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End Effects in Poly(styrene)/Poly(ethylene oxide) Copolymers

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ABSTRACT: We have studied phase boundaries and critical scattering on equivalent systems of homopolymer blends and diblock copolymers with different end groups terminating the polymer chains. The aim is to investigate the effect of end groups relative to the effect of the covalent junction in diblock copolymers. Either effect intuitively causes corrections with a V^{-1} dependence on the molar volume V . Besides the experimental phase boundaries, the Flory–Huggins interaction parameter has been determined and is discussed. The polymer systems studied is based on poly(styrene), PS, and poly(ethylene oxide), PEO, where the latter polymer chain is terminated by either a hydroxy or a methoxy group. The change from hydroxy to methoxy end groups caused a change in the phase boundary of 90K and 45K for homopolymer blends ($\bar{V} = 1970 \text{ cm}^3/\text{mol}$) and diblock copolymers ($\bar{V} = 17\,700 \text{ cm}^3/\text{mol}$), respectively.

Introduction

The early theories^{1,2} of both homopolymer blends and diblock copolymers are mean field theories based on a common segmental interaction parameter, the Flory–Huggins parameter Γ . More sophisticated^{3,4} theories take fluctuation renormalizations into account but remain with the assumption of a segmental Γ parameter. Recent experiments^{5–7} have shown, however, that the Flory–Huggins parameter is not the same for homopolymer blends and diblock copolymers. A theoretical explanation for this difference has been given on the basis of the lattice cluster theory,⁸ showing that the nonrandom mixing contributions of the block junction yield a V^{-1} correction to Γ of block copolymers, V being the molar volume. The additional V^{-1} terms were predicted to be stronger than end effect corrections, assuming that the end groups being bonded to only one monomer unit.

End group effects were studied in both PS/PEO homopolymer blends and the corresponding diblock copolymers using PEO polymers with methoxy and hydroxy termination. The end group effect could thereby be directly compared to the block junction effect in diblock copolymers. Phase boundaries were determined from cloud point or rheology while composition fluctuations were measured by and small-angle neutron scattering. The composition fluctuations were analyzed by theories, which take strong fluctuations near the phase boundary into account. As a result, we got the Flory–Huggins parameter, which is set free from fluctuations and therefore principally can be compared to mean field theories. The energy contribution associated with the hydrogen bonding of the hydroxy end group to the PEO chain was calculated numerically by density functional theory and compared to the measured differences of the Flory–Huggins parameter. The relatively strong hydrogen bond interaction per molecule is classified as an end effect but should be distinguished from the much weaker effect of end monomers being bonded to only one neighbor.⁸

Theoretical Concepts

Thermodynamics Including Fluctuations. The structure factor $S(Q)$ of homopolymer blends can, on the

basis of the random phase approximation, be described by the Ornstein–Zernicke form

$$S(Q) = \frac{S(0)}{1 + \xi^2 Q^2} \quad (1)$$

where $S(0)$ is the susceptibility of composition fluctuations, Q is the momentum transfer, and ξ is the correlation length. Experimentally, this structure factor $S(Q)$ can be observed directly by neutron scattering experiments as a function of the scattering vector $Q = 4\pi/\lambda \sin(\theta)$, λ being the radiation wavelength and 2θ the scattering angle. $S(0)$ is the extrapolated (maximum) intensity of the structure factor for $Q \rightarrow 0$. The structure factor, eq 1, has a Lorentzian shape characterized by the correlation length ξ .

Theoretically, the susceptibility is related to the Gibbs free energy according to $S(0)^{-1} = \partial^2(G/RT)/\partial\Phi^2$. Generally, the susceptibility follows the scaling behavior⁵

$$S(0)^{-1} = C_+^{-1} \tau^\gamma \quad (2)$$

as a function of the reduced temperature $\tau = 1 - T_C/T$. For homopolymer blends, two universality classes are observed. At temperatures close to the critical temperature T_C , the 3-dimensional Ising model is valid with the critical amplitude C_+ and the critical exponent $\gamma = 1.239$, whereas at temperatures far away from T_C , the mean field behavior is found with the critical amplitude C_+^{MF} and the critical exponent $\gamma = 1$, respectively. The crossover between the two distinct scaling relations is described by the Ginzburg number Gi , which is proportional to the reduced crossover temperature.

On the basis of renormalization group methods to first order in the parameter $\epsilon = 4 - d$, d being the dimensionality of the system, Belyakov and Kiselev³ expressed a crossover function, which have proven to describe the susceptibility over the whole temperature range very well:

$$\hat{\tau} = (1 + 2.333\hat{S}(0)^{\Delta/\gamma})^{(\gamma-1)/\Delta} [\hat{S}(0)^{-1} + (1 + 2.333\hat{S}(0)^{\Delta/\gamma})^{-\gamma/\Delta}] \quad (3)$$

The crossover function describes the renormalized re-

duced temperature $\hat{\tau} = \tau/Gi$ as a function of the renormalized susceptibility $\hat{S}(0) = S(0)Gi/C_+^{\text{MF}}$. The phenomenological approach, which replaces the critical exponents by the critical exponents of the 3d-Ising model $\gamma = 1.239$ and $\Delta = 0.51$, yields the final eq 3. The critical mean field amplitude is related to the Flory–Huggins parameter according to

$$C_+^{\text{MF}} = \frac{1}{2}(\Gamma_s + \Gamma_o) = \frac{1}{2} T_C^{\text{MF}}/\Gamma_h \quad (4)$$

where Γ_o and Γ_h are respectively the entropic and the enthalpic terms of the Flory–Huggins parameter: $\Gamma = \Gamma_h/T - \Gamma_o$, and Γ_s is the value at the spinodal critical point, given by $\Gamma_s = 1/V_1 + 1/V_2$. The mean field critical temperature originates from the high-temperature behavior and is related to the “real” critical temperature by $T_C^{\text{MF}} = T_C/(1 - Gi)$. The thermal composition fluctuations induce additional entropy in the system, and thus lower T_C , i.e., stabilize the disordered phase of the system.

The structure factor of a diblock copolymer was first given by Leibler.² The system being a one-component system (when ideally monodisperse) does not show fluctuations at large length scales. This means that the structure factor $S(Q) \propto Q^2$ is low at small scattering angles Q (correlation hole). At high scattering angles, the structure factor shows the Q^{-2} dependence, due to the self-similarity of chain segments. Therefore, a peak is observed in the structure factor, reflecting the overall size of the copolymer, $R_g \sim 1/Q^*$. The structure factor has the form²

$$S(Q) = \frac{V}{F(x, f) - 2\Gamma_{\text{ren}}V} \quad (5)$$

where the function F is a combination of generalized Debye functions, which depends on the volume fraction of the one block, f , the squared product of the scattering angle Q and the overall radius of gyration: $x = (QR_g)^2$. The susceptibility of diblock copolymers is given by the peak intensity $S(Q^*)$. The mean field critical point is reached when Γ_s approaches the value $2\Gamma_s V = F(x^*, f)$. Fluctuation corrections were described by the theory of Fredrickson and Helfand,⁴ which introduces a renormalized interaction parameter:

$$\Gamma_{\text{ren}} V = \Gamma V - \tilde{Gi} \sqrt{S(Q^*)/V} \quad (6)$$

The additional “fluctuation” term is proportional to a Ginzburg number $\tilde{Gi} = \tilde{\nu}/\tilde{N}^{1/2}$ and implicitly to the susceptibility. The parameter $\tilde{\nu}$ reads $c^3 d\lambda/2$ according to theory⁴ and achieves 128.8 for the symmetric chain length ratio $f = 0.5$. The parameter $\tilde{N}^{1/2} = R_0^3/V$ is proportional to the number of chains perturbing a single chain with the end-to-end distance R_0 . Therefore, the Ginzburg number of this one-component system scales only with $N^{-1/2} \propto V^{-1/2}$, and the fluctuations have therefore much more significance when compared to homopolymer blends, where Gi scales as $Gi \propto N^{-1}$ due to the probability of two interpenetrating components. For a three-component polymer system,⁹ fluctuation renormalized effects are even weaker. Hypothetically, the scaling $Gi \propto N^{-\nu/2}$ for systems with ν polymer components seems to be reasonable. This kind of a scaling breaks down, however, when the entropic part of the interaction parameter plays a dominating role,

which has been shown by pressure experiments.^{10,11} The order–disorder transition temperature is predicted by the Fredrickson–Helfand theory in terms of the Flory–Huggins parameter:

$$\Gamma_{\text{ODT}} V = 10.5 + 41(\tilde{Gi}/\tilde{\nu})^{2/3} \quad (7)$$

Thus, the disordered state is stabilized, and the “real” temperature of the order–disorder transition is lowered by the fluctuations compared to the mean-field estimation alike that of homopolymer blends. The entropic character of fluctuations is more obvious in the representation of eq 7 than for homopolymer blends.

Flory–Huggins Parameter as a Mean-Field Parameter. The Flory–Huggins parameter can be determined on the basis of neutron scattering experiments⁵ by applying the more sophisticated fluctuation theories in a wide temperature range. By these methods the experimental Flory–Huggins parameter is set free from fluctuations and can be compared to mean-field theories. The lattice cluster theory of Dudowicz and Freed¹² predicts the influence of monomer structures and compressibility on the Flory–Huggins parameter within a mean-field approximation.

Historically, the interaction parameter was assumed to be identical for homopolymer blends and diblock copolymers in the concept of Flory and Huggins. Quite large differences of the Flory–Huggins parameter were observed in an experimental comparison of a corresponding homopolymer blend and diblock copolymer.^{5–7} This difference was understood as a junction effect with a V^{-1} scaling, according to the portion of the junction to the total interaction parameter. The empirical Flory–Huggins parameter reads⁵

$$\Gamma^{\text{block}} = (\Gamma_h^{\text{blend}} - A_h/V)/T - (\Gamma_o^{\text{blend}} - A_o/V) \quad (8)$$

This dependence was already expressed by Dudowicz and Freed⁸ from the lattice cluster theory and proposed to describe the experimental results of a PEP–PEE diblock copolymer. The junction corrections of diblock copolymers were predicted to be an order of magnitude larger than the end effects, which consider the end monomers being bonded to only one monomer.

Ab Initio Calculation of Hydrogen Bond Strength. Density functional theory (DFT) ab initio calculations were performed with the DMOL³ program.¹³ We used the BLYP density-functional^{14,15} and the DNP basis set¹⁶ in the DMOL program. Default geometry optimization parameters were chosen in the DMOL program.

A measure for the hydrogen bond strength were obtained by calculating the interaction energy between two ethylene oxide oligomers (trimers). The oligomers were terminated with a hydroxy and a methoxy group in the two ends, respectively. The oligomers were placed in a conformation allowing for a hydrogen bond between the terminal –OH on one oligomer and a central ether oxygen on the other oligomer (see Figure 1a). The oligomer containing the H-bond donating group was placed such that the H-bond pointed along a SP³ lone pair of the acceptor oxygen and the van der Waals contacts between the two oligomers were minimal. The structure was then geometry optimized, and the energy difference between the complex and the two isolated oligomers (in their optimized structures) was taken as a measure for the H-bond strength. We did not attempt

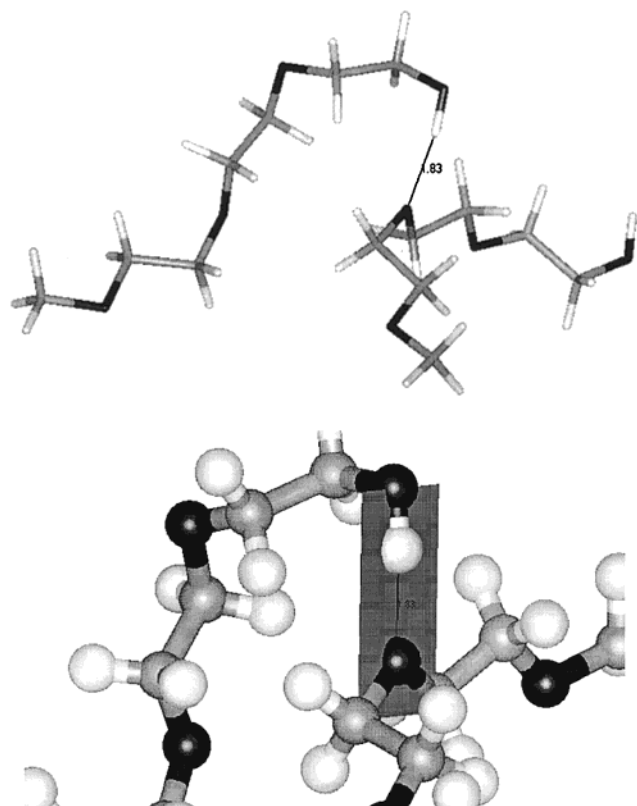


Figure 1. (a, top) Complex of ethylene oxide trimers showing the optimized geometry used to calculate hydrogen-bond strength: white = hydrogen; gray = carbon; black = oxygen. (b, bottom) Close-up on the geometry of the hydrogen bond. The plane is a least-squares plane for O–H, C–O–C atoms.

to correct for basis set superposition errors or to average interaction energies over different structures.

The interaction energy was 14.5 kJ/mol. The optimized structure showed a hydrogen bond with an O–H distance of 1.83 Å. The O–H–O was nearly linear and bisecting the C–O–C angle (Figure 1b). This H-bond geometry is observed in many structures¹⁷ though it is less common than the initial conformation before geometry optimization, where the H-bond points in the direction of the SP³ lone pair.

Experimental Section

Sample Synthesis and Characterization. The poly(styrene)-*block*-poly(ethylene oxide) (PS-PEO) diblock copolymers were synthesized by anionic polymerization under inert argon atmosphere in two steps, following a procedure of Hillmeyer.¹⁸ The poly(styrene) block was synthesized in cyclohexane of 30 °C with *sec*-butyllithium as initiator. After 2 h, when a conversion of over 99.9% was achieved, an excess of ethylene oxide monomer was added to the living polymer solution in order to end-cap the styrene polymer with one ethylene oxide monomer. After half an hour, the living polymers were terminated by acetic acid. After an additional waiting period of half an hour, the polymer solution was concentrated by evaporating the solvent, and the polymer could be precipitated in methanol. The polymer was filtered and dried under high vacuum.

Naphthylpotassium was synthesized following an established procedure.¹⁹ The dry poly(styrene)-alcohol polymer was dissolved in THF at 50 °C under inert argon atmosphere. Potassium naphthalene was added with a syringe by means of a titration. After the solution kept a slight green color for 10 min, the ethylene oxide monomer was added for polymerization. The conversion could be followed by pressure measurements. A conversion of 99.9% took typically 40 h. The

Table 1. Homopolymer Blends Studied^a

	$M_n(\text{PS})$ [g/mol]	$M_n(\text{PEO})$ [g/mol]	\bar{V}_n [cm ³ /mol]	T_C [K]	$\Phi_{C,\text{vol}}$
h-PS/PEO(MME)	1360	1450	1380	417 ^b	0.42
d-PS/PEO(MME)	1460	1450	1380	391.4 ^c	0.43
h-PS/PEO(MME)	2100	2000 ^(F)	2010	485 ^b	0.41
d-PS/PEO(MME)	2150	2000 ^(F)	1970	482.2 ^c	0.45
h-PS/PEO(MME)	2530	2000 ^(F)	2190	499 ^b	(0.42)
h-PS/PEO(DME)	2100	2000 ^(F)	2010	395 ^b	0.42
d-PS/PEO(DME)	2150	2000 ^(F)	1970	392.5 ^c	0.41
h-PS/PEO(DME)	2530	3000 ^(H)	2710	488 ^b	0.43
d-PS/PEO(DME)	2720	3000 ^(H)	2710	458.8 ^c	0.43

^a (F), (H) bought from Fluka and Hoechst. M_n is from stoichiometry. \bar{V}_n is calculated from densities at 413 K ($\rho_{\text{h-PS}} = 0.969$ g/cm³, $\rho_{\text{d-PS}} = 1.044$ g/cm³, $\rho_{\text{PS}} = 1.064$ g/cm³). ^b T_C and Φ_C is measured by cloud point. ^c T_C and Φ_C is measured by SANS.

polymerized living polymer solution was split in two containers. One section was terminated by acetic acid and the other one by methyl iodide. After half an hour, the ready polymers were washed in chloroform and an aqueous sodium carbonate solution for three times. The final chloroform solution was concentrated by a rotorvapor and dried under high vacuum. The two diblock copolymers are called PS-PEO-OH and PS-PEO-me in the following.

The pure homopolymers were synthesized by standard procedures, which compare to synthesis of the single blocks of the diblock copolymer. The poly(ethylene oxide) was synthesized with an activated ethylene glycol monomethyl ether, which proved to be better than simple methanol. The poly(ethylene oxide) homopolymer was also terminated by the two mentioned ways, and thus monomethoxypoly(ethylene oxide) (PEO(MME)) and dimethoxypoly(ethylene oxide) (PEO(DME)) was yielded. Some commercial PEO(MME) from Fluka and Hoechst was methoxylized in THF solution by adding sequentially sodium hydride and methyl iodide. All PEO polymers were washed with chloroform and water.

The number-average molecular weights listed in Table 1 are determined from the synthesis stoichiometry. The molar masses of the homopolymers (PS and PEO) and of the first block of the diblock copolymers (PS-OH) were confirmed by size exclusion chromatography (SEC) measurements with THF as solvent and an array of standard polymers within an accuracy of better than 10%. Another cross check was made by MALDITOF for single polymers. The diblock copolymers were measured by SEC and ¹H NMR (only protonated samples). The chain length ratios of ¹H NMR measurements agreed with stoichiometry within 2%. We therefore trusted in the stoichiometry of the deuterated samples. A possibility of MALDITOF did not give results since the molar masses were too high. Molar mass distributions were determined by SEC and were found to be narrow ($M_w/M_n < 1.1$).

The order-disorder transition temperatures have been determined by rheology.²⁰ Figure 2 represents the elastic modulus of two symmetric diblock copolymers upon heating. At the apparent order-disorder transition temperature T_{ODT} the elastic modulus decreases strongly. The lower molar mass sample has a lower T_{ODT} than the higher molar mass sample. For the partially deuterated samples the T_{ODT} has been determined by SANS experiments, which is described below.

The phase diagrams of homopolymer blends can be measured by observing the cloud points (Figure 3). The single protonated samples were filled into a glass tube. The composition was determined by weight. The highly evacuated and sealed glass tubes were then heated in an oil bath. At high temperatures the polymers mixed. The average of several cooling and heating runs yielded an experimental cloud point, which should be a measure of the binodal within the according error bars. The critical composition is expected to be at the maximum cloud-point temperature.

Small-angle neutron scattering (SANS) experiments were performed at the DR3 reactor at the Risø National Laboratory in Denmark. A new furnace was constructed to hold three quartz glass cuvettes, which were sealed off under

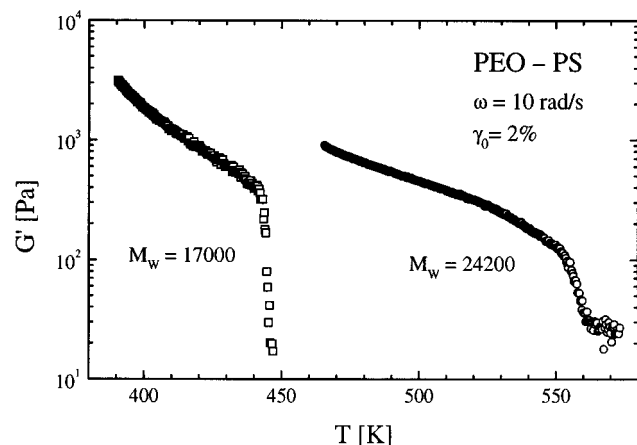


Figure 2. Dynamical mechanical elastic moduli as a function of temperature for the samples h-PS-PEO-OH(4) (\square) and h-PS-PEO-OH(1) (\circ). The parameters used were $\omega = 10$ rad/s, $\gamma_0 = 2\%$ in a shear sandwich geometry. The heating rate was 2 K/min.

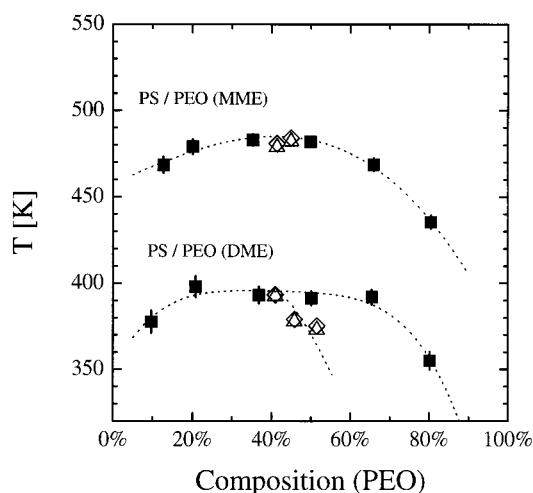


Figure 3. Experimental phase diagram obtained from cloud point (\blacksquare) and SANS measurements. By SANS measurements the binodal (\diamond) and spinodal (\triangle) temperature were obtained independently. The detailed SANS experiments close to the critical point determine the critical point by the difference between binodal and spinodal temperature.

vacuum. With these cuvettes our samples could be heated to 280 °C without degrading. A cross check was made by thermogravimetric analysis (TGA) under a nitrogen atmosphere, where degradation was observable for temperatures higher than 290 °C. The three glass cuvettes were placed in an aluminum drawer, which was inserted into the copper furnace. Thus, three samples could run with the same temperature program without waiting any additional time for equilibration. The temperature of the furnace was controlled between 10 and 300 °C with an accuracy of 0.05 K by an Eurotherm controller. A separate temperature element close to the samples allowed to read off the exact sample temperature. The counter cooling system ran with water at constant temperature of 5 °C.

The scattering data were corrected for background scattering and detector sensitivity. The data were radially averaged and calibrated in absolute units by a 1 mm water standard. The resulting absolute macroscopic cross section $d\Sigma(Q)/d\Omega$ in units of cm^{-1} is related to the structure factor $S(Q)$, according to $d\Sigma(Q)/d\Omega = S(Q)\Delta\rho^2/N_A$, where $\Delta\rho$ is the difference of the coherent scattering length densities of the polymer components ($\rho_{\text{d-PS}} = 0.099 \text{ mol/cm}^3$, $\rho_{\text{PEO}} = 0.010 \text{ mol/cm}^3$), and the Avogadro number is N_A . The scattering experiments were performed in the momentum transfer range of $0.009/0.007/0.004 \text{ \AA}^{-1} \leq Q \leq 0.070/0.054/0.035 \text{ \AA}^{-1}$, by using the neutron

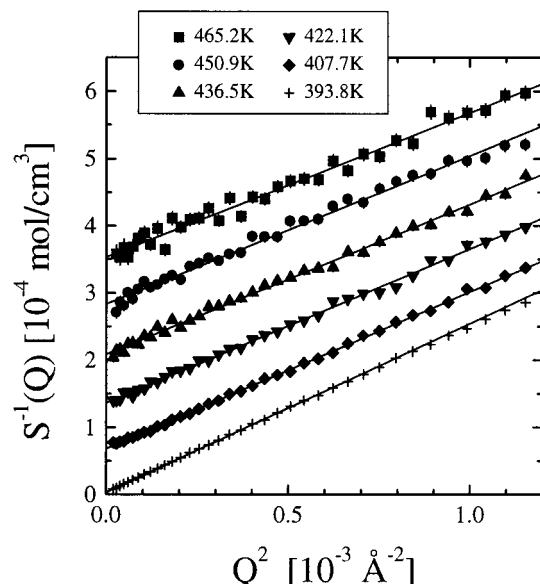


Figure 4. Zimm plot of the structure factor of the d-PS/PEO(DME) blend with the average molar volume of $1970 \text{ cm}^3/\text{mol}$ for different temperatures. Measurements were taken with a 6 m detector distance. Upon lowering the temperature the critical point is approached.

wavelength of 7.7 Å, the detector distances of 3/4/6 m, and identical collimation distances.

SANS Results

The experimental structure factor of the d-PS/PEO(DME) homopolymer blend with molecular masses of 2150/2000 g/mol is shown in Figure 4 in the Zimm representation. At high temperatures the structure factor is low, and therefore the extrapolated inverse susceptibility is high. Upon lowering the temperature, the structure factor increases and the inverse susceptibility decreases. This behavior is typical for an upper critical solution temperature (UCST) system.

The experimental structure factor of 2 diblock copolymers with different end groups is compared in Figure 5. The structure factor of the d-PS-PEO-OH(5) has a larger value than that of the d-PS-PEO-me(5). With the same contrast factor, this means that the experimental temperature of 443.7 K is most close to the order-disorder transition temperature of the d-PS-PEO-OH(5). We used the theory of Leibler (eq 5) with the experimental resolution function to describe the peak of the structure factor.^{21,22} The peak maximum of the desmeared structure factor is the susceptibility used in the following.

The inverse susceptibility of the two PS/PEO homopolymer blends with different PEO end groups is plotted in Figure 6 and compositions equal to respectively $\phi = 0.45$ and $\phi = 0.41$ for the d-PS/PEO(MME) and d-PS/PEO(DME) blends. The inverse susceptibility is decreasing on lowering the temperature in the one-phase region. Upon further cooling the binodal line is crossed, and the observed inverse susceptibility increases again. Since the composition of the blends is very critical, and the inverse susceptibility approaches almost any small number, there is no observable difference between the binodal and spinodal temperature, e.g., $T_B = T_C$ for the given composition.²³ The clear curvature of the inverse susceptibility is demonstrated by drawing the mean-field line at high temperatures,

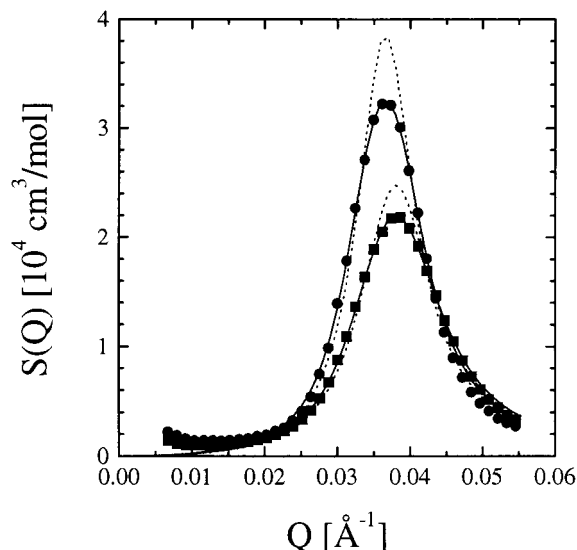


Figure 5. Structure factor as a function of the scattering vector Q for the d-PS-PEO-OH(5) (●) and the d-PS-PEO-me(5) (■). Measurements were taken with a 4 m detector distance at a temperature of 443.7 K. The solid lines represent fits of the Leiber function including the resolution function of the instrument. The dotted lines depict the desmeared Leiber function.

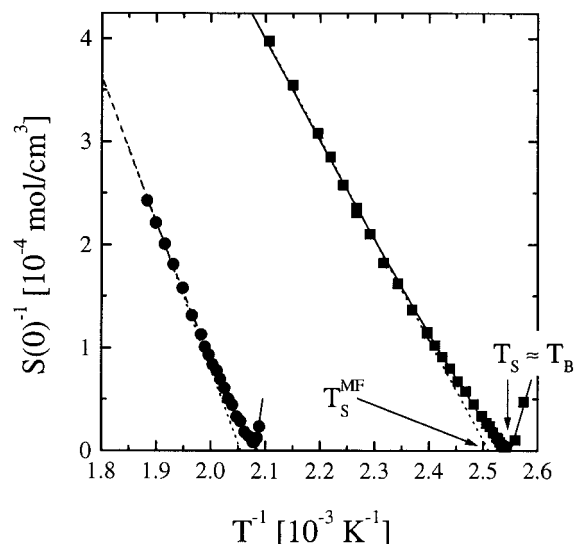


Figure 6. Inverse susceptibility as a function of the inverse temperature for the d-PS/PEO(MME) (●) and the d-PS/PEO(DME) (■) blends with the average molar volume of 1970 cm³/mol. The fits of the crossover function are depicted by a dashed and solid line for the d-PS/PEO(MME) and the d-PS/PEO(DME), respectively. The dotted straight lines correspond to the mean-field approximation, which extrapolates to the critical mean-field temperature T_s^{MF} . The spinodal temperature T_s extrapolates from the inverse susceptibility $S^{-1}(0) \rightarrow 0$, and the binodal temperature T_B is observed from the increase of the inverse susceptibility. Within the experimental error we find $T_s = T_B$.

which extrapolates to a higher critical mean-field temperature T_C^{MF} . For the d-PS/PEO(DME) blend the whole temperature range of T_B , T_C , and T_C^{MF} is about 90 K lower than for the d-PS/PEO(MME) blend.

The crossover function of Belyakov and Kiselev describes the susceptibility of the homopolymer blends over the whole temperature range in the one-phase region. This was technically done by solving the inverse temperature as a function of susceptibility. Since eq 3 is already solved for the reduced temperature \tilde{t} , the final

Table 2. Diblock Copolymers Studied^a

	f_{PEO}	M_n [g/mol]	V_n [cm³/mol]	T_{ODT} [K]
d-PS-PEO-OH (4)	0.5 ^c	11 400	10 800	
h-PS-PEO-OH (4)	0.5 ^b	17 000	16 700	445 ^d
d-PS-PEO-OH (5)	0.5 ^c	18 700	17 700	437 ^e
d-PS-PEO-OH (6)	0.5 ^c	20 200	19 200	457 ^e
d-PS-PEO-OH (3)	0.5 ^c	21 800	20 700	497 ^e
h-PS-PEO-OH (1)	0.51 ^b	24 200	23 800	553 ^d
d-PS-PEO-me (4)	0.5 ^c	11 400	10 800	
h-PS-PEO-me (4)	0.5 ^b	17 000	16 700	323 ^d
d-PS-PEO-me (2)	0.5 ^c	17 800	16 900	336 ^e
d-PS-PEO-me (5)	0.5 ^c	18 700	17 700	392 ^e
d-PS-PEO-me (6)	0.5 ^c	20 200	19 200	433 ^e
d-PS-PEO-me (3)	0.5 ^c	21 800	20 700	459 ^e
h-PS-PEO-me (1)	0.51 ^b	24 200	23 800	572 ^d

^a M_n is from stoichiometry; V_n is calculated from densities at 413 K. ^b f_{PEO} is from NMR. ^c f_{PEO} is from stoichiometry. ^d T_{ODT} is measured by rheology. ^e T_{ODT} is measured by SANS.

result seems quite similar:

$$\frac{1}{T} = \frac{1}{T_C} (1 - Gi(1 + 2.333(S(0)Gi/C_+^{MF})^{\Delta/\gamma})^{(\gamma-1)\Delta} [C_+^{MF}/(S(0)Gi) + (1 + 2.333(S(0)Gi/C_+^{MF})^{\Delta/\gamma})^{-\gamma/\Delta}]) \quad (11)$$

With standard nonlinear fitting programs (f.i. Origin5.0) the fitting was performed on the inverse temperature vs inverse susceptibility data set, leaving the critical temperature T_C , the Ginzburg number Gi , and the mean-field critical amplitude C_+^{MF} as free fitting parameters. The results from the fitting procedure are presented in Table 3. The accessible temperature range of the d-PS/PEO(DME) system with the average molar volume of 2710 cm³/mol was too narrow for a three-parameter fit, and thus the Ginzburg number was fixed with a value of 0.006. Here we used the empirical $Gi \propto V^{-2}$ law²⁴ for the extrapolation from the lower molar volume system.

For the diblock copolymers the inverse susceptibility decreases on lowering the temperature in the one-phase region as well (Figure 7). The behavior is much more curved when compared to the homopolymer blend, indicating that fluctuation renormalizations are much more important. Upon further cooling the inverse susceptibility shows a sudden decrease at the order-disorder transition temperature T_{ODT} , which is found to be lower for the d-PS-PEO-me(5) compared to the d-PS-PEO-OH(5). This temperature difference of 45 K is lower compared to that of homopolymer blends.

The susceptibility of the diblock copolymer in the one-phase region can be solved as a function of the inverse temperature. This was done with eqs 5 and 6 by the formula of Kardar, since the elimination of Γ_{ren} results in a third-order polynomial of $S(Q^*)^{-1/2}$. The discriminant $D = 8/27(\Gamma - \Gamma_s)^3 + \hat{c}^2$ tells whether there are one or three solutions. The only physical one is presented in the following

$$S^{-1}(Q^*) = -\frac{8}{3}(\Gamma - \Gamma_s) \cos^2\left(\frac{1}{3} \arccos\left(\hat{c}\left(-\frac{2}{3}(\Gamma - \Gamma_s)\right)^{-3/2}\right)\right) \quad \text{for } D < 0$$

$$\left(\sqrt[3]{\hat{c} + \sqrt{D}} - \frac{2}{3}(\Gamma - \Gamma_s)/\sqrt[3]{\hat{c} + \sqrt{D}}\right)^2 \quad \text{for } D \geq 0 \quad (12)$$

with the parameter $\hat{c} = \tilde{G}iV^{-3/2}$. The fitting procedure was applied for eq 12 after replacing Γ with the

Table 3. Homopolymer Blend Parameters from SANS Measurements^a

	d-PS/PEO (MME)	d-PS/PEO (MME)	d-PS/PEO (DME)	d-PS/PEO (DME)
V_n [cm ³ /mol]	1380	1970	1970	2710
T_C [K]	391.4 ± 0.1	482.2 ± 0.2	392.5 ± 0.1	458.8 ± 0.2
$Gi \times 100$	3.2 ± 0.8	2.3 ± 0.4	1.25 ± 0.20	0.6 (set)
C_+^{MF} [cm ³ /mol]	190.9 ± 6.3	245.0 ± 6.3	319.6 ± 7.5	220.3 ± 12
Γ_σ [10 ⁻³ mol/cm ³]	1.20 ± 0.09	1.04 ± 0.05	0.562 ± 0.037	0.40 ± 0.06
Γ_h [K mol/cm ³]	1.06 ± 0.03	1.01 ± 0.02	0.622 ± 0.013	0.53 ± 0.03

^a T_C , Gi , and C_+^{MF} originate from the fitting of the crossover function.

Table 4. Diblock Copolymer Parameters from the SANS Measurements^a

	d-PS-PEO-OH (4)	d-PS-PEO-OH (5)	d-PS-PEO-OH (6)	d-PS-PEO-OH (3)
V_n [cm ³ /mol]	10800	17700	19200	20700
T_{ODT} [K]		437 ± 1	457 ± 1	497 ± 2
\tilde{Gi}	4.8 (set)	3.9 ± 0.6	3.6 (set)	3.5 (set)
Γ_σ [10 ⁻³ mol/cm ³]	0.152 ± 0.018	0.121 ± 0.036	-0.013 ± 0.006	0.033 ± 0.006
Γ_h [K mol/cm ³]	0.531 ± 0.008	0.456 ± 0.056	0.351 ± 0.003	0.384 ± 0.003

	d-PS-PEO-me (4)	d-PS-PEO-me (2)	d-PS-PEO-me (5)	d-PS-PEO-me (6)	d-PS-PEO-me (3)
V_n [cm ³ /mol]	10800	16900	17700	19200	20700
T_{ODT} [K]		336 ± 3	392 ± 1	433 ± 1	459 ± 4
\tilde{Gi}	4.8 (set)	3.24 ± 0.12	3.8 ± 0.3	3.6 (set)	3.5 (set)
Γ_σ [10 ⁻³ mol/cm ³]	0.105 ± 0.018	-0.112 ± 0.011	0.009 ± 0.030	-0.047 ± 0.006	-0.036 ± 0.012
Γ_h [K mol/cm ³]	0.435 ± 0.008	0.285 ± 0.008	0.368 ± 0.025	0.322 ± 0.003	0.326 ± 0.007

^a \tilde{Gi} , Γ_σ , and Γ_h originate from the fitting of the Fredrickson-Helfand theory.

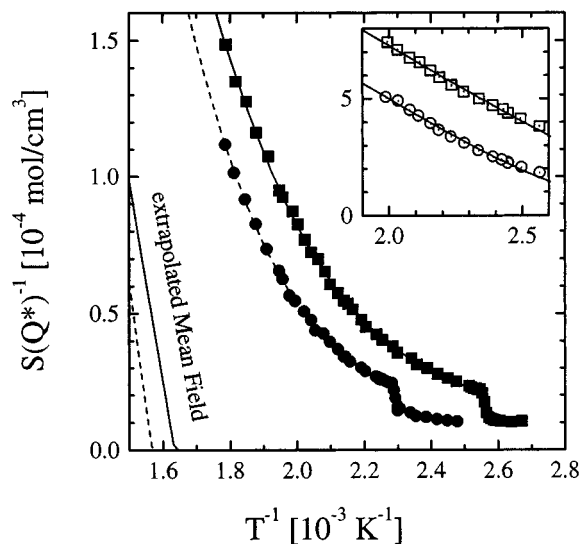


Figure 7. Inverse susceptibility as a function of the inverse temperature for the d-PS-PEO-OH(5) (●) and the d-PS-PEO-me(5) (■). The fits of the Fredrickson-Helfand theory are depicted by a dashed and solid line for the d-PS-PEO-OH(5) and the d-PS-PEO-me(5), respectively. The straight lines of the same line type correspond to the extrapolated mean-field approximation. The order-disorder transition temperature T_{ODT} is observed at the sudden drop of the inverse susceptibility. The inset depicts the inverse susceptibility of the d-PS-PEO-OH(4) (○) and the d-PS-PEO-me(4) (□) with corresponding Fredrickson-Helfand theory.

temperature dependence $\Gamma = \Gamma_h/T - \Gamma_\sigma$. The three free fitting parameters were the enthalpy and entropy portion of the Flory-Huggins parameter Γ_h and Γ_σ and the parameter \tilde{c} , which is proportional to the Ginzburg number.

The fits of the Fredrickson-Helfand theory (eq 12) are shown by the curved lines in Figure 7. The corresponding mean-field lines in the limit of vanishing fluctuations ($\tilde{Gi} \rightarrow 0$) are depicted with straight lines of the same style. The inverse susceptibility of two differ-

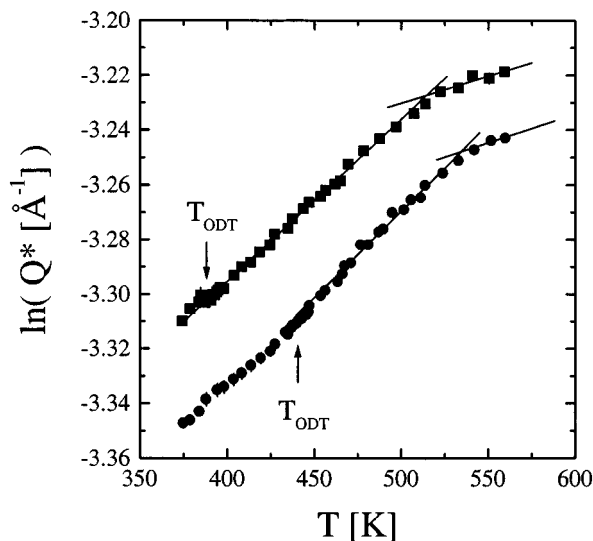


Figure 8. Logarithmic peak position Q^* as a function of the temperature for the d-PS-PEO-OH(5) (●) and the d-PS-PEO-me(5) (■). The change of slope is indicated by straight lines. The order-disorder transition temperatures are just indicated as a reference.

ent samples with much lower molar masses (11 400 g/mol) is plotted vs the inverse temperature in the inset of Figure 7. The curvature has already decreased so much that the Ginzburg number had to be extrapolated from the high molar mass samples with the scaling $\tilde{Gi} \propto V^{-1/2}$. The corresponding fitted theory is plotted by solid lines in Figure 7. The results from the fitting procedure are summarized in Table 4. The Ginzburg number was also set fixed in the case of a too narrow temperature range.

In Figure 8 the peak position Q^* is plotted as a function of temperature for the d-PS-PEO-me(5) and d-PS-PEO-OH(5). The d-PS-PEO-OH(5) has a smaller Q^* , which speaks for a slightly stretching of the diblock copolymer. Within statistics, no discontinuity of the

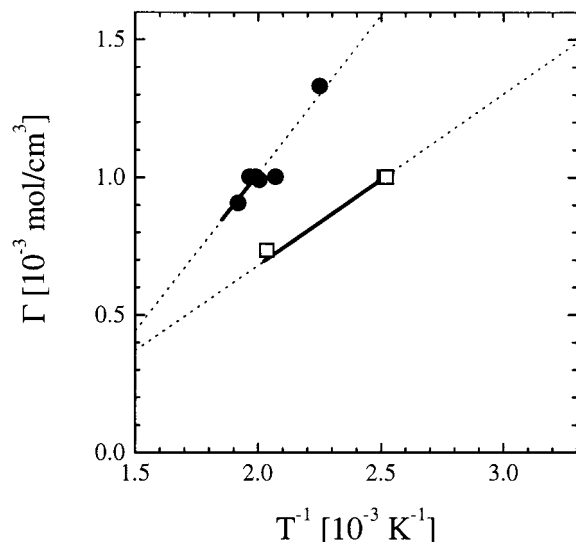


Figure 9. Flory–Huggins parameter of the homopolymer blends PS/PEO(MME) (●) and PS/PEO(DME) (□) from phase boundary measurements is compared to the SANS measurements. The experimental SANS temperature range is indicated by the thick lines, which are extrapolated by dotted lines.

peak position at the order–disorder transition is observed. This is despite a discontinuity of Q^* at the T_{ODT} , first observed in a pressure study.²⁵ The temperature behavior of $\ln Q^*$ can be described by two linear regimes, which cross over at a temperature of about 525 K. The slope changes from $(0.60 \pm 0.01) \times 10^{-3} \text{ K}^{-1}$ to $(0.20 \pm 0.05) \times 10^{-3} \text{ K}^{-1}$ for the d-PS–PEO–me(5) and from $(0.67 \pm 0.01) \times 10^{-3} \text{ K}^{-1}$ to $(0.25 \pm 0.06) \times 10^{-3} \text{ K}^{-1}$ for the d-PS–PEO–OH(5) (compare ref 20). From the temperature dependence of the unperturbed coil size $\kappa = \partial \ln r_0^2 / \partial T = 0.40 \times 10^{-3} \text{ K}^{-1}$ and $0.23 \times 10^{-3} \text{ K}^{-1}$ for PS and PEO, respectively, one would estimate the temperature dependence of the unperturbed diblock copolymer to be $0.32 \times 10^{-3} \text{ K}^{-1}$. Despite the sign, the estimated κ of the unperturbed diblock copolymer is of the same order of magnitude compared to the observed $\partial \ln Q^* / \partial T$ at high temperatures. The low-temperature value of $\partial \ln Q^* / \partial T$ exceeds the bare coil thermal expansivities by far, which seems to be connected to the neighborhood of T_{ODT} .

Discussion

The homopolymer blend Flory–Huggins parameter obtained from respectively neutron scattering and cloud point measurements is compared in Figure 9. The SANS Flory–Huggins parameter is represented from the samples with average molar volumes of $1970 \text{ cm}^3/\text{mol}$ and results from the fitting of the crossover function of the measured susceptibility at many different temperatures. Within the experimental temperature range the Flory–Huggins parameter is presented by a thick line, which is extrapolated to either side by a dotted line. Cloud points were measured either on the protonated samples in an oil bath with the eye or on the partially deuterated samples with neutron scattering experiments (Table 1). The mean-field temperature is calculated as the Ginzburg number corrected critical temperature, $T_c^{\text{MF}} = T_c / (1 - G\chi)$, where the Ginzburg number was measured exactly by the neutron scattering experiments and was extrapolated due to the empirical $G\chi \propto N^{-2}$ law for polymers at atmospheric pressure.²⁴ The corresponding Flory–Huggins parameter was cal-

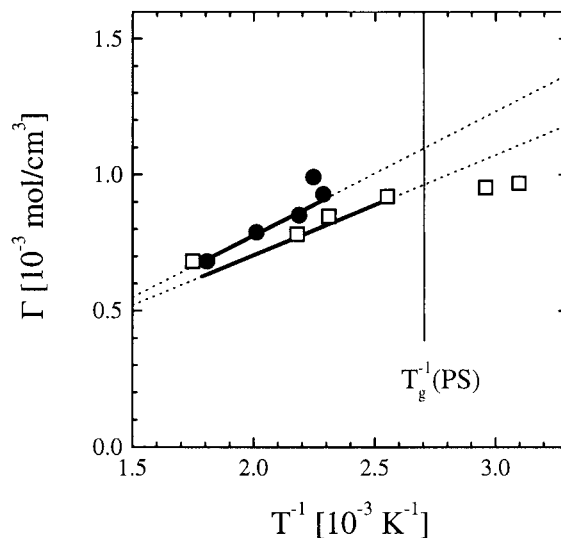


Figure 10. Flory–Huggins parameter of the diblock copolymers PS–PEO–OH (●) and PS–PEO–me (□) from phase boundary measurements is compared to the SANS measurements. The experimental SANS temperature range is indicated by the thick lines, which are extrapolated by dotted lines. The phase boundary measurements with temperatures below the glass transition temperature $T_g(\text{PS})$ show a clear disagreement.

culated by $\Gamma = 1/V_1 + 1/V_2$. Thus, the cloud point measurements yield only single points in the Γ – T^{-1} plane. The single measured phase boundaries agree very well with the SANS Flory–Huggins parameter, even for the PS/PEO blend with the low molar volume of $1380 \text{ cm}^3/\text{mol}$.

The diblock copolymer Flory–Huggins parameter of the SANS and the phase boundary measurements is compared in Figure 10 in the same manner as in Figure 9. The SANS Flory–Huggins parameter is presented for the samples with the molar volume of $17700 \text{ cm}^3/\text{mol}$ and results from the fitting of the Fredrickson–Helfand theory of the measured susceptibility at different temperatures. The order–disorder transition temperature was measured either by rheology or by SANS (Table 2). The corresponding Flory–Huggins parameter was calculated by eq 7, which includes the fluctuation corrections. The Ginzburg number $G\chi$ was measured exactly by the neutron scattering experiments and was extrapolated by the predicted $G\chi \propto N^{-1/2}$ law. The single measured phase boundaries agree well with the SANS Flory–Huggins parameter. Only the low molar mass samples have small deviations, which might be related to the fact that these samples have T_{ODT} below the glass transition of the PS.

Another focus of Figures 9 and 10 is the comparison of the Flory–Huggins parameter for different end groups in the homopolymer blend or the diblock copolymer. The methoxy and hydroxy termination of the PEO block were concerned in this study. The homopolymer blend PS/PEO(MME) has a clearly higher interaction parameter than the PS/PEO(DME), whereas the difference is much smaller for the PS–PEO–OH and the PS–PEO–me diblock copolymers. According to the differences of the Flory–Huggins parameter, the phase boundary can be shifted up to 90K and 45K by the different termination of the PEO in the homopolymer blend and the diblock copolymer, respectively.

While Figures 9 and 10 represent the SANS results only for specific samples, the detailed results from SANS

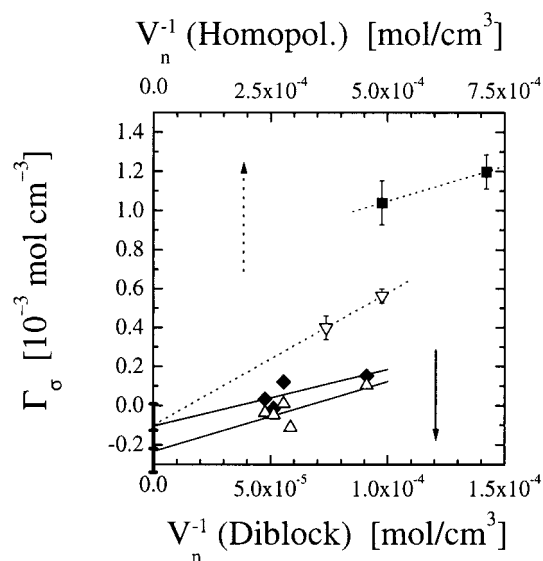


Figure 11. Entropic portion of the SANS Flory-Huggins parameter for the PS-PEO-me (Δ), the PS/PEO(DME) (∇), the PS-PEO-OH (\blacklozenge), and the PS/PEO(MME) (\blacksquare). The x -axis has different scales for the diblock copolymers and the homopolymer blends. The solid straight lines are least-squares fits of the diblock copolymers and are depicted with the error bar of the intercept. The dotted lines correspond to the homopolymers.

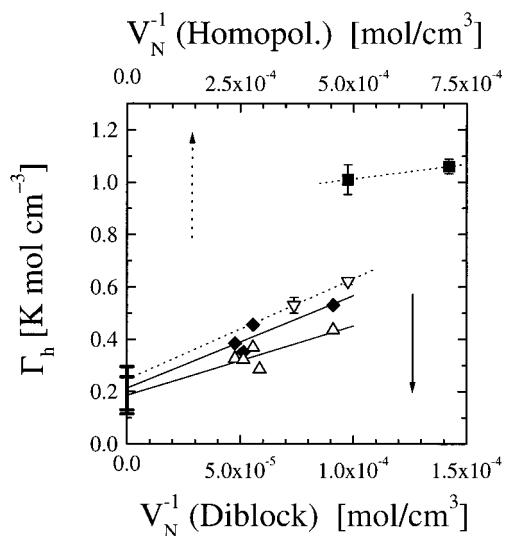


Figure 12. Enthalpic portion of the SANS Flory-Huggins parameter for the PS-PEO-me (Δ), the PS/PEO(DME) (∇), the PS-PEO-OH (\blacklozenge), and the PS/PEO(MME) (\blacksquare). The solid straight lines are least-squares fits of the diblock copolymers and are depicted with the error bar of the intercept. The dotted lines correspond to the homopolymers.

studies are represented in Figures 11 and 12. Here the entropic and enthalpic portions of the Flory-Huggins parameter are presented for the homopolymer blends and the diblock copolymers as a function of the reciprocal molar volume. This representation is motivated by the comparison of the Flory-Huggins parameter of a homopolymer blend with the corresponding diblock copolymer (eq 8) and should also have the same mathematical form for end group effects. The straight line of the entropic contribution Γ_σ of the d-PS-PEO-me diblock copolymers has an intercept of $\Gamma_\sigma = (-0.23 \pm 0.11) \times 10^{-3} \text{ mol/cm}^3$, which represents the value for infinite molar volume. This additive negative entropy is in agreement with the "lattice cluster theory for

pedestrians",^{26,27} which states that the Flory-Huggins entropy of mixing Γ_S is overcounted, and yields a value of $\Gamma_\sigma = -0.17 \times 10^{-3} \text{ mol/cm}^3$. A line with the same intercept (within error bars) connects Γ_σ of the two corresponding homopolymer blends d-PS/PEO(MME) and thus confirms the concept of the junction in diblock copolymers. The d-PS-PEO-OH diblock copolymers find an intercept of $\Gamma_\sigma = (-0.10 \pm 0.11) \times 10^{-3} \text{ mol/cm}^3$, which is almost the same than for the d-PS-PEO-me diblock copolymers. The agreement would be expected for different end groups in the infinite molar volume limit. Only the d-PS/PEO(MME) homopolymer blends differ from the whole concept distinctively. One might speculate that the molar volumes are already that low, that higher-order corrections (V^{-2}) lead to deviations from a linear dependence.

The same qualitative behavior of the enthalpic portion of the Flory-Huggins parameter is found for all four polymer systems (Figure 12). It should be mentioned that the intercepts amount to $\Gamma_h = 0.19 \pm 0.07$ and $0.21 \pm 0.08 \text{ K mol/cm}^3$ for the methoxy- and hydroxy-terminated diblock polymers and thus agree much better than the entropic portions.

We now compare the Γ_h for differently terminated diblock copolymers with the identical molar volume and consecutively for two homopolymer blends with differently terminated PEO's. The enthalpy difference of the differently terminated diblock copolymers with the molar volume of $17\,700 \text{ cm}^3/\text{mol}$ amounts to 0.088 K mol/cm^3 , which corresponds to hydrogen bond energy of $\epsilon = 13 \text{ kJ/mol}$ (according to $\epsilon = 2\Delta\Gamma_h(V/2)R$). For the homopolymer blends the enthalpy difference is 0.39 K mol/cm^3 , which corresponds to $\epsilon = 13 \text{ kJ/mol}$ (according to $\epsilon = 2\Delta\Gamma_h VR$) on the hydrogen bond. The experimentally determined hydrogen-bond energy agrees well with calculations in the local density quantum chemical model, which yielded 14.5 kJ/mol . So the intuitive picture of end group effects describes a common hydrogen-bond energy, which agrees with the local density quantum model.

Conclusion

In this study we compared the effect of different end groups and the covalent junction in diblock copolymers on the thermodynamics, which intuitively influence the Flory-Huggins parameter with a V^{-1} term. The different hydroxy and methoxy termination can change the phase boundary in homopolymer blends by 90K and in diblock copolymers by 45K . The change of the enthalpic portion of the Flory-Huggins parameter was explained by the hydrogen-bond energy of hydroxy end group, which was calculated by the DMOL³ program using the density functional theory. The intuitive picture of V^{-1} corrections of end groups and the covalent junction was confirmed in trends by the molar volume dependence of the Flory-Huggins parameter.

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