, and Glass Transition Temperature of the Polystyrene Samples and the P(S-*co*-2VP) Copolymers

code	% 2VP	M_V (g/mol) × 10^{-3}	T_g (°C)[a]
HMPS		240	103.9
LMPS		9.8	96.4
RMA1	5.9	84.6	106.0
RMA2	8.6	68.6	104.5
RMA3	11.5	56.7	105.4
RMA4	16.1	65.1	106.0
RMA5	16.1	80.9	106.2
RMA6	17.3	55.1	106.0
RMA7	20.2	49.6	104.7
RMA8	23.2	58.2	91.9
RMA9	31.2	62.4	95.7
RMA10	35.9	46.3	91.9

[a] Inflection point, heating rate 10 °C/min.

a serum cap, were degassed by the usual freeze−thaw method. The monomer mixture was allowed to warm to the desired temperature of 80 or 60 °C in a thermostatic bath, whereafter the initiator solution was added. Reaction times were 3 h (80 °C) or 16 h (60 °C) to allow a conversion to about 10%. To stop the polymerization, hydroquinone was added. The polymers were precipitated in hexane, filtered off, and dried at 40 °C in a vacuum. For the copolymerization reactions involving 2-vinylpyridine only the reaction temperature of 60 °C was used.

Characterization. The composition of the copolymers was determined by elemental analysis. Viscosity-average molecular weights (M_V) were measured in toluene at 25 °C using the Mark−Houwink relation[9] $[\eta] = 7.5 \times 10^{-5} M_V^{0.76}$. The glass transition temperatures were determined using a Perkin-Elmer DSC-7 employing a heating rate of 10 °C /min. The results are collected in Table 1 for the copolymers with 4-vinylpyridine and in Table 2 for the copolymers with 2-vinylpyridine. As expected, the glass transition temperatures increase with increasing amounts of 4VP (2VP) except for the highest amounts of vinylpyridine where they decrease again. The reason for this effect is unclear, but it must somehow be related to chemical correlations (blocky, head-to-head versus head-to-tail, etc.). This is furthermore supported by the fact that the glass transition becomes rather broad (30 °C) for high vinylpyridine content copolymers. Pure P4VP and P2VP have a glass transition temperature of 148 and 104 °C, respectively.

Blend Preparation and Measurements. Blends of 50/50 wt % polystyrene and copolymer were prepared by dissolving equal amounts of both compounds in chloroform, followed by evaporation of chloroform. The glass transition temperatures of the blends, before and after aging, were measured with DSC2920 of TA-Instruments in the modulated mode with a modulation of 0.5 °C, a period of 60 s, and a heating rate of 1 °C/min.

Annealing of the blends was performed at 86.5 °C in a thermostatic block after the samples were heated to 160 °C to promote equilibration in the liquid state.

Results and Discussion

It is well-known that most polymer pairs are immiscible in the melt. Because of the high molar mass of the components involved, only a very small positive exchange interaction, i.e., a very small positive χ parameter value, can be tolerated.[10] If, as is usually the case, two polymers are almost completely immiscible (i.e., strong segregation regime), it is obviously impossible to determine the corresponding interaction parameter from phase behavior observed. One possible alternative is to take very short chain lengths, i.e., oligomers or even low molar mass analogues.[11,12] However, a more convenient way is to use appropriate random copolymers. Almost two decades ago, a simple mean-field theory was introduced to describe the phase behavior in random copolymer blends in terms of the various groups present.[13−15] Here we are interested in the special case of a blend of a polymer P(A) and a random copolymer P(A_x-*co*-B_{1-x}). The Gibbs free energy of mixing per segment for such a blend, assuming monodisperse polymers with chain lengths N_1 and N_2, is given by

$$\frac{\Delta g_m}{kT} = \frac{\varphi}{N_1} \ln \varphi + \frac{1-\varphi}{N_2} \ln(1-\varphi) + \chi\varphi(1-\varphi) \quad (1)$$

In this particular case the interaction parameter is given by the following expression (in terms of solubility parameters already presented long ago by Scott[16])

$$\chi = (1-x)^2 \chi_{AB} \quad (2)$$

Now, miscibility requires

$$\chi \le \chi_c = \frac{1}{2}\left(\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}}\right)^2 \quad (3)$$

which can obviously be satisfied taking $1 - x$ sufficiently small. This equation demonstrates that an estimate for χ_{AB} may be obtained using a range of $1 - x$ values. In our case the value of $\chi_{S,4VP}$ ($\chi_{S,2VP}$) can be determined by studying the critical copolymer composition $1 - x$ for which PS and P(S_x-*co*-$4VP_{1-x}$) (P(S_x-*co*-$2VP_{1-x}$)) are on the borderline of miscibility. This method has been used successfully in the past among others to obtain interaction parameter values between styrene and *o*- or *p*-fluorostyrene.[17,18]

The use of appropriate random copolymer blends involving monomers with a large unfavorable exchange interaction implies that only a small incorporation of the comonomer (i.e., 4VP or 2VP in our case) can be tolerated. This in turn implies that the glass transition temperatures (T_g's) of the homopolymer (PS) and the copolymer (P(S-*co*-4VP), P(S-*co*-2VP)) will be very similar. As a consequence, the simple criterion according to which two T_g's correspond to phase separation and one composition-dependent T_g corresponds to miscibility cannot always be easily applied. However, precisely for this reason, we developed a decade ago an alternative thermal analysis procedure involving physical aging (i.e., thermal annealing in the glassy state).[19−23] As is well documented in the literature now, if a phase-separated blend involving polymers with similar glass

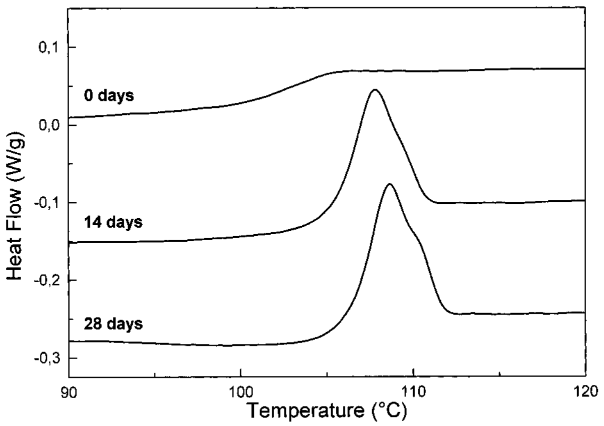

Figure 1. Total heat flow curves of a 50−50 wt % blend of high molar mass polystyrene (HMPS, Table 1) and random copolymer P(S-*co*-$4VP_{0.107}$) (RMO8, Table 1) as a function of annealing time in the glassy state at 86.5 °C.

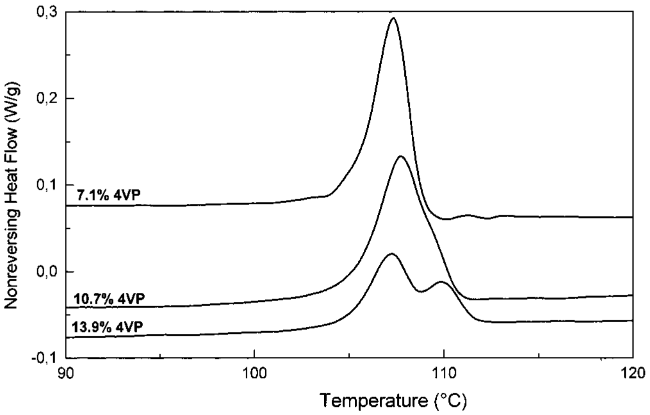

Figure 2. Nonreversing heat flow curves of 50−50 wt % blends of high molar mass polystyrene (HMPS) and random copolymers P(S-*co*-$4VP_{0.071}$), P(S-*co*-$4VP_{0.107}$), and P(S-*co*-$4VP_{0.139}$) (RMO7, RMO8, and RMO9; Table 1) after annealing for 11 days in the glassy state at 86.5 °C.

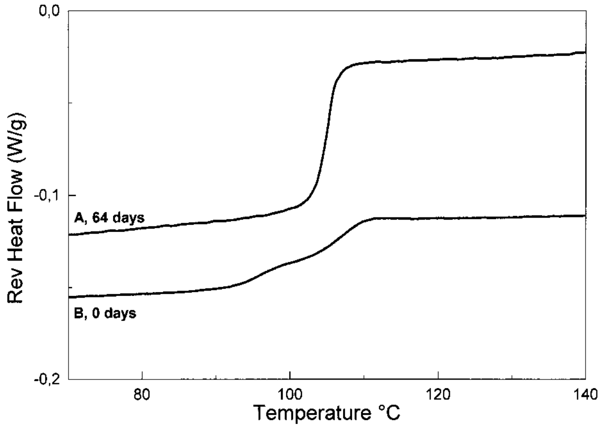

Figure 3. Reversing heat flow curves of 50−50 wt % blends of low molar mass polystyrene (LMPS, Table 1) and (A) P(S-*co*-$4VP_{0.139}$) (RMO9, Table 1) and (B) P(S-*co*-$4VP_{0.188}$) (RMO10, Table 1). Sample A annealed for 64 days at 86.5 °C; sample B not annealed.

transition temperatures is annealed in the glassy state approximately 15 °C below their glass transition temperature, a subsequent differential scanning calorimetry (DSC) scan will exhibit two separate enthalpy relaxation peaks. If, on the other hand, the blend is homogeneous, the same procedure will show a single enthalpy recovery peak only. Where necessary, i.e., if the respective glass transition temperatures were too close, this procedure has been applied to our blends. With the advent of modulated differential scanning calorimetry additional options became available,[24−26] which will be illustrated here by presenting reversing and nonreversing heat flow curves besides the usual total heat flow. For selected cases the phase behavior concluded from the thermal analysis procedure has furthermore been verified by optical microscopy using phase contrast.

The composition of all blends investigated is 50−50 wt %. Since the molar masses of the homopolymer PS and the random copolymers used are different, this implies an approximation. A blend observed to be homogeneous for this composition may actually be phase separated at a somewhat different composition. Because this only occurs for blends having a critical point (lower critical solution temperature) near the temperature of equilibration (160 °C), the effect will be small. Figure 1 shows the total heat flow curves for a blend of the high molar mass PS sample (HMPS, Table 1)) and the random copolymer P(S-*co*-$4VP_{0.107}$) (RMO8, Table 1) as a function of annealing *time* at 86.5 °C. It is quite obvious that after sufficiently long annealing times the enthalpy recovery peaks of the two different phases start to separate, resulting in an enthalpy recovery peak with a shoulder. At even longer annealing times two separate peaks will become visible; however, the result presented suffices to demonstrate this particular sample to be phase separated. Figure 2 presents the nonreversing heat flow curves for three different blends involving HMPS and random copolymers of styrene and 4-vinylpyridine with 7.1, 10.7, and 13.9% 4VP annealed for 11 days at 86.5 °C. For the blend of the random copolymer with the highest amount of 4VP (i.e., 13.9%) this annealing time is already long enough to give rise to two separate enthalpy recovery peaks, and the phase-separated state of the system is obvious. For the random copolymer with 10.7% 4VP the annealing time of 11 days is just on the borderline; however, as confirmed by Figure 1, this system is also phase-separated. There are no indications that the enthalpy recovery peak of the blend of HMPS and the random copolymer containing the least amount of 4VP, i.e., 7.1%, is composed of two separate peaks. That in this case we are really dealing with a homogeneous system is confirmed by much longer annealing time studies. Finally, as a last example, Figure 3 shows the reversing heat flow curves of blends of the low molar mass PS (LMPS, Table 1) with a copolymer involving 13.9% 4VP and another copolymer with 18.8% 4VP. The reversing heat flow curve of the former shows no sign of phase separation even after annealing for 64 days at 86.5 °C. A reversing heat flow curve of a sufficiently long annealed phase-separated sample shows two separate specific heat jumps; the total heat flow curve and the nonreversing heat flow curve will exhibit two separate peaks as illustrated in Figures 1 and 2. Hence, it is safe to conclude that this particular system is homogeneous. The blend involving the copolymer with 18.8% 4VP on the other hand is characterized by a reversing heat flow curve exhibiting two T_g's already without any annealing, convincingly demonstrating that this system is phase-separated.

Table 3 summarizes the pertinent observations for blends of polystyrene and random copolymers of styrene and 4-vinylpyridine. On the basis of these data, employ-

Table 3. Lower and Upper Bounds for the Flory−Huggins Interaction Parameter $\chi_{S,4VP}$

code	$1 - x$	N_{P4VP}	N_{PS}	state	$\chi_{S,4VP}$
RMO2+HMPS	0.086	322	2308	mixed	≤0.40
RMO3+HMPS	0.118	305	2308	separated	>0.22
RMO5+LMPS	0.169	248	94	mixed	≤0.49
RMO6+LMPS	0.214	267	94	separated	>0.30
RMO7+HMPS	0.071	672	2308	mixed	≤0.35
RMO8+HMPS	0.107	603	2308	separated	>0.17
RMO9+LMPS	0.139	528	94	mixed	≤0.56
RMO10+LMPS	0.188	598	94	separated	>0.29

Table 4. Lower and Upper Bounds for the Flory−Huggins Interaction Parameter $\chi_{S,2VP}$

code	$1 - x$	N_{P2VP}	N_{PS}	state	$\chi_{S,2VP}$
RMA9+LMPS	0.312	594	94	mixed	≤0.107
RMA10+LMPS	0.359	441	94	separated	>0.088
RMA3 +HMPS	0.115	540	2308	mixed	≤0.154
RMA4+HMPS	0.161	619	2308	separated	>0.072

ing eq 3, lower and upper bounds for $\chi_{S,4VP}$ can be derived. Because we are dealing with polydisperse polymers, the precise relation differs from eq 3. Koningsveld and co-workers[27] demonstrated that this equation remains a very good approximation provided weight-average chain lengths are used. Because these data are not available for the copolymers, we used the viscosity-averaged molar masses to obtain the chain lengths, taking the styrene monomer as a segment. It should be noted that the results are relatively insensitive to the precise value of the chain length. The thus obtained bounds are presented in Table 3, from which we may conclude that

$$0.30 < \chi_{S,4VP} \leq 0.35 \qquad (4)$$

Since the χ parameter value is in general temperature dependent, this inequality is supposed to hold near 160 °C, where the equilibration took place. This value is relatively large; however, it is still considerably smaller than for styrene and acrylonitrile, for which values as large as $\chi_{S,AN} \cong 0.6-0.8$ have been reported.[28−31] It is also considerably smaller than the range of values obtained by Clarke and co-workers,[6] except for their lower bound of 0.38 derived from contact angle measurements of a PS droplet on a P4VP layer which actually is very close to our results. For block copolymers of polystyrene and poly(4-vinylpyridine) inequality (4) implies that the incompatibility parameter will in general still satisfy $\chi N < 100$, implying a strong rather than super strong segregation regime.

To corroborate the validity of our approach, a similar study has been performed using 2VP-containing polymers (Table 2). Table 4 summarizes the pertinent results of this miscibility study involving the random copolymers of styrene and 2-vinylpyridine from which the following inequality is obtained:

$$0.09 < \chi_{S,2VP} \leq 0.11 \qquad (5)$$

This result is in excellent agreement with the well-established value of $\chi_{S,2VP} = 0.1$.[2]

Concluding Remarks

Miscibility studies of blends of polystyrene and random copolymers of styrene and 4-vinylpyridine demonstrate convincingly that the value of the Flory−Huggins parameter $\chi_{S,4VP}$ is of the order of 0.30−0.35, considerably smaller than derived recently from measurements involving strong segregation properties such as micellar spacing and interface thickness. Our conclusions, on the other hand, are based on a weak segregation property, i.e., the borderline of miscibility in random copolymer blends, and the analysis is based on the simplest mean-field description available. The validity of our approach is supported by the fact that applied to styrene and 2-vinylpyridine it results in a value of the interaction parameter that is in excellent agreement with the commonly accepted value. The values for $\chi_{S,4VP}$ obtained by Clarke et al.[6] from the micelle spacing vary from 1.4 to 7.5, which suggests serious deficiencies in the theoretical expressions on which the evaluation is based. Finally, Clarke et al.[6] used the interfacial width between PS and P4VP to derive a lower bound $\chi_{S,4VP} > 1.0$. This value is also considerably larger than found in the present study. In this respect it should be noted that the precise expression for the interfacial thickness and interfacial tension has been the subject of many studies.[32−37] In a most recent study Ermoshkin and Semenov[37] observed a model based on the Flory−Huggins interaction term to be inadequate for the PS/PMMA system. In conclusion, we believe phase behavior studies of random copolymer blends to be one of the best methods to obtain a reliable estimate of the value of the Flory−Huggins interaction parameter involved.

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