

Thermal composition fluctuations near the isotropic Lifshitz critical point in a ternary mixture of a homopolymer blend and diblock copolymer

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We have studied thermal composition fluctuations of a ternary symmetric homopolymer/diblock copolymer system of PEE/PDMS/PEE-PDMS [PEE and PDMS being poly(ethyl ethylene) and poly(dimethyl siloxane), respectively] in its disordered state with small angle neutron scattering for concentration Φ of diblocks up to 15%. The phase diagram shows three characteristic regimes; (1) below the Lifshitz concentration $\Phi_{LL} \cong 9\%$; (2) in the very near vicinity of the Lifshitz concentration; and (3) above Φ_{LL} . In the regime (1) of low diblock content the maximum neutron intensity is obtained at $Q=0$ and phase separation into macroscopic large domains is observed at low temperatures. With increasing diblock content the thermal fluctuations indicate a crossover from 3d-Ising to isotropic Lifshitz critical behavior with critical exponents of the susceptibility $\gamma = (1.62 \pm 0.01)$ and correlation length $\nu = (0.99 \pm 0.04)$ appreciably larger than in the 3d-Ising case. In the structure factor this crossover is accompanied by a strong reduction of the Q^2 term leading to the dominance of the Q^4 term; the restoring force of the thermal fluctuations is strongly reduced as the Q^2 term is proportional to the surface energy. Near the Lifshitz critical temperature a further crossover was observed leading to the appreciably larger critical exponents $\gamma = (2.44 \pm 0.08)$ and $\nu = (1.22 \pm 0.08)$ and a stabilization of the disordered regime visible through a decrease of the phase boundary by nearly 10 K. This crossover is interpreted by the formation of fluctuation induced inhomogeneous diblock distribution at the interface of the thermal fluctuations. (2) In the intermediate regime between 9% and 12% diblock content the Lifshitz line was crossed twice upon increasing the temperature from low to high temperatures; at low and high temperatures the structure factor $S(Q)$ shows diblock character (maximum of $S(Q)$ at $Q \neq 0$) while at intermediate temperature blendlike character (maximum of $S(Q)$ at $Q=0$). At low temperatures a transition to a bicontinuous microemulsion phase is proposed. (3) At diblock content of 15% a weak order-disorder transition was observed. The data in the Lifshitz critical range and larger than the Lifshitz line could be interpreted by a recently developed theory of Kielhorn and Muthukumar who considered the effect of thermal fluctuations in ternary homopolymer/diblock copolymer samples and from which the Flory-Huggins parameter could be evaluated. © 2000 American Institute of Physics. [S0021-9606(00)50512-1]

I. INTRODUCTION

The characterization of different states of matter and the phase transitions between them is of fundamental scientific interest. Each phase transition belongs to a universality class with a set of unique critical exponents describing material properties in the vicinity of the phase transition. The critical fluctuations and the associated classification have been studied experimentally and theoretically in great details in both polymer blends¹⁻⁵ and in diblock copolymers.^{2,6-8} Upon ap-

proaching the critical point by changing the external fields such as temperature a crossover from the universality classes of mean field to a “fluctuation” renormalized state is observed. The renormalized state is for homopolymer blends in the 3d-Ising universality class^{3,4} while the state of diblock copolymers is of the Brascovskii type.⁶⁻⁸ The temperature defining the crossover from mean field to renormalized critical characteristics is estimated by the Ginzburg criterion, which in the incompressible mean field theory predicts a $1/N$ and $1/\sqrt{N}$ (N is degree of polymerization) scaling behavior

for blends^{1,2} and diblock copolymers,⁶ respectively. In reality, however, the renormalized ranges appear to be significantly larger in both blends⁵ and block copolymers.⁷ In blends the larger 3d-Ising critical range has been attributed to the effect of compressibility,⁹ and it is likely that this also plays an important role in the critical behavior of copolymers.¹⁰

When systems belonging to different universality classes of critical phenomena are combined, the various phase transitions influence each other and create new phenomena. In this paper we investigate the interference of macroscopic and microscopic phase transitions in a model polymer system composed of a critical blend of two homopolymers mixed with small amounts of the corresponding symmetrical diblock copolymer. The molar sizes of the ternary system have been tuned in such a way, that the critical temperature of the pure homopolymer blend is closely matched to the order-disorder temperature of the pure diblock copolymer. With the molar volumes $V_A = V_B$ for the homopolymers *A* and *B* and with the molar volume *V* for the diblock copolymer, the Flory-Huggins parameters Γ must then obey the conditions $\Gamma_{\text{ODT}} \equiv \Gamma_C$, Γ_{ODT} and Γ_C representing the Flory-Huggins parameter of the diblock copolymer and the blend at the order-disorder transition and at the critical point, respectively. Within mean field approximation the molar volumes must fulfil the ratio $V/V_A = V/V_B \equiv 5$. To first order the combined effect of the enthalpy and the entropy of mixing should neither increase nor decrease the line of critical points in such homopolymer/copolymer phase diagram. Still, because of the loss in configurational entropy in the ordered phase, Γ_{ODT} will decrease upon the addition of homopolymers.¹¹ If more homopolymer is added, the microdomain size continuously increases until in the thermodynamic limit at $Q^* = 0$ where the domains are of macroscopic size. Thus, in mean field theory the critical lines of a homopolymer mixture and the corresponding diblock copolymer meet together at a multicritical point. This point represents a new universality class which is generally referred to as the isotropic Lifshitz type.¹¹⁻¹³

The critical behavior near the Lifshitz critical point is expected to be strongly influenced by thermal fluctuations, giving rise to larger critical exponents, and suppression of the phase boundaries. This is a consequence of the large critical dimensions relative to the dimensional space, *m*, in which the wave vector instability occurs, and which for the studied polymer system is with $m = d = 3$ equal to the dimension of space. It is the current belief that the upper critical dimension for the isotropic Lifshitz point is $d_U = 8$.¹²⁻¹⁴ This large value of d_U makes it further difficult to calculate critical exponents by the usual $\epsilon \equiv (d_U - d)$ expansion technique; it should be compared with the upper critical dimension of binary blends, where $d_U = 4$.

In a recent study on a ternary system of relatively high molar mass symmetric polyolefins composed of two homopolymers and the corresponding diblock copolymer: PE/PEP/PE-PEP [PE being polyethylene and PEP being poly(ethylene propylene)], mean field Lifshitz-type behavior was observed near the predicted isotropic Lifshitz critical point;¹⁵ the critical exponents of the susceptibility and correlation length were determined with $\gamma = 1$ and $\nu = 0.25$, respec-

tively, and the structure factor followed the characteristic mean field Lifshitz behavior, $S(Q) \propto Q^{-4}$. This is opposed to the common $S(Q) \propto Q^{-2}$ characteristic known for binary blends, and is observed for samples of less copolymer content.¹⁵ In the very near vicinity of the mean field Lifshitz critical point, however, the influence of fluctuations clearly manifested itself by the absence of the Lifshitz critical point, and instead the appearance of a one-phase channel of polymeric microemulsion.¹⁶ An equivalent one-phase gap was observed between the micro- and macrophase separated states in the more low-molar mass system of PEE-PDMS, PEE and PDMS being poly(ethyl ethylene) and poly(dimethyl siloxane), respectively.¹⁷⁻¹⁹ Moreover, in the near vicinity of the mean field Lifshitz point, this system showed critical exponents that are significantly larger relative to both mean field and 3d-Ising behavior.¹⁷ In another SANS study on the PE-PP, PE, and PP mixture, PE and PP being poly(ethyl ethylene) and head-to-head poly(propylene), respectively, a qualitatively similar phase behavior was found; in particular, the microemulsion phase could be identified by the use of contrast variation technique.²⁰

In the present paper further detailed experimental results obtained from small angle neutron scattering (SANS) are presented on the latter PEE/PDMS/PEE-PDMS system. Part of the experimental data ranging from pure homopolymer blend to the regime close to the Lifshitz concentration, $\Phi_{\text{LL}} \equiv 0.09$, have already been published in Ref. 17. In that publication we focused on the crossover phenomena from mean field to 3d-Ising critical behavior characteristic for pure blends and small values of Φ , and from mean field to Lifshitz critical behavior near $\Phi = \Phi_{\text{LL}}$. The critical exponents of the Lifshitz critical point and the Ginzburg number are appreciably larger than for the 3d-Ising case as expected from the larger upper dimension, as summarized in Fig. 16 below, and as given in Table V and VI. In the following we will present experimental data below and above the Lifshitz line and give an interpretation mainly on the basis of the Kielhorn-Muthukumar theory.¹³ In the first part we will review some of the main theoretical background of the present work and then present the experimental data and their analysis.

II. THEORETICAL BACKGROUND

The investigated ternary mixtures of a critical binary polymer blend and the corresponding copolymer were always prepared as a symmetric mixture with equal amounts of the two monomers by the same homopolymer concentration and a symmetric diblock copolymer. As one of the monomers was partially deuterated with the same degree of deuterium, according to the neutron scattering contrast the structure factor measures thermal composition fluctuations with respect to the total monomer fractions and which corresponds to a scalar ($n = 1$) order parameter represented by the local concentration $\Phi = \Phi(r)$. The basic thermodynamic features of those systems near their consolute line are sufficiently well described by the common Landau expansion of the free energy according to

$$H = \frac{1}{2} \int d^d x \{ c_2 (\nabla \Phi)^2 + c_4 (\nabla^2 \Phi)^2 + r \Phi^2 + u \Phi^4 + u_6 \Phi^6 \} \quad (1)$$

with this order parameter.^{21,22} A principal effect of diblock copolymers dissolved with a homopolymer blend is a reduction of the surface energy which according to the Hamiltonian, Eq. (1), is described by a reduction of the parameter c_2 . This parameter is positive at low copolymer content, becomes zero at the concentration of the Lifshitz critical point (Lifshitz line), and negative for large copolymer content. The Hamiltonian Eq. (1) accounts for the composition fluctuations in the homogeneous (disordered) one-phase regime. The composition fluctuations are described by the structure factor $S(Q)$, Q being the momentum transfer, and can be measured directly in a scattering experiment as the scattered intensity with Q given by $Q = (4\pi/\lambda) \sin \theta$, λ being the wavelength of the used radiation, and θ being half of the scattering angle.

For positive c_2 -values the structure factor $S(Q)$ as obtained from the Hamiltonian, Eq. (1), has the characteristic behavior of polymer blends; $S(Q)$ is maximum at $Q=0$, and the susceptibility, r^{-1} , is correspondingly given by this $S(Q=0)$ value, $r^{-1} \equiv S(0)$. At the critical temperature T_C of macrophase separation the susceptibility diverges, i.e., the inverse susceptibility $r \equiv S^{-1}(0)$ is zero. For negative c_2 -values the structure factor, $S(Q)$, has the basic characteristics of block copolymer melts, i.e., the maximum value of $S(Q)$ appear at a finite Q -value, $Q=Q^*$. The susceptibility is then given by the structure factor at this Q^* -value. Within mean field theory of symmetric copolymers the $S(Q^*)$ -value will diverge at the critical point, and beyond that the system will order on a mesoscopic length scale through microphase separation.

The Lifshitz critical point is determined by the two conditions $c_2=0$ and $r=S^{-1}(0)=0$. With $c_2 \approx 0$ in the vicinity of the Lifshitz point, the forth order term of the gradient energy, c_4 , becomes a leading term in the free energy, Eq. (1), giving rise to the characteristic Lifshitz $S(Q) \propto Q^{-4}$ behavior of the structure factor.

A. Structure factor of a three component polymer blend–diblock copolymer mixture in mean field approximation

The expression for the structure factor of a three component mixture of a polymer blend and the corresponding diblock copolymer is described within the random phase approximation according to^{6,8,13}

$$S^{-1}(Q) = F(Q)/V - 2\Gamma, \quad (2)$$

where Γ is the effective Flory–Huggins (FH) parameter, $\Gamma = \Gamma_h/T - \Gamma_\sigma$, including both an enthalpic term, Γ_h and an entropic term Γ_σ . $F(Q)$ is the inverse form factor, which can be calculated in terms of the partial structure factors S_{AA} , S_{BB} , and S_{AB} describing the correlation between the monomers of type A and B,¹¹

$$F(Q)/V = \frac{S_{AA}(Q) + S_{BB}(Q) + 2S_{AB}(Q)}{S_{AA}(Q)S_{BB}(Q) - S_{AB}^2(Q)}.$$

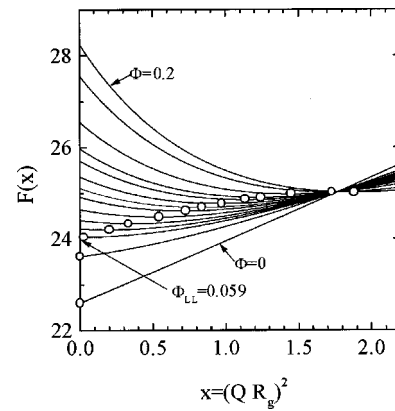


FIG. 1. Inverse form factor for different diblock concentrations calculated based on Eq. (4). The circles indicate the maximum value of the form factor.

For a ternary system composed of a critical mixture of A and B homopolymers of equal volume, $V_A = V_B$, and conformation (and thereby also of equal concentration $\Phi_A = \Phi_B$ and equal partial structure factors S_{AA} and S_{BB} , $S_{AA} = S_{BB}$) and an AB diblock with volume V , $F(Q)$ can be reduced to

$$F(Q)/V = 2[S_{AA}(Q) - S_{AB}(Q)]. \quad (3)$$

Assuming that the polymers in the mixture remain as unperturbed Gaussian chains, $F(Q)$ can be written in terms of the Debye-function,

$$g_D(x) = 2[f x + \exp(-f x) - 1]/x^2$$

as

$$F(x) = 4[(1 - \Phi)\alpha g_D(1, x\alpha) - \Phi g_D(1, x) + 4\Phi g_D(0.5, x)], \quad (4)$$

where $x = R_g^2 Q^2$, R_g being the radius of gyration of the diblock copolymer; and α the ratio of the molar volumes of the homopolymers relative to the diblock copolymer, $\alpha = \sqrt{V_A V_B}/V$.^{8,13} Figure 1 shows the inverse form factor $F(x)$ given by Eq. (4), as calculated with parameters equal to those of the experimentally investigated samples discussed below and given in Table I. From the minimum values of $F(x)$ one gets both the Flory–Huggins parameter Γ_S at the spinodal and critical point, and the corresponding characteristic $Q=Q^*$ value. For concentrations, Φ , smaller than the Lifshitz critical value according to $\Phi_{LL} = 2\alpha^2/(1 + 2\alpha^2) = 0.0596$ the critical point occurs for $Q=0$, corresponding to macrophase separation.^{11,23} For larger Φ the maximum occurs at a steadily growing Q^* value, corresponding to microphase separation. These critical values of (Γ_S, Q^*) are depicted by the open circles in Fig. 1, and plotted vs diblock concentration Φ in Figs. 2(a) and 2(b). The values for Γ_S are further summarized in Tables II and III.

The structure factor in Eqs. (2) and (3) can be expanded into powers of Q^2 ,

$$S^{-1}(Q) = S^{-1}(0) + L_2 Q^2 + L_4 Q^4 + \dots, \quad (5)$$

with the coefficients given in terms of the parameters of the Hamiltonian in Eq. (1). The first term is $S^{-1}(0) = r$, as discussed above, and equal to the inverse susceptibility, $S^{-1}(0) = 2(\Gamma_S - \Gamma)$, for concentrations less than the Lifshitz

TABLE I. Sample characteristics.

Sample	Polymer blend		Diblock copolymer	
Polymer	Polyethyl- ethylene	Polydimethyl- siloxane	Polyethyl- ethylene	Polydimethyl- siloxane
Chem structure	PEE (C ₄ H _{5.2} D _{2.8})	PDMS (SiOC ₂ H ₆)	PEE (C ₄ H _{5.2} D _{2.8})	PDMS (SiOC ₂ H ₆)
d (g/cm ³)	0.91	0.98	0.91	0.98
Ω (cm ³ /mol)	66	77.7	66	77.7
σ (Å)	5.35	5.92	5.35	5.92
$\Sigma c_i b_i / \Omega_i$ (10 ¹⁰ cm ⁻²)	1.79	0.0628	1.79	0.0628
V_W (cm ³ /mol)	2010	2270	12000	168
N	30.5	29.2		
Volume fraction PEE	$\Phi = 0.516$		$f = 0.5$	
Γ_S (10 ⁻³ mol/cm ³)	0.942		0.875	

value. The coefficients L_2 and L_4 are proportional to, respectively, c_2 and c_4 in the Hamiltonian Eq. (1), and can be determined in terms of the polymer parameters and concentration Φ ,¹³

$$c_2 \sim L_2 = (R_g^2/V)[4\alpha^2(1-\Phi) - 2\Phi]/[3\alpha^2(1-\Phi)^2], \quad (6a)$$

$$c_4 \sim L_4 = (R_g^4/V)[(1-\Phi)^2(4\alpha^4 + 16\alpha^2 - 9\alpha + 4) - (1-\Phi)(16\alpha^2 - 9\alpha + 8) + 4]/[36(1-\Phi)^3\alpha^3]. \quad (6b)$$

At the Lifshitz concentration, the characteristic mean field behavior, $S^{-1}(Q) \propto Q^4$, clearly appears from this equation.

B. Effect of thermal fluctuations in blend/copolymer mixtures

Near the Lifshitz line of a three component blend/diblock mixture thermal composition fluctuations are expected to become strong as its upper critical dimension, $d_U = 8$, is twice as large as that of binary polymer blends. This large value of d_U is related to the reduction of the surface energy described through the c_2 -term in the Hamiltonian, Eq. (1), and which acts as a threshold force for thermal composition fluctuations. The structure factor of blend/diblock mixtures was recently derived beyond the mean field approximation by Kielhorn and Muthukumar.¹³ They used the Hartree approximation in the Brazovskii formalism, equivalent to the procedure developed by Fredrickson and Helfand for pure

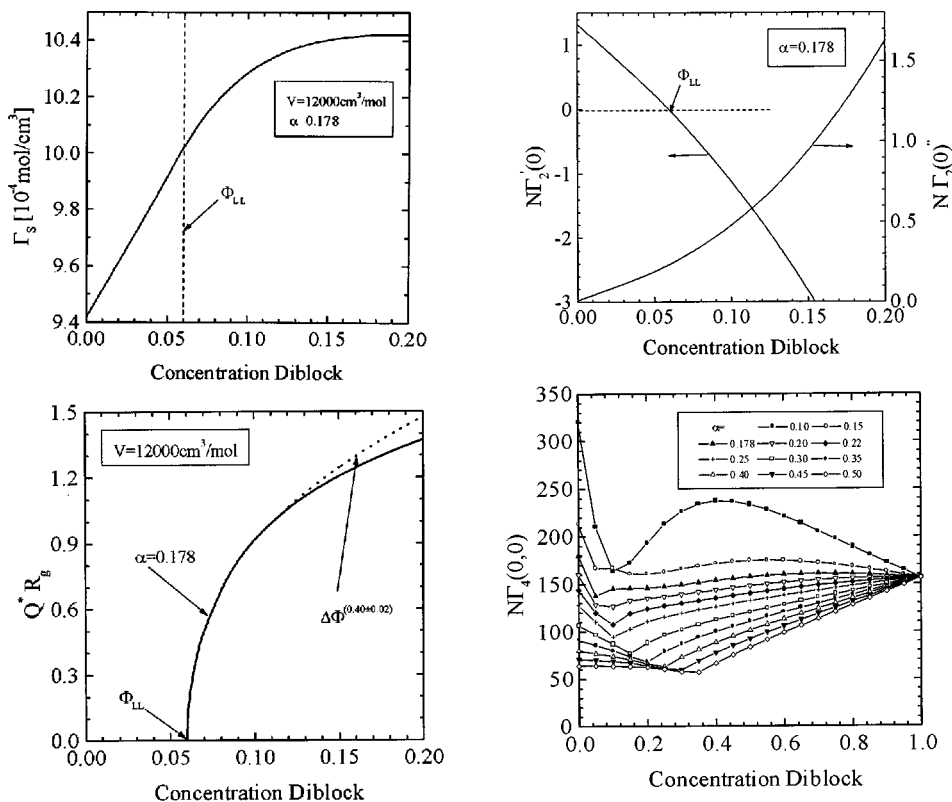


FIG. 2. (a) Theoretical Flory-Huggins parameter at the spinodal and critical point evaluated from the minimum of $F(x)$ in Fig. 1. (b) The value of $Q = Q^*$ representing the maximum of $S(Q)$ evaluated from $F(x)$ in Fig. 1. Below the Lifshitz line $Q^* = 0$ and near the Lifshitz line Q^* follows a scaling behavior with good approximation. (c) First and second derivative of the second order vertex function. (d) Fourth order vertex function for various $\alpha = \sqrt{N_{\text{PEE}} N_{\text{PDMS}}} / N_{\text{PEE-PDMS}}$ and diblock concentration. Note, that the concentration Φ of (d) covers the range 0–1, while that of (a), (b), and (c) covers 0–0.2 only.

TABLE II. Parameters of samples larger than Lifshitz line from the structure function $S(Q)$.

Φ (%)	T_{ODT} (°C)	G	\tilde{G}_i	$\Gamma_S(10^{-3} \text{ mol/cm}^3)$	$\Gamma_h(\text{mol K/cm}^3)$	$\Gamma_\sigma(10^{-4} \text{ mol/cm}^3)$	$\Gamma_{\text{ODT}}V$
9.3	63	0.187	1.5 ± 0.1	1.025	0.33 ± 0.005	2.2 ± 0.2	...
10	81	0.396	1.3 ± 0.5	1.029	0.52 ± 0.01	$-(2.9 \pm 0.3)$...
10.9	75	0.325	1.1 ± 0.3	1.032	0.43 ± 0.005	$-(0.65 \pm 0.12)$...
12.1	37	0.464	1.2 ± 0.1	1.036	0.44 ± 0.005	$-(0.84 \pm 0.15)$...
14.9	30	0.456	1.3 ± 0.1	1.041	0.39 ± 0.004	0.18 ± 0.09	15.3
100 ^a	83.3	0.54	1.4 ± 0.2	0.875	0.29 ± 0.04	$-(2.7 \pm 0.6)$	13

^aHas been evaluated from the Fredrickson–Helfand theory [Eq. (17)] with $\bar{N}=900$ as evaluated assuming $\sigma=6.5 \text{ \AA}$.

diblock copolymer melts.⁶ The structure factor, Eq. (2), was thereby approximated and parameterized into a more simple form according to

$$S^{-1}(Q) = a/(b + Q^2) + c + dQ^2 \quad (7)$$

with the parameters, $a \equiv A/(\sigma^2 V)$, $b \equiv B/\sigma^2$, $c \equiv C/V$, and $d \equiv D\sigma^2/V$, where σ is the statistical segment length of the copolymer and is related to the radius of gyration according to $R_g^2 = \sigma^2 V/6\Omega = \sigma^2 N/6$, Ω and N being the respectively monomer molar volume and the degree of polymerization. The effects of thermal fluctuations are included by the renormalized parameters A , B , C , and D . These parameters were calculated assuming that the general shape of $S(Q)$ is unaltered compared to the mean field result. The detailed expressions are given in Eqs. (3.9)–(3.12) of Ref. 13. The susceptibility $S(Q^*)$ is thereby given in the form of

$$S^{-1}(Q^*) = 2[\Gamma_C V - \Gamma_{\text{ren}} V]/V \quad (8)$$

with the renormalized Flory–Huggins parameter Γ_{ren} that includes the effect of thermal fluctuations. The detailed form of Γ_{ren} is given separately for the two cases, $\Phi > \Phi_{\text{LL}}$ and $\Phi < \Phi_{\text{LL}}$ corresponding to the susceptibility represented by respectively $S(Q^*)$ at finite Q^* and $S(0)$. In the “block copolymerlike” case of $\Phi > \Phi_{\text{LL}}$, Γ_{ren} is given as¹³

$$\Gamma_{\text{ren}} V = \Gamma V - G \sqrt{6x^* d_+} \times \frac{b/Q^{*2} - \sqrt{1 + b/(dQ^{*4}S(Q^*))} + 2 - 1/(dQ^{*2}S(Q^*))}{\sqrt{1/(dQ^{*2}S(Q^*)) - 2 + 2\sqrt{1 + b/(dQ^{*4}S(Q^*))}}}. \quad (9)$$

The parameter G is determined by the degree of polymerization N , the monomer molar volume, Ω , and the relative volume fractions of the polymer components Φ_A , Φ_B , and Φ according to

$$G = \frac{N\Gamma_4(0,0)}{16\pi\sqrt{d_+}} \frac{1}{\sqrt{\bar{N}}} \quad (10)$$

and with the parameters d and d_+ given by [Eq. (3.9) in Ref. 13],

$$d \equiv d_+ \sigma^2 / \Omega; \quad d_+ = 1/[12(\Phi_A + f\Phi)[\Phi_B + (1-f)\Phi]]. \quad (11)$$

The parameter $\Gamma_4(0,0)$ is the fourth order vertex function, which was evaluated by the same procedure as used by Leibler⁸ but is a function of f , Φ_A , Φ_B , and α .¹³ In Fig. 2(d) for the studied samples the numbers of $N\Gamma_4(0,0)$ have been given for various diblock concentrations Φ and α . The parameter $\sqrt{\bar{N}} = (R_0^3/V)$ ($R_0 = \sqrt{6}R_g$ is the end-to-end distance of the polymer) is the average number of chains in the volume R_0^3 ; its reciprocal value is a measure of the effect of thermal fluctuations as discussed for blends on p. 112 of Ref. 1 and therefore proportional to the Ginzburg number as will be defined in Eq. (18). The value of \bar{N} was estimated with 900 assuming a mean statistical segment length of $\sigma = 6.5 \text{ \AA}$ (Fig. 19). There exists the following identity: $dQ^{*2}V \equiv 6d_+x^*$, i.e., $R_g^2 \equiv dV/6d_+$. So, the statistical segment length σ can be evaluated from the parameters d and d_+ and the monomer molar volume Ω according to $\sigma = \sqrt{\Omega(d/d_+)}$.

TABLE III. Parameters of samples less than the Lifshitz concentration evaluated from the susceptibility $S(0)$ with Eq. (12) and the crossover function (+). The 0 and 4.3 samples could not appropriately be described by Eq. (12). $\bar{N}=900$ was evaluated assuming $\sigma=6.5 \text{ \AA}$.

Φ (%)	T_c (°C)	G	$\Gamma_S(10^{-3} \text{ mol/cm}^3)$	$\Gamma_h(\text{mol K/cm}^3)$	$\Gamma_\sigma(10^{-4} \text{ mol/cm}^3)$	b_0	c_0^a
0 ⁺	141.4	...	0.937	0.44	1.14
4.3 ⁺	129.7	...	0.984	0.44	1.34
6	121.2	0.41	1.002	0.44 ± 0.01	1.17 ± 0.09	0.01 ± 0.005	0.25
6.7	104.9	0.4	1.008	0.36 ± 0.01	$-(0.9 \pm 0.2)$	0.29 ± 0.05	0.19
7.4	109.5	0.39	1.014	0.31 ± 0.005	$-(2.2 \pm 0.1)$	0.04 ± 0.01	0.14
8.3	86.7	0.39	1.02	0.35 ± 0.008	$-(1.1 \pm 0.2)$	0.4 ± 0.05	0.06

^aCalculated c_0 .

In the “blendlike” case of $\Phi < \Phi_{LL}$, where the susceptibility is represented by $S(0)$, the renormalized FH-parameter is given according to Ref. 13,

$$\Gamma_{\text{ren}} = \Gamma V - G[b_0 - V/S(0)] - \sqrt{b_0 V/S(0)} / \sqrt{V/S(0) + b_0 c_0 + 2\sqrt{b_0 V/S(0)}} \quad (12)$$

with the parameters, $b_0 = 12d_+ (6d_+ - N\Gamma_2'(0)) / (N\Gamma_2''(0))$ and $c_0 = N\Gamma_2'(0) / 6d_+$, $N\Gamma_2(x)$ being the second order vertex function⁸ which within mean field approximation is equal to the inverse structure factor according to $N\Gamma_2(x) \equiv V/S(Q)$.¹³ Its derivatives with respect to x are obtained from Eq. (5) according to $N\Gamma_2'(0) = L_2 V/R_g^2$ and $N\Gamma_2''(0) = 0.5L_4 V/R_g^4$; both derivatives of $\Gamma_2(0)$ have been plotted in Fig. 2(c).

C. The scaling ansatz for blend/copolymer mixtures

The decrease of the surface energy with increasing copolymer content leads to a structure factor near the critical temperature, which in analogy with the mean field case, Eq. (5), can be given as

$$S_{-1}(Q) = S^{-1}(0) + l_2 Q^2 + l_4 Q^4, \quad (13)$$

with the coefficient l_4 of the additional Q^4 term proportional to the c_4 term in the Hamiltonian, as discussed above. For convenience the structure function is written in the following form:¹²

$$S^{-1}(Q) = S^{-1}(0) [1 + (Q\xi)^2 + Kp^{-2}(Q\xi)^4], \quad (14)$$

where the susceptibility according to scaling laws follow the relation,

$$S^{-1}(0) = C_+^{-1} t^\gamma \quad (15)$$

with the reduced temperature $t = (T - T_C)/T$, and the critical amplitude C_+ .²¹ The parameter ξ , given by

$$\xi = \sqrt{S(0)l_2}$$

is the correlation length of the thermal fluctuations and the prefactor Kp^{-2} is given as

$$Kp^{-2} = l_4 / (l_2^2 S(0)).$$

The parameter p is a scaling field amplitude, which is given by the square gradient term of the Hamiltonian Eq. (1) as

$$p = c_2 / \sqrt{4c_4|r|} = c_2 / \sqrt{4c_4|S^{-1}(0)|}$$

and is thus a measure of the deviation from the Lifshitz point.¹²

At the Lifshitz critical temperature the correlation length ξ losses its meaning as $l_2 = 0$. ξ has then to be redefined from the then dominating Q^4 term in Eq. (14); the corresponding scaling field p is constant. At smaller copolymer content, the Q^4 term in the structure factor in Eqs. (5) and (15) becomes negligible, and ξ follows the usual scaling law $\xi_0 t^{-\nu}$; p is given as $p^2 \propto \xi^{(2+\eta)/l_4}$ and l_2 as $l_2 \propto \xi^\eta$ (Ref. 24) with the Fisher exponent $\eta = 2 - \gamma/\nu$ obtained from the critical expo-

nents γ and ν of the susceptibility and correlation length, respectively. ξ and p become accordingly both infinite at the critical temperature.

The Lifshitz critical point leads to a new critical exponent β_Q describing the change in Q^* with Φ . By increasing the copolymer content past the Lifshitz concentration, i.e., in the range $\Phi_{LL} \leq \Phi \leq 1$, Q^* changes from zero to finite values according to the scaling law²²

$$Q^* \propto |\Phi - \Phi_L|^{\beta_Q}. \quad (16)$$

The exponent is found to be, $\beta_Q = 0.4$ according to the results in Fig. 2(b), it is a theoretical result within mean field approximation.

D. Effect of thermal fluctuations in diblock copolymers

Composition fluctuations in *diblock copolymers* are relevant only on the length scale of polymer chains. This is the reason that $S(Q)$ shows an interference peak at a finite value of Q^* . The renormalized Flory–Huggins parameter for diblock copolymers can be approached from Eq. (9) in the limit $b/(dQ^* S(Q^*)) \ll 1$ according to

$$\Gamma_{\text{ren}} V = \Gamma V - \tilde{\text{Gi}} \sqrt{S(Q^*)/V} + G/\sqrt{S(Q^*)/V} \quad (17)$$

with the Ginzburg number $\tilde{\text{Gi}}$

$$\tilde{\text{Gi}} = 6x^* d_+ G(1 + b/Q^{*2}) \quad (18)$$

and with $x^* = (R_g Q^*)^2$ as before.¹³ The corresponding expression for Γ_{ren} derived for pure diblock copolymers by Fredrickson–Helfand,⁶

$$\Gamma_{\text{ren}} V = \Gamma V - \tilde{\text{Gi}} \sqrt{S(Q^*)/V} \quad (19)$$

is the same as Eq. (17) with the third term equal to zero.

E. Effect of thermal fluctuations in polymer blends

The theoretical approaches for the susceptibility of polymer blends is conceptually different from those of the above discussed ones for block copolymer like systems. In case of *polymer blends* the susceptibility $S(0)$ is interpreted with the asymptotic crossover model derived by Belyakov and Kiselev,^{25,26}

$$\hat{t} = (1 + 2.333\hat{S}(0)^{\Delta/\gamma})^{(\gamma-1)/\Delta} \times [\hat{S}^{-1}(0) + (1 + 2.333\hat{S}(0)^{\Delta/\gamma})^{-\gamma/\Delta}]. \quad (20)$$

The exponents $\gamma \cong 1.24$ and $\Delta = 0.5$ are the critical exponents of the 3d-Ising model. The rescaled reduced temperature $\hat{t} = t/\text{Gi}$ ($t = |T_C - T|/T$) is formulated as a function of the rescaled susceptibility $\hat{S}(0) = S(0)\text{Gi}/C_{\text{MF}}$. The parameters Gi , C_{MF} , and T_C are the experimental parameters characterizing the system. Gi is the Ginzburg number and C_{MF} the mean field critical amplitude of $S(0)$. In the asymptotic limits $t \gg 1$ and $t \ll 1$ the susceptibility in Eq. (20) follows the well-known scaling laws $S(0) = C_{\text{MF}} t^{-1}$ of the mean field approximation, and $S(0) = C_+ t^{-\gamma}$ of the 3d-Ising model, respectively. Experimentally, $S(0)$ is obtained from the Ornstein–Zernike approximation,²¹

$$S^{-1}(Q) = S^{-1}(0) + I_2 Q^2.$$

The Ginzburg number is related to the ratio between the critical amplitudes of the 3d-Ising and the mean field susceptibilities according to Refs. 5, 21, and 26

$$Gi = 0.069 (C_+ / C_{MF})^{1/(\gamma-1)}. \quad (21)$$

Within the FH-model the susceptibility is given as $S(0)/V = [2(\Gamma_C V - \Gamma V)]^{-1}$ with the FH-parameter $\Gamma = \Gamma_h/T - \Gamma_\sigma$ and the respective enthalpic and entropic contributions Γ_h and Γ_σ (Refs. 1 and 2). The mean field critical amplitude is thus related to the FH-parameters according to

$$C_{MF} = 1/2[\Gamma_S + \Gamma_\sigma] = T_C^{MF}/2\Gamma_h \quad (22)$$

which in the limit $\Gamma_\sigma = 0$ leads to the scaling relation $Gi \propto V^{-1}$ (Ref. 5). In order to evaluate the enthalpic term one needs the “mean field” critical temperature T_C^{MF} which is related to the “real” critical temperature T_C according to $T_C^{MF} = T_C/(1 - Gi)$ (Ref. 26). Thermal composition fluctuations stabilize, in analogy with the block copolymer systems, the disordered phase of the system, and lower thereby T_C .

III. EXPERIMENT

Small-angle neutron scattering technique was used to measure the structure factor of thermal composition fluctuations in a number of ternary mixtures of similar size PEE and PDMS homopolymers and symmetric PEE-PDMS diblock copolymer with varying concentrations Φ ranging from volume fractions $\Phi = 0$ to $\Phi = 15\%$. PEE is the acronym for partially deuterated poly(ethyl ethylene), and PDMS is poly(dimethylsiloxane).

A. Sample preparation

The homopolymers PEE and PDMS and the symmetric diblock copolymer PEE-PDMS were all synthesized by anionic polymerization followed by catalytic hydrogenation.²⁷ The PEE-monomers were partly deuterated during the catalytic saturation. Based on the measured densities, the chemical formula of the PEE monomers in both the homopolymers and the block copolymer are of $C_4D_{2.8}H_{5.2}$. The degree of deuteration was not measured independently, but it is known that only limited isotope exchange takes place during such a process.²⁸ The level of exchange depends on the reaction conditions. The samples were all saturated under similar conditions and the measured densities are consistent with an equal degree deuteration. The molecular characteristics are summarized in Table I. The ratio of the degree of polymerization of the homopolymers and copolymer is $\alpha = \sqrt{N_{PEE}N_{PDMS}/N_{PEE-PDMS}} = 0.178$.

B. Small-angle neutron scattering

The scattering experiments were performed at the KWS1 small-angle neutron scattering (SANS) diffractometer at the FRJ-2 research reactor of the Forschung Zentrum, Jülich (FZJ).²⁹ The composition fluctuations were measured *in situ* at the corresponding temperatures. The scattered neutron intensity was corrected for background contributions and calibrated in absolute units by a Lupolen secondary standard.

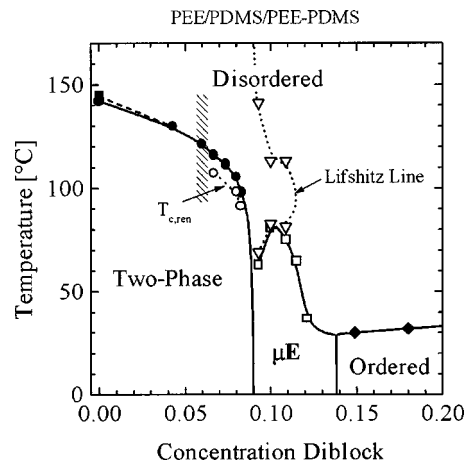


FIG. 3. Experimental phase diagram of PEE/PDMS/PEE-PDMS. The filled circles (●) represent the critical temperatures of the 3d-Ising and isotropic Lifshitz case separated by the dashed area, the open circles (○) the critical temperatures of the renormalized Lifshitz case, the solid square (■) the binodal, the diamonds (◆) the order-disorder transition, and the triangles (▽) the Lifshitz line, and the open squares (□) are the crossover to microemulsion characteristics. The order-disorder transition at $\Phi = 0.18$ was independently determined by rheology.

IV. EXPERIMENTAL RESULTS AND INTERPRETATION

A. Phase diagram

The phase diagram of the ternary PEE/PDMS/PEE-PDMS mixture with the near critical PEE/PDMS blend and the diblock copolymer of content Φ is shown in the range of $\Phi = 0$ –20% in Fig. 3. It was determined from the behavior of the susceptibility at the phase boundaries as will be discussed in the following. The phase diagram in Fig. 3 will give us orientation in the presentation of the experimental data. A phase diagram of this system including the whole concentration range is published elsewhere.¹⁸

The phase diagram in Fig. 3 is divided into five sections: The disordered regime at high temperatures is separated by the Lifshitz line (LL). At Φ lower than the Lifshitz line, the maximum intensity occurs at $Q = 0$ while for Φ larger than the Lifshitz line the maximum intensity is observed at a finite Q^* -value. Theoretically, the Lifshitz line is estimated to be 6% according to $\Phi_{LL} = 2\alpha^2/(1 + 2\alpha^2)$ (Ref. 11). The observed Lifshitz line, however, is observed at a larger Φ and it depends on temperature; its smallest Lifshitz concentration is found at 9.3% and its largest value around 100 °C at 10.9%. At low and high temperatures the Lifshitz line appears constant at about 9%. For block copolymer contents above the Lifshitz line mesoscopic ordering is expected to occur below an ordering temperature. Such an ordering was observed, however, only for copolymer contents at $\Phi = 14.9\%$ and above. Below $\Phi = 14.9\%$ experiments were performed in some cases down to -10 °C without any indications of an ordering transition from the susceptibility alone. Apparent changes in the temperature dependence of the Flory-Huggins parameter [Fig. 18(a)] and changes in the temperature and concentration dependence of Q^* near $T = 65$ °C and $\Phi \approx 11.5\%$ (Fig. 10) give further indications of a crossover to a separate regime between 9% and 14% diblock content which together with the results in Ref. 16 has been inter-

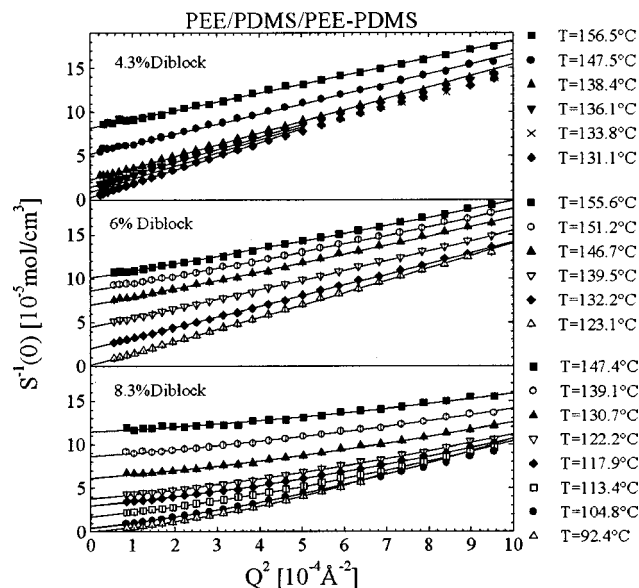


FIG. 4. Structure factor in Zimm representation for three diblock concentrations. At 4.3% $S(Q)$ is described by the Ornstein–Zernike law, at 6% and above contributions from the Q^4 term becomes visible.

preted as a bicontinuous microemulsion phase and which is indicated by the symbol μE in the phase diagram.

For Φ below the Lifshitz line, ordering occurs on a macroscopic scale by phase separation. The binodal and the spinodal phase boundaries are depicted in the phase diagram. The $\Phi=0$ system is at a slightly off-critical concentration while for the systems with finite copolymer content critical behavior was observed where the phase decomposition coincided with infinite susceptibility. So, the solid line represents the critical points. The Lifshitz critical point is a multiple critical point connecting the line of transitions to macrophase separation with the line of microphase separation, as already discussed in the theoretical parts above. The Lifshitz point can, however, only be realized within mean field approximation; according to the Ginzburg criterion thermal fluctuations stabilize the disordered phases differently in blends and in diblock copolymers and thereby destroy the Lifshitz point.^{11–13} The phase diagram shown in Fig. 3, including the ordered μE -phase is qualitatively similar to the diagram found in an analogous polymer mixture of PE/PEP/PE-PEP.¹⁶

B. Structure factor and susceptibility below the Lifshitz line

In Fig. 4 the structure factor $S(Q)$ of three samples with copolymer content below the Lifshitz line has been plotted for various temperatures vs the momentum transfer Q in Zimm representation, e.g., $S^{-1}(Q)$ vs Q^2 . The solid lines represent fits of Eq. (13) from which three parameters, namely the susceptibility $S(0)$ and the coefficients l_2 and l_4 are obtained. At $\Phi=4.3\%$ $S(Q)$ is sufficiently well described by the Ornstein–Zernike approximation with $l_4=0$ similarly to blends. For larger Φ the Q^4 term in $S(Q)$ becomes visible as demonstrated for the $\Phi=6\%$ and 8.3% samples and be-

comes more relevant for the 8.3% sample as is expected from the reduction of the surface energy caused by the diblock component.

In Fig. 5 the inverse susceptibility $S(0)$ has been plotted vs the inverse temperature $1/T$ for the five investigated samples with Φ less than the Lifshitz line. The critical temperatures determined from $S^{-1}(0)=0$ decreases with increasing Φ ; the solid and open points in the phase diagram of Fig. 3 depict them. The $\Phi=4.3\%$ sample behaves similarly to pure blends; $S^{-1}(0)$ shows at high temperature mean field characteristics, and near the critical point 3d-Ising critical behavior with a crossover regime given by the Ginzburg number in Eq. (21). This is demonstrated by the corresponding fitted solid line obtained from the crossover function by Belyakov *et al.* in Eq. (20).^{25,26} This crossover function has successfully been used by us for the interpretation of polymer blends.⁵ The second dashed line in the figure represents the asymptotic 3d-Ising scaling law with the critical exponent $\gamma=1.24$ as calculated from the parameters of the crossover function.

The susceptibilities of the other samples plotted in Fig. 5 with slightly larger Φ could be analyzed with the expressions of the susceptibility $S(0)$ derived from Eq. (8) with $Q^*=0$ and the corresponding renormalized FH-parameter of Eq. (12). The fits are depicted by solid lines; they describe the stronger curvature of the experimental data rather well. For the 8.3% sample the data points near T_C are not well described and T_C is fitted at a lower temperature. The parameters obtained from the fit are the FH-parameter Γ , and b_0 and c_0 . The two latter parameters are related to the first and second derivative of the second order vertex function at $Q=0$ as discussed in Sec. II B. Their numerical values are collected in Table III. A discussion of these data on the basis of scaling laws and the corresponding critical exponents and amplitudes will be given later in Sec. III E.

C. Structure factor and susceptibility near the Lifshitz line

The SANS data of the samples between 9% and 11% diblock concentration Φ show at low and high temperatures the characteristic behavior of diblock copolymers, i.e., $S(Q)$ shows maximum at finite Q^* -value, but at intermediate temperatures that of homopolymer blends, i.e., $S(Q)$ maximum at $Q=0$. The curved Lifshitz line shown in the phase diagram (Fig. 3) reflects this behavior. Apparently, the Lifshitz line is not constant in diblock copolymer content as expected from theory. The measured structure factors of the three investigated samples are shown in Fig. 6. The corresponding susceptibilities, $S(0)$ or $S(Q^*)$ are plotted in Fig. 7 vs the inverse temperature, while the l_2 coefficient of Q^2 and the Q^* -values of the maximum intensity have been plotted in Fig. 8 and 9 as a function of temperature. The structure factor $S(Q)$ has been fitted with the approximate expression of Eq. (7) as demonstrated by the solid lines. The Flory–Huggins parameter, the Ginzburg number, and the statistical segment length have been evaluated for each temperature of the experiment from the expressions of a , b , c , d in Ref. 13 and Eq. (9) and directly from $S(0)$ with Eq. (12), assuming that the parameters in Eq. (12) are constant with temperature.

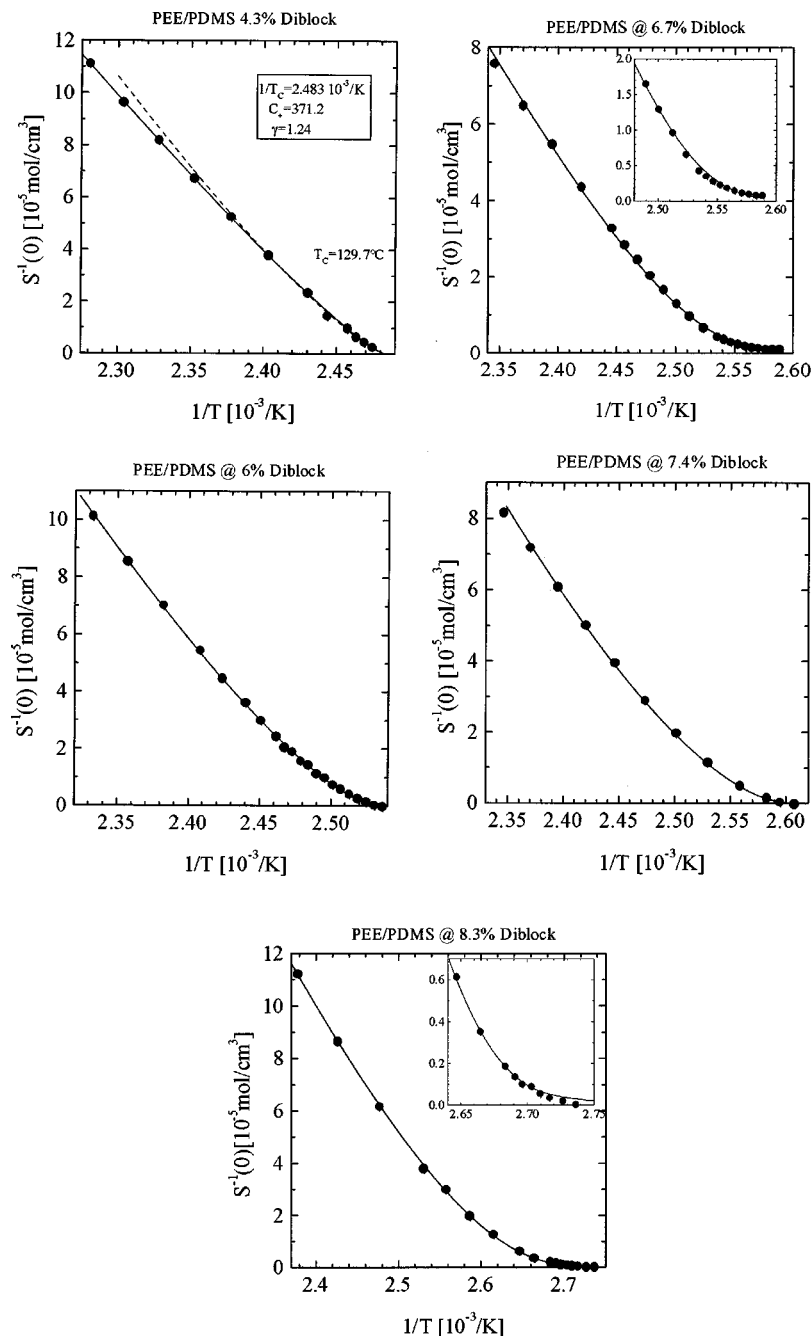


FIG. 5. Inverse susceptibility vs inverse temperature. $S(0)$ in the 4.3% sample follows a crossover function between mean field and 3d-Ising case (dotted curve) while $S(0)$ of the other samples show stronger renormalization according to fluctuations; they are fitted by a theory using a Hartree approximation in the Bradzovskii formalism.

Their resulting numerical values are collected in the Tables II and IV, and will be discussed later. In Fig. 7 $S^{-1}(Q^*)$ has also been fitted with Eq. (17) representing the limit of a diblock copolymer as indicated by the solid line. This fit describes the data well, it is a guide for the eye and their parameters have not been given here.

Even though the general characteristics of the structure factor, and the related parameters, are similar for the three samples with, respectively, 9.3%, 10%, and 10.9% copolymers, the 9.3% sample shows a remarkable deviation. Both the $S(0)$ -and the $S(Q^*)$ -values decrease continuously in the 10% and the 10.9% samples, as is best seen from the plots in Fig. 7. The 9.3% sample, however, shows a significant different behavior. After a continuous decrease of $S(Q)$ in the microemulsion-phase between 34 and 54 °C a relatively

strong increase is observed in $S(Q)$ near $Q=0$ between 54 °C and 78 °C even though with its maximum value is still at a finite, though small, Q^* -value. Upon further increase in T , a strong decrease of $S(Q)$ is observed, with its peak-position approached at $Q=0$. This means that near the low-temperature part of the Lifshitz line, the one-phase stabilizing effect of the diblock copolymers must be remarkably reduced as the long-range fluctuation modes have strongly increased. At higher temperatures the intensity is again reduced, and above 141 °C re-entrance to the phase with the character of a diblock copolymer appears. It appears from the inset in the plot of the 9.3%-data in Fig. 6, showing the data measured at 150 °C, that the statistics of the block copolymer like $S(Q)$ is quite bad. The conclusion that reentrance to block copolymer like characteristics is, however, strongly

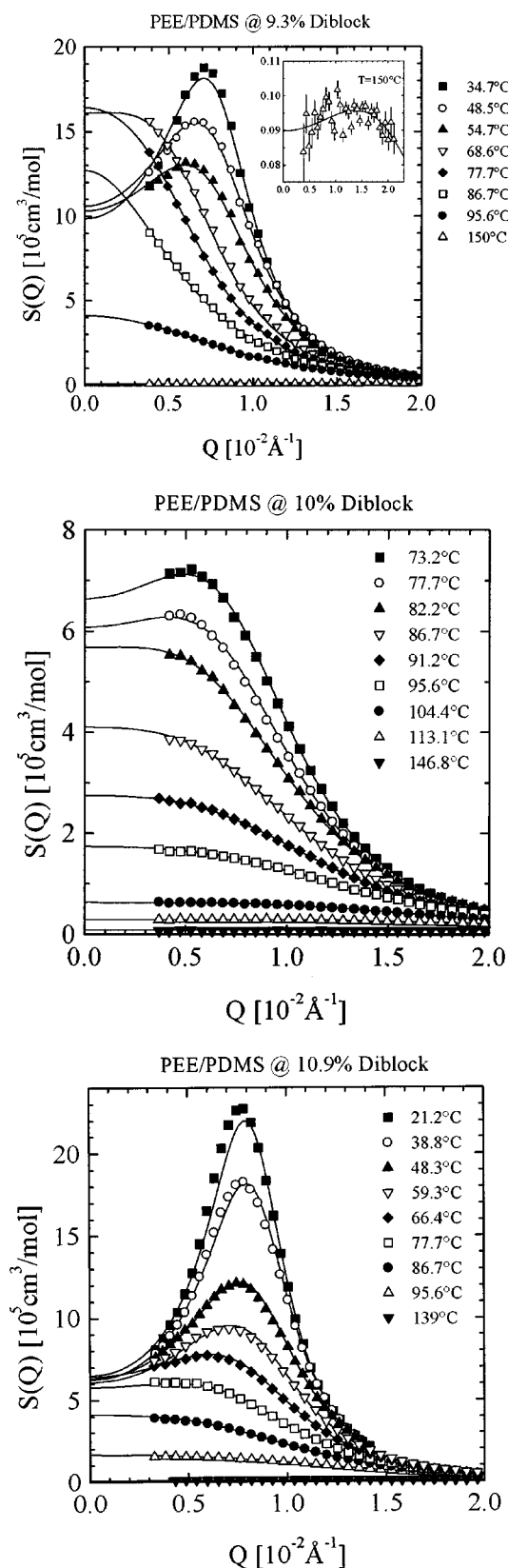


FIG. 6. Structure factor for concentrations between 9.3% and 10.9%. In this concentration range, transitions from diblock to blend and from blend to diblock character are observed by increasing the temperature.

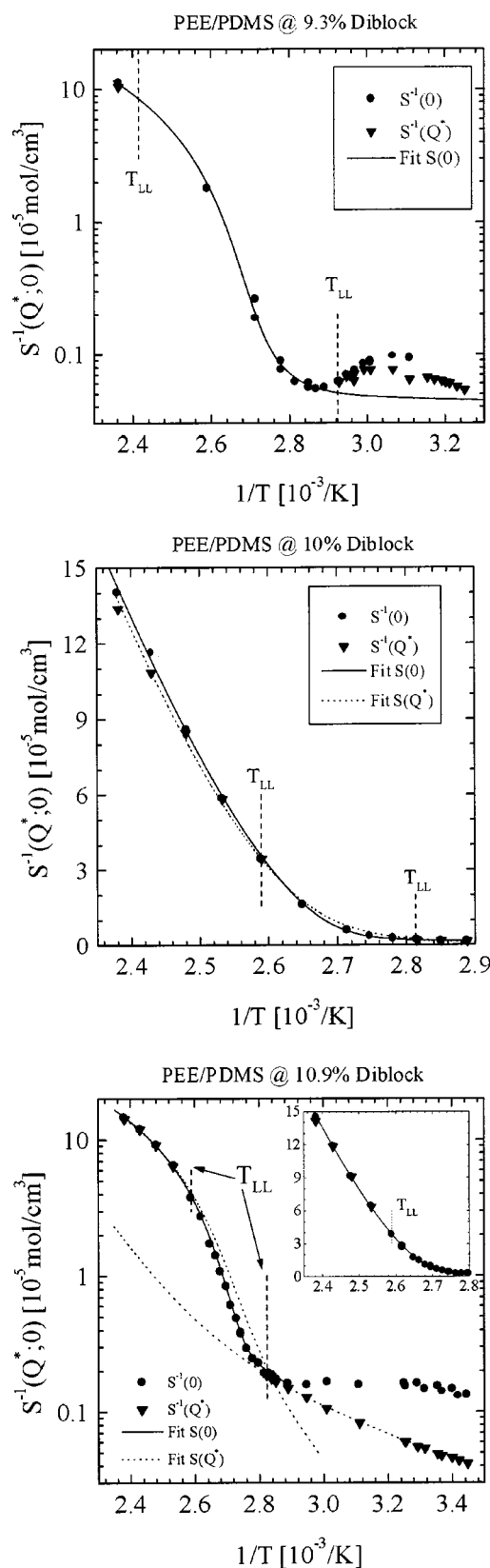


FIG. 7. $S(0)$ and $S(Q^*)$ values from different PEE/PDMS/PEE-PDMS systems as obtained from $S(Q)$ in Fig. 6 and the corresponding fits. $S(0)$ and $S(Q^*)$ are given logarithmically, while the inset shows the data on linear scale.

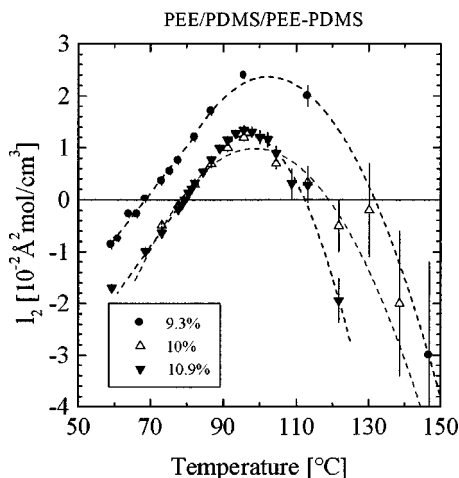


FIG. 8. Coefficient l_2 of the Q^2 term of the inverse structure factor. The negative and positive numbers determine the respective diblock and blend character. The Lifshitz line is defined for $l_2=0$.

supported by the temperature dependence of l_2 , given in Fig. 8, showing a pronounced maximum.

Both $S(Q)$ and $S(Q=0)$, as shown in Figs. 6 and 7, have been fitted with the theoretical expressions according to, respectively, Eqs. (8), (9), and (12). The fit of $S(0)$ is depicted as a solid line in the figure, and the resulting fit-parameters are collected in Table IV. Only the 10% sample is well described by theory in the whole measured temperature range. The temperature range of this sample exceeded, however, only slightly the lower Lifshitz line. For the 9.3% sample the theoretical $S(0)$ describes the experimental data only above the lower Lifshitz temperature, while the decrease of $S(0)$ near the lower Lifshitz temperature is not described by theory. The 10.9% sample shows also significant deviations; the $S(0)$ -susceptibility is only well described above the lower Lifshitz temperature and the $S(Q=Q^*)$ -value above and below the Lifshitz temperature can only be fitted with different sets of parameters. This observed discrepancy between $S(0)$ and theory might be a further indication for an ordered regime below the lower Lifshitz line.

Crossing the Lifshitz temperature becomes clearly visible from the temperature behavior of the coefficient l_2 of the Q^2 term of the inverse structure factor in Eq. (13), and which has been plotted in Fig. 8 for three Φ -values. The positive and negative values of l_2 corresponds to the respective blend and diblock character of the samples. There is yet no theoretical description of the observations in Fig. 8. Within the mean field approximation the Lifshitz line is predicted to occur at a constant diblock concentration Φ as the vertex function $\Gamma'_2(0)$ becomes zero at the Lifshitz concentration shown in Fig. 2(c), which means that L_2 in $S(Q)$ of Eq. (5) becomes zero at this concentration. The parameter l_2 obtained via Eq. (13) is of course influenced by thermal fluctuations which are not included in the mean field parameters $\Gamma'_2(0)$ and L_2 in Eq. (5). A theoretical expression for l_2 is not known to us.

An even more clear impression of the Lifshitz line is obtained from the Q^* -values of the $S(Q)$ -peak, as shown in

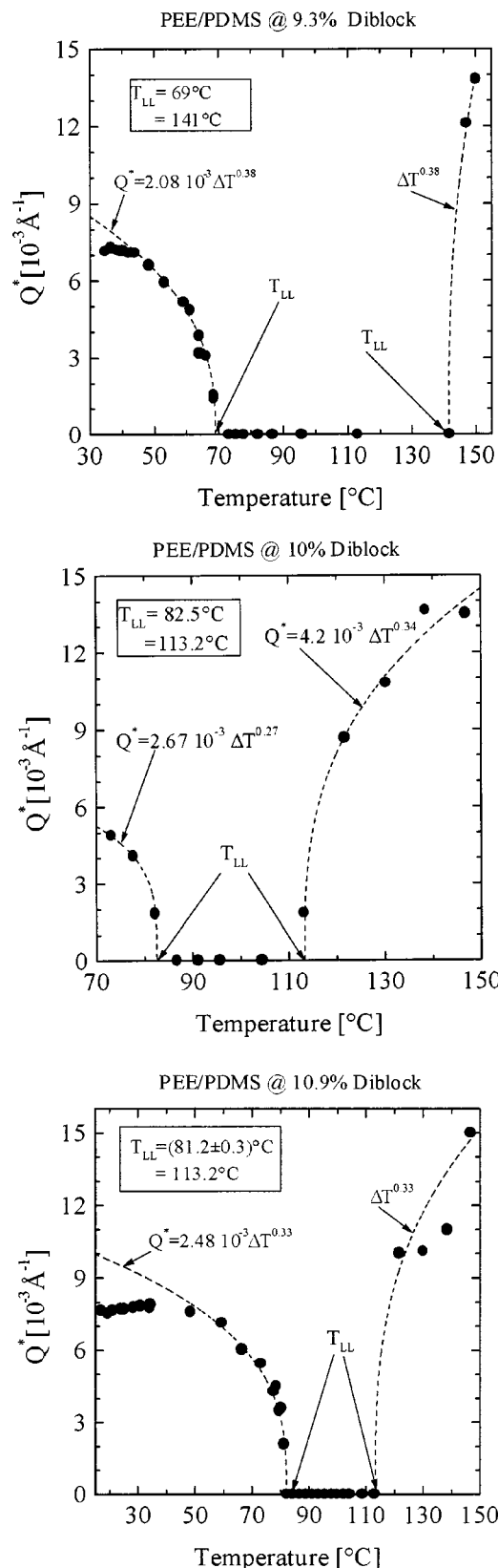


FIG. 9. Q^* values vs temperature for three concentrations. The ranges of diblock and blend character are clearly seen. Near the Lifshitz temperatures Q^* can be fitted by a scaling ansatz.

Fig. 9 giving Q^* vs temperature. At the Lifshitz temperature Q^* becomes zero. The behavior of Q^* near the Lifshitz line can approximately be described by a scaling law $Q^* \propto |T - T_{LL}|^{-\beta_T}$ with an exponent β_T between 0.3 and 0.4 when

TABLE IV. Parameters of samples larger than the Lifshitz line from $S(0)$.

Φ (%)	Γ_h (mol K/cm ³)	$\Gamma_\sigma(10^{-4}$ mol/cm ³)	b_0	c_0^a
9.3	0.7 ± 0.06	$-(0.93 \pm 1.5)$	3.9 ± 1	-0.03
10	0.49 ± 0.04	2.38 ± 1.03	2.2 ± 0.3	-0.09
10.9	0.44 ± 0.02	1.06 ± 0.6	1.48 ± 0.08	-0.18
12.1	0.48 ± 0.03	2.03 ± 0.7	2.8 ± 0.1	-0.3
14.9	0.33 ± 0.01	$-(1.07 \pm 0.2)$	3.1 ± 0.04	-0.61

^aCalculated c_0 .

approaching T_{LL} from both low and high temperatures. Q^* becomes only to some extent constant at low temperatures far from the Lifshitz line. The change of Q^* with Φ , as predicted from the mean field theory, has been plotted in Fig. 2(b), very near the Lifshitz concentration a power law behavior with an exponent of 0.4 is predicted. Corresponding experimental Q^* values measured at 65, 100, and 145 °C have been plotted vs Φ in Fig. 10. As in a first order phase transition the Q^* value seems to discontinuously change at the Lifshitz concentration which is about 11.5% and 9% at 100 °C and 145 °C, respectively, and then further increase with diblock concentration approaching the value of the pure diblock copolymer. At 65 °C two steps of Q^* are visible one at the corresponding Lifshitz concentration of 9% the other at 11.5%. The latter step at 11.5% might be a further indication for a transition to a microemulsion phase [see also discussions in context with Fig. 18(a)]. The dashed lines have been plotted as a guide for the eye. For a more detailed analysis and proof of the microemulsion phase one surely needs more experimental data from more diblock concentrations and also from application of the D/H contrast variation techniques.²⁰ It seems, however, clear from the data in Fig. 10 that no scaling with Φ occur near the Lifshitz line as predicted by theory [see Fig. 2(b)] and as it is observed at constant Φ between 9% and 11% with changing temperature (see Fig. 9).

D. Structure factor and susceptibility beyond the Lifshitz line

Two samples beyond 12% diblock concentration have been studied and the results are presented in Figs. 11–14. Figure 11 shows the structure factor $S(Q)$ of the 12.1% and 14.9% samples, as plotted in a semilogarithmic representation. For all temperatures between 143 and 17 °C the maximum value of $S(Q)$, and thereby the susceptibility, was observed at finite Q^* -values indicating that Φ is beyond the Lifshitz line at all temperatures. The solid lines in the figures are the result of the theoretical scattering function given in

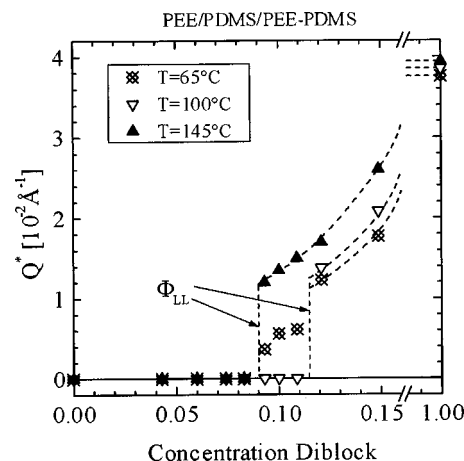


FIG. 10. Q^* vs concentration at 145, 100, and 65 °C. Q^* changes discontinuously at the Lifshitz concentration and increases very fast to the value of the pure diblock copolymer. At 65 °C two transitions at 9% and 11.5% diblock concentration are observed. The transition at 11.5% might be interpreted as an order–disorder transition to a bicontinuous microemulsion structure.

Eq. (7). The corresponding $S(Q=0)$ and $S(Q=Q^*)$ -values are plotted in Fig. 12 and Q^* together with x^* are given in Fig. 13. The solid lines in Fig. 12 represent best fits of the renormalized susceptibility, according to Eq. (8) for the $S(Q^*)$ and $S(0)$ values, and the corresponding renormalized FH-parameter of Eq. (17) and of Eq. (12). The parameters from the fit of $S(0)$ are summarized in Table IV. The values of $S(Q=0)$ and $S(Q=Q^*)$ show the same characteristic temperature dependence. For the 14.9% sample a slight deviation of the susceptibility from its theoretical description is observed at 30 °C, reflecting the order–disorder transition to a lamella phase. A corresponding discontinuity is also observed in the $S(0)$ and Q^* -values (Figs. 12 and 13). In the 12.1% sample, there was no similar changes for temperatures down to 14 °C, showing that the sample did not order into a lamella phase, to at least down to 14 °C. The Q^* -value for the peak position is theoretically predicted to be constant, as shown in the calculations given in Fig. 2(b). In reality, however, Q^* changes with temperature, likely as a consequence of the influences of the degree of the thermal composition fluctuations. Close to $T \cong 100$ °C a relative pronounced change appear in the temperature dependence of the Q^* -value, resulting in an only weak T dependence at low temperature. The observed change of slope of the Q^* -data for the 12.1% sample at 98 °C might result from the close approach to the Lifshitz line.

Figure 14 shows the susceptibility $S(Q=Q^*)$ and the peak position, Q^* , of the pure diblock copolymer. A clear

TABLE V. Critical parameters of the isotropic Lifshitz critical range. The 4.3% sample has been analyzed by the crossover function between mean field and 3d-Ising ranges.

Φ (%)	T_C (°C)	G_i (10^{-2})	C_+ (cm ³ /mol)	γ	ξ_0 (Å)	ν	$\eta = 2 - \gamma/\nu$
4.3	129.7	1.5 ± 0.6	323 ± 148	1.24	...	0.632	0.038
6	121.9	...	293 ± 60	1.37 ± 0.03	3.5 ± 0.3	0.84 ± 0.01	0.37 ± 0.01
6.7	116	...	227 ± 30	1.62 ± 0.02	2.7 ± 0.6	0.95 ± 0.03	0.29 ± 0.01
7.4	111.4	...	269 ± 34	1.61 ± 0.02	2.2 ± 0.5	1 ± 0.03	0.39 ± 0.01
8.3	97.9	...	279 ± 63	1.62 ± 0.03	1.9 ± 0.6	1.03 ± 0.05	0.43 ± 0.02

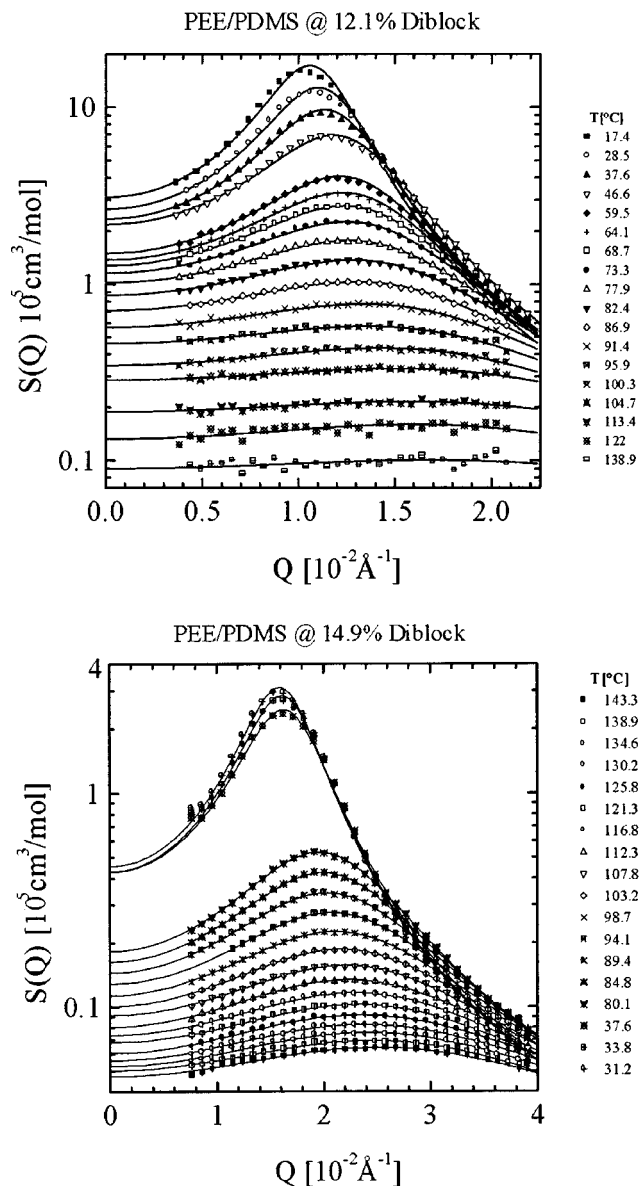


FIG. 11. Structure factor for two concentrations with exclusively diblock character (see phase diagram in Fig. 3). The solid lines represent a fit of $S(Q)$ in Eq. (7).

step wise change of the susceptibility is seen at the order-disorder phase transition at 83.3 °C. The solid line represents the theoretical expression in Eq. (17) and the corresponding fit parameters are given in Table II. The peak position Q^* linearly decreases with decreasing temperature in the disordered regime and shows a clear change in its behavior below the order-disorder transition.

E. Lifshitz critical range and crossover behavior

We now discuss the behavior of thermal composition fluctuations in the disordered regime below the Lifshitz line from another point of view, namely, in terms of critical exponents of the susceptibility and the corresponding correlation length obtained from asymptotic scaling laws. The structure factor $S(Q)$ of three samples have been plotted in Fig. 4 for various temperatures in Zimm representation S^{-1} vs Q^2 . The solid lines represent fits according to Eq. (13) from

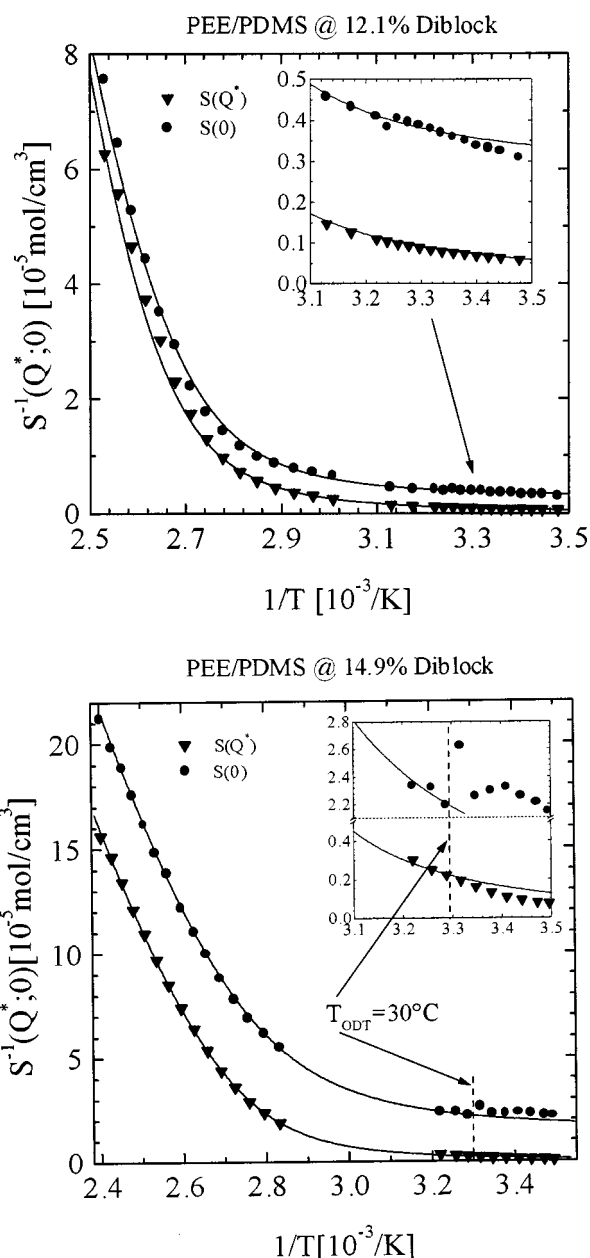


FIG. 12. $S(Q^*)$ and $S(0)$ vs inverse temperature $1/T$. The data are fitted by the theory of Kielhorn and Muthukumar. For the 14.9% sample a weak order-disorder transition was found at 30 °C; such a transition was not observed for the 12.1% sample.

which the susceptibility $S(0)$ and the two coefficients l_2 and l_4 emerges. In the $\Phi = 4.3\%$ sample, $S(Q)$ is sufficiently well described by the Ornstein-Zernike approximation corresponding to $l_4 = 0$. For larger block copolymer contents the Q^4 term becomes visible and relevant. The inverse susceptibility $S^{-1}(0)$ vs $1/T$ is shown in Figs. 5 and 15. The $\Phi = 4.3\%$ mixture behaves similarly to blends, namely, from high to low temperatures a transition from *mean-field* to *3d-Ising critical behavior* is observed. This is demonstrated by the corresponding fit (solid line) of the crossover function by Belyakov et al.²⁵ as already discussed. The second line through some of the 4.3% data represents the asymptotic 3d-Ising scaling law with the critical exponent $\gamma = 1.24$ as

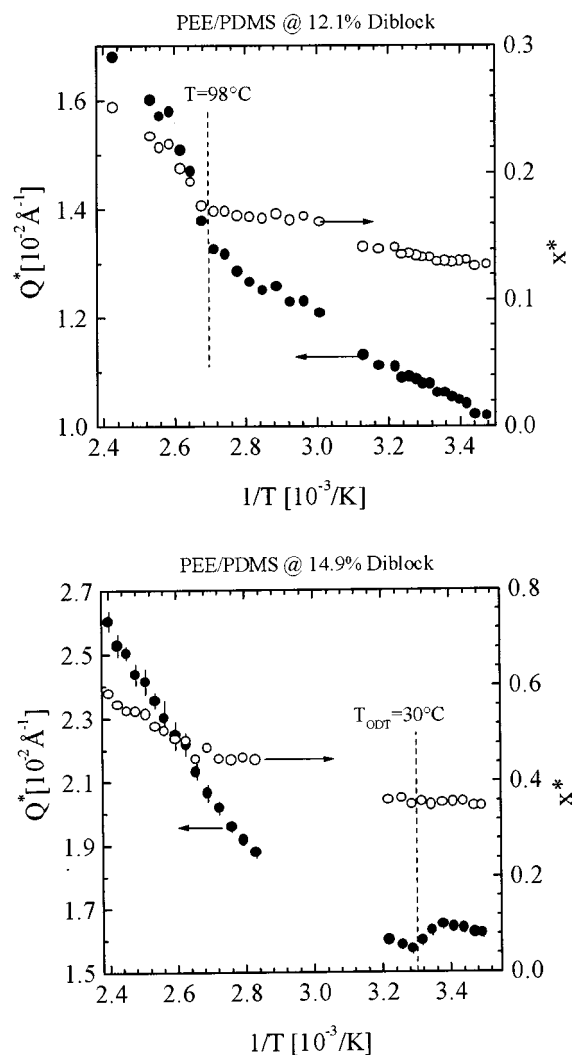


FIG. 13. Q^* values of $S(Q)$ from Fig. 11 vs $1/T$. Strong shifts of the peak maximum are observed with temperature. In the 12.1% sample a much stronger slope is observed at higher temperature above 100 °C. This might be related to the close approach to the Lifshitz line at this temperature.

evaluated from the crossover function. The inverse susceptibilities of the diblock concentration $\Phi = 6\%$, 7.4% , and 8.3% are characterized by curvatures far beyond that of the $\Phi = 4.3\%$. Such larger curvature corresponds to an increase of the ν -exponent, indicating a crossover to the universality class of the *isotropic Lifshitz case*. These susceptibilities could be analyzed over the whole temperature range by the scaling law according to $S^{-1}(0) = C_+^{-1}t^\gamma$ with the reduced temperature, $t = (T - T_C)/T$, and the critical exponent, γ , as demonstrated by the solid lines. This also means that the Ginzburg number corresponding to the critical range above T_C has strongly increased in comparison with the 4.3% sample. A similar analysis has also been performed for the correlation length according to $\xi = \xi_0 + t^{-\nu}$ with the critical exponent ν . The obtained critical exponents are collected in Table VI and are shown vs the copolymer content in Fig. 16.

In two samples with concentration 6.7% (not shown in Fig. 15 for clarity) and 8.3% an additional crossover was observed very near the critical temperature and phase separation was observed at a lower critical temperature plotted as

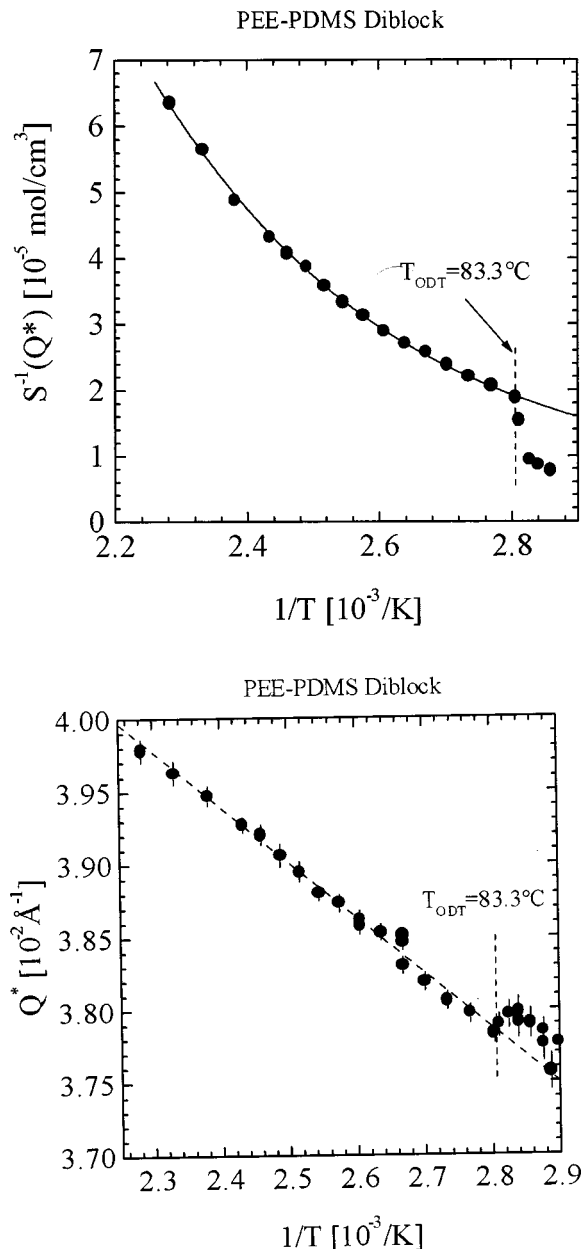


FIG. 14. Susceptibility and Q^* for the pure diblock copolymer. A relatively strong change of the order parameter is observed at the order–disorder temperature. In the disordered regime the susceptibility was fitted by the Fredrickson–Helfand theory according to Eq. (17).

open dots in the phase diagram. In this range the susceptibilities were analyzed by the same scaling law as demonstrated for the 8.3% sample in the inset of Fig. 15; the corresponding appreciably larger exponents and the critical temperatures are summarized in Table VI and plotted in Fig. 16. On the other hand, in the 7.4% sample phase separation occurred at the higher critical temperature shown as a full dot in the phase diagram and no additional crossover was observed. This experiment was performed with larger temperature steps and therefore the sample spent much less time in the region of strong thermal fluctuations. The experimental procedure was always the same; after the sample reached the desired temperature within the limits of less than 0.1 K two experimental runs of 10 and 30 min were started. Based on

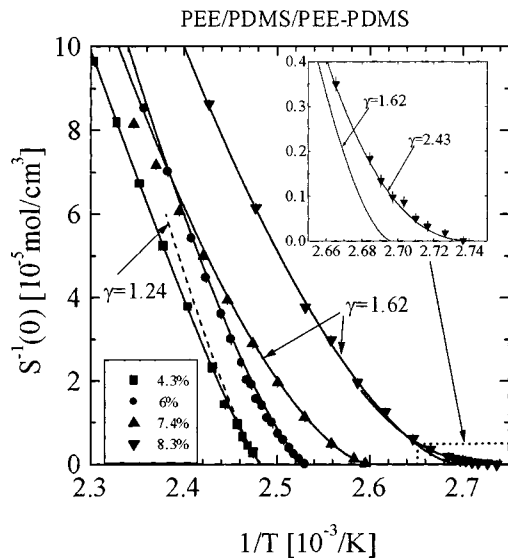


FIG. 15. Inverse susceptibility vs inverse temperature. $S(0)$ in the 0.043 sample follows a crossover function between mean field and 3d-Ising case while $S(0)$ of the other samples follows a scaling law with larger critical exponents.

these data we conclude that for the samples between 6% and 9% diblock content two consolute lines can be realized experimentally. These are plotted by the open and full dots in the phase diagram, respectively; phase separation occurs either at the upper or at the lower lines, depending on whether the crossover to the new universality class can occur or not. Such a crossover, however, is observed only if the experiments are performed sufficiently slowly. We abbreviate this as the *renormalized Lifshitz critical behavior*. An interpretation of this crossover might be related to rearrangements of the diblock copolymers as caused by the strong thermal composition fluctuations near T_C and which further stabilize the sample against phase decomposition. Such an effect was indeed observed in a ternary symmetric homopolymer/diblock copolymer system by a simulation study on spinodal decomposition; in the early to intermediate time regime the block copolymers became accumulated at the interface of the domains.³⁰ In our experiments we already observed this effect in the disordered phase near the critical point. Such a behavior was not observable in the simulations as one started from a mean field free energy expression neglecting thermal fluctuation. Because of the observed large thermal fluctuations near the critical point an early stage (e.g., a linear regime) of spinodal decomposition is not observable as the fluctuation modes already interact in the disordered regime leading to nonlinear effects right from the beginning of the phase decomposition process.^{2,31} This crossover might be quite analogous to the transition to a *renormalized 3d-Ising*

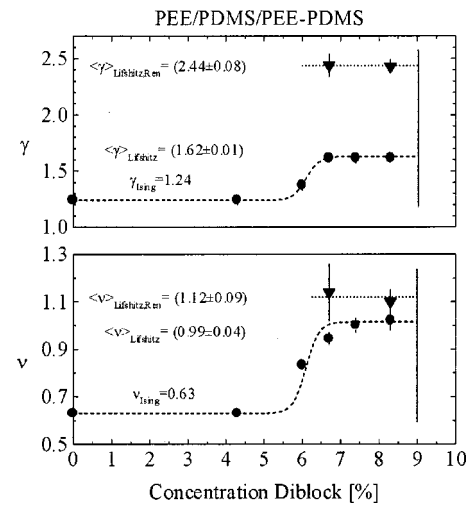


FIG. 16. Critical exponents of susceptibility and correlation length. At about 6% diblock content a crossover from 3d-Ising to isotropic Lifshitz critical behavior is observed. Near T_C a further crossover to a renormalized Lifshitz critical behavior was observed.

critical behavior, which have been observed in some binary polymer blends,^{32,33} in those blends an inhomogeneously distributed free volume could account for such a crossover behavior.

F. The Q^4 term of $S(Q)$ near the Lifshitz critical point

The structure factor plotted in Fig. 4 in the Zimm presentation shows that in the ranges where thermal composition fluctuations are described within the 3d-Ising universality class the coefficient l_4 in Eq. (13) is negligible and $S(Q)$ is described by the Ornstein–Zernike approximation. The crossover to the Lifshitz critical behavior shown for the critical exponents in Fig. 16 starts at 6% diblock concentration. At this Φ we also begin to observe a contribution from l_4 to $S(Q)$ from a slight deviation from linearity in the presentation of Fig. 4. This contribution becomes stronger at larger Φ as is visible for the 8.3% sample. This observation is a clear experimental indication of the connection between the crossover between the critical universality classes of 3d-Ising and isotropic Lifshitz cases and the reduction of the c_2 and l_2 terms in the Hamiltonian [Eq. (1)] and structure factor $S(Q)$ [Eq. (13)], respectively, being proportional to the restoring forces of thermal composition fluctuations. The strength of the Q^4 term can be also characterized by Kp^{-2} in the structure factor of Eq. (14) and which is plotted in Fig. 17 vs the correlation length ξ in double logarithmic scale. Approaching the critical temperature ξ becomes infinite and Kp^{-2} approaches zero as is expected for diblock compositions less than the Lifshitz value.¹² At constant ξ the Kp^{-2} increases

TABLE VI. Parameters in the renormalized case.

Φ (%)	T_c (°C)	C_+ (cm ³ /mol)	γ	ξ_0 (Å)	ν	$\eta = 2 - \gamma/\nu$
6.7	107.4	78	2.44 ± 0.1	3.5	1.14 ± 0.12	$-(0.14 \pm 0.02)$
7.4		not observed because of a faster cooling rate by larger temperature steps				
8.3	91.4	55	2.43 ± 0.06	2.4	1.1 ± 0.05	$-(0.21 \pm 0.01)$

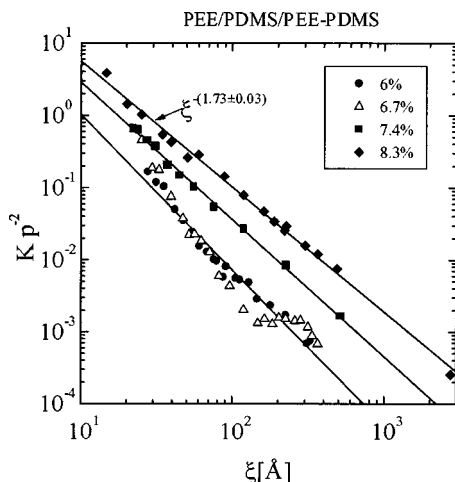


FIG. 17. Coefficient of the Q^4 term of $S(Q)$ in Eq. (14) vs the correlation length. This coefficient follows a scaling law approaching zero at the critical temperature as is expected for diblock concentrations smaller than the Lifshitz concentration. For constant correlation length the coefficient strongly increases according to the decrease of the surface energy proportional to c_2 in the Hamiltonian. The appearance of a finite Kp^{-2} is accompanied by the crossover from 3d-Ising to the isotropic Lifshitz case; this is reasonable as the restoring force for thermal composition fluctuations proportional to c_2 becomes weaker.

by about one order of magnitude changing the diblock composition from 6.7 to 8.3% and which is the result of a decreasing c_2 parameter in the Hamiltonian [Eq. (1)].

G. Flory–Huggins parameter, Ginzburg number, and segment length

The analysis of the structure factor $S(Q)$ measuring thermal composition fluctuations in the disordered state of the three component polymer mixture was mainly performed on the basis of the formalism developed by Kielhorn and Muthukumar in Ref. 13 and which takes the effects of thermal fluctuations into consideration, as reviewed above in Sec. II B. For samples with a diblock concentration larger than the Lifshitz line with the maximum of $S(Q)$ occurring at a finite Q , the most general application started with the analysis of $S(Q)$ by Eq. (7) (see solid lines in Figs. 6 and 11) which for each equilibrium state delivers four parameters, namely, a , b , c , d . Based on these four values and their expressions given in Ref. 13, the FH-parameter, the Ginzburg parameter, and the statistical segment length were calculated for each temperature from Eq. (9). The so obtained FH-parameter has been plotted in Fig. 18(a) vs $1/T$. The data mainly follow a straight line according to $\Gamma = \Gamma_h/T - \Gamma_\sigma$ with the enthalpic and entropic contributions whose numbers have been plotted in Fig. 18(b) and are given in Table II. The FH-parameters in Fig. 18(a) follow a straight line at high temperatures while at temperatures just below the lower Lifshitz line deviations are observed as indicated by the arrows. This means that at low temperature the theoretical approach does no longer describe the experimental data; a transition to a different state could be the reason for this deviation. With reference to the results of Bates *et al.*¹⁶ we interpret this behavior and the temperatures as indicated by arrows in Fig.

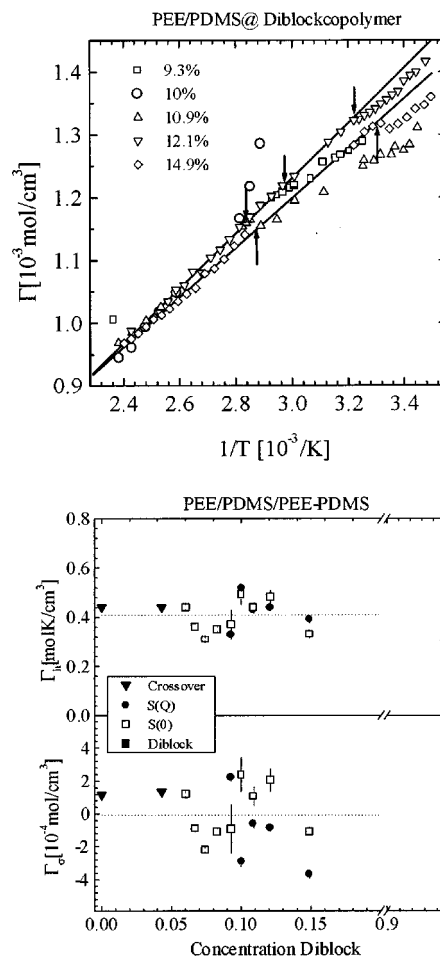


FIG. 18. (a) Flory–Huggins parameter vs $1/T$ as evaluated from $S(Q)$ with Eqs. (8) and (9). The deviations from the straight lines at low temperatures are interpreted related to an ordering transition to a bicontinuous microemulsion structure. (b) Flory–Huggins parameter for all investigated samples; they were derived from the fitted straight lines in (a) and from Eqs. (20) and (12), depending on whether the sample is in the 3d-Ising or isotropic Lifshitz critical region.

18(a) as the borderline to a bicontinuous microemulsion phase. This borderline has been plotted in the phase diagram of Fig. 3.

In addition, the FH-parameter was evaluated from $S(0)$ using Eqs. (8) and (12), which for diblock concentrations smaller than the Lifshitz line becomes the system susceptibility. In order to analyze $S(0)$ the parameters in Eq. (12) had to be assumed independent of temperature. The just mentioned formalism could not be applied for diblock concentrations smaller than 5%; for those samples the thermal fluctuations show the critical behavior of the 3d-Ising universality class as in binary polymer blends, including the crossover to the mean field behavior. So, the FH-parameter of the pure blend and 4.3% sample was evaluated from the fitted crossover function in Eq. (20) and has been depicted in Fig. 18(b).

The statistical segment length σ is another parameter obtained from the parameter d in the parameterized form of the structure factor of Eqs. (7) and (11). It describes the polymer conformation according to its relationship with the radius of gyration ($R_g^2 = \sigma^2 N/6$). In Fig. 19 the values of σ

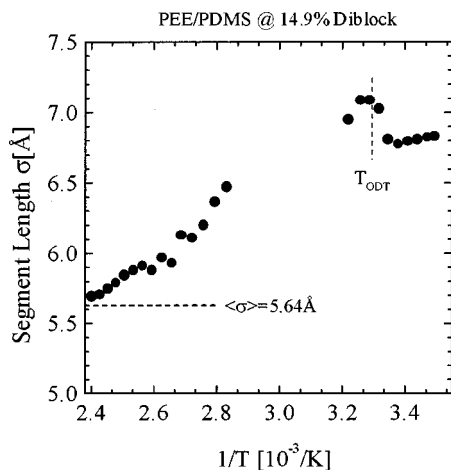


FIG. 19. Statistical segment length for the sample with 14.9% diblock concentrations as obtained from the fit. At high temperatures the conformation of an ideal coil is approached while at lower temperature the coils become stretched.

of the 14.9% sample is shown as an example; at high temperatures one finds in all samples a very good agreement with the expected value $\langle\sigma\rangle=5.64\text{ \AA}$ from the literature.³⁴ Upon decreasing the temperature a marked increase in the segment length reflects a stretching of the polymers.

V. DISCUSSIONS AND CONCLUSIONS

We presented SANS experiments on the three component mixture composed of the near critical polymer blend PEE/PDMS and the corresponding diblock copolymer. The ratio of the molar volumes between homogeneous and diblock copolymer is $\alpha=0.178$. From measurements of the static structure factor $S(Q)$ the phase boundaries between the disordered states at high temperatures and, respectively, the micro- and the macrophase separated states at low temperatures were determined for the PEE/PDMS/PEE-PDMS system. These results are summarized in the phase diagram in Fig. 3. The macrophase separation is realized as a usual second order phase transition in the low diblock copolymer limit. For higher copolymer content, microphase separation appears as a first order phase transition to a lamella ordered state above 14% diblock content with a periodicity given by the size of the diblock copolymer and to a bicontinuous microemulsion phase between roughly 9% and 14% diblock concentration. The phase boundary of the latter phase was proposed indirectly from anomalies of the concentration dependence of Q^* (Fig. 10), the FH-parameter [Fig. 18(a)] and from information in Ref. 16. In the disordered regime, the fluctuations are reflected through the structure factor maximum, $S(0)$ and $S(Q^*)$, which represents the susceptibility and the maximum amplitude of the thermal fluctuation modes. The fluctuations resulting in respectively macro and microphase separation is occurring for a maximum in $S(Q)$ at, respectively, $Q=0$, and $Q=Q^*$, Q^* being finite. The Lifshitz line separating these two disordered ranges was identified experimentally, as shown in the phase diagram in

Fig. 3. According to the mean field theory the Lifshitz line should be at a constant block copolymer content in contrast to the observation.

Beyond the characteristic border lines presented in the phase diagram in Fig. 3 the “critical” characteristics of the thermal composition fluctuations in the disordered regime were determined, including the identification of the cross-over behavior from the universality classes of 3d-Ising to the isotropic Lifshitz and to a renormalized Lifshitz case leading to a lower phase boundary indicated by the crossed area and the open dots, respectively. In the ternary PEE/PDMS/PEE-PDMS system the mean field approximation can, however, only be a rather poor approximation. In particular, critical fluctuations will become strong near the isotropic Lifshitz critical point since the stabilizing effects from the surface energy, expressed by the c_2 term and by the l_2 term in Eqs. (1) and (13), respectively, becomes small. This effect is expressed by an upper critical dimension, which is derived as $d_U=8$ at the Lifshitz line.^{12–14} The Lifshitz point, however, is destroyed by these thermal composition fluctuations, as according to the Ginzburg criterion the stabilization of the disordered phases is much weaker in blends than in diblock copolymers.^{11,13} On the other hand in the ternary system of PE/PEP/PE-PEP, where the appearance of a microemulsion phase was first established¹⁶ the observed critical exponents remained the mean field values.¹⁵ This situation is different from the present system and must be related to the order of magnitude smaller molar volume of the polymers in the PEE/PDMS system, relative to the PE/PEP system. At the Lifshitz point the Ginzburg number scales with $N^{-2/5}$ in comparison with blends where a N^{-1} is proposed, which means an appreciably stronger sensitivity of Gi with molar volume.

A detailed analysis of the structure factor $S(Q)$ and $S(0)$ were performed with the theoretical approach formulated by Kielhorn and Muthukumar¹³ which for homopolymer blends/copolymer systems takes fluctuations into consideration on the basis of the Hartree approximation. The resulting fits, which are represented by the solid lines in the corresponding figures, represent the experimental data rather well. Three characteristic different diblock concentration ranges appear in the phase diagram. First, we considered the two samples of largest diblock content at 12.1% and 14.9%. In these samples the susceptibility always occurs at the finite Q^* value. The fit of $S(Q)$ is presented in Fig. 11 from which the parameters are collected in Table II. In addition $S(0)$ was fitted as depicted in Fig. 12 and the corresponding parameters are collected in Table IV. The susceptibility $S(Q^*)$ itself was fitted by Eq. (17) representing the Fredrickson–Helfand approach and is demonstrated by the solid line. The corresponding parameters are not given. The transition to an ordered state is observed in the 14.9% sample, as highlighted in the inset of Fig. 12 showing the deviations of $S(0)$ from their theoretical prediction. The deviations are still weak in comparison to that of the pure diblock sample, shown in Fig. 14. A similar deviation was not observed for the 12.1% sample and those with lower diblock content.

The samples between 9% and 11% diblock content show an intermediate behavior between the characteristic behavior of blends and diblock copolymers. This is most clearly seen

in the plots of Fig. 9 showing the peak position Q^* vs temperature. According to these figures the samples show the characteristic behavior of diblocks both at low and at high temperatures, while at intermediate temperature the behavior is polymer blend like with the susceptibility given at $Q=0$ of $S(Q)$. These observations imply that the Lifshitz line depends on the diblock content as depicted by the dashed curve in the phase diagram in Fig. 3. Near the Lifshitz line the Q^* approaches with temperature zero exponentially with an exponent roughly between 0.3 and 0.4, which is quite similar to the theoretical exponent of Q^* upon approaching the Lifshitz line by changing concentrations, as proposed by the mean field calculation shown in Fig. 2(b). The change of Q^* with concentration depicted for three temperatures in Fig. 10, however, shows a different behavior; at the Lifshitz concentration a stepwise increase of Q^* is observed as is typical for an order parameter change at a first order phase transition. At 65 °C even two stepwise changes of Q^* are observed, while at 9% diblock content the Lifshitz line is passed the second step to a finite Q^* is observed at 11.5%. This change in Q^* we interpret as the phase transition border to a bicontinuous microemulsion phase in consistence with results from Ref. 16. The $S(Q)$ of these samples is shown in Fig. 6, and their $S(Q^*)$ and $S(0)$ in Fig. 7; the solid and dashed lines represent the corresponding fits whose parameters are collected in Tables II and IV. An irregularity was observed in the 9.3% sample in so far as a continuous increase of $S(Q^*)$ and $S(0)$ with decreasing temperature was not observed; at the lower Lifshitz line a decrease of $S(Q^*)$ and $S(0)$ is observed. This means that in this sample the long wavelength fluctuations became partly unbounded from the diblock copolymers if approaching the lower Lifshitz line.

In the samples with a diblock content lower than the Lifshitz line the susceptibility is always represented by $S(0)$ which have been plotted in Fig. 5. The solid lines represent the corresponding fits with Eqs. (12) and (13); their parameters are collected in Table III. The Kielhorn–Muthukumar theory could not be applied for the 4.3% sample; in this case the fluctuations showed the characteristic behavior of polymer blends, namely a crossover behavior from cases of mean field approximation to the 3d-Ising model. The corresponding solid line represents a fit of the crossover function in Eq. (20) and the dashed line the scaling law according to the 3d-Ising model with the critical exponent $\gamma=1.24$.

The main parameters obtained from application the Kielhorn–Muthukumar theory to $S(Q)$ and $S(0)$ are the FH-parameter, the Ginzburg number \tilde{Gi} , and polymer conformation. The enthalpic and entropic terms of the FH-parameter from all samples are shown in Fig. 18 and are summarized in Tables II–IV. The values obtained from $S(Q)$ and $S(0)$ and Eqs. (12) and (16) are the same within the error bars and independent from the diblock content. The enthalpic term of the FH-parameter of the pure blend and the 4.3% samples derived from the crossover function Eq. (20) is the same as for the other three component samples while a roughly 30% smaller value was found for pure diblock copolymer. Distinctly different entropic terms were evaluated for the 0 and 4.3% sample and the pure diblock copolymer being of the order of 10^{-4} and negative for the latter sample. The en-

tropic terms of Γ for the other three component samples show a rather strong scattering within the same order of magnitude of the pure diblock and of the 0 and 4.3% samples. The apparent difference of the FH-parameter of binary polymer blends and the corresponding diblock copolymers has been discussed in Refs. 10, 35, and 36. The conclusion of Refs. 10 and 36 was that the absolute values of the FH-parameters are always smaller in diblock copolymers which is consistent with the data of the present work.

The Ginzburg parameter \tilde{Gi} in Table II is rather constant for the diblock copolymer and the three component mixtures. The corresponding Ginzburg number of the 0 and 4.3% sample evaluated from the crossover function is about two orders of magnitude smaller than for the diblock copolymer. Similar ratios were also found for another system.¹⁰

The values for the segment length are plotted in Fig. 19 for the 14.9% sample. At high temperature the statistical segment length approaches the value given in literature for the corresponding linear polymer components. The polymers become stretched by decreasing the temperature. A slight shrinkage of the chains is observed by passing the order–disorder temperature.

The susceptibilities for a diblock content of 6% and larger as depicted in Fig. 5 have also been interpreted from the point of view of scaling laws, valid asymptotically close to a critical point and plotted in Fig. 15. These scaling laws are characterized by the critical exponents and amplitudes. The numerical numbers of the critical exponents of the susceptibility and correlation length are depicted in Fig. 16. For concentrations with block copolymer content below 5.5% the thermal fluctuations are described by the universality class of the 3d-Ising behavior. Between $\Phi=5$ and 7%, approximately, the system crosses gradually over to the isotropic Lifshitz critical behavior characterized by a critical exponent ($\gamma=1.62$) significantly larger than the 3d-Ising value ($\gamma=1.24$). Even larger critical exponents were obtained after the crossover to the Lifshitz renormalized state very close to the critical temperature ($\gamma=2.44$). The critical exponents γ and ν are related by the Fisher scaling relation to the Fisher exponent η presented in Tables II and III. The experimental η values are of the order of one magnitude larger than those of polymer blends in the 3d-Ising regime, and become negative in the renormalized state. A crossover from 3d-Ising to an isotropic Lifshitz and renormalized isotropic Lifshitz critical behavior is observed even though the Lifshitz critical point itself cannot be reached experimentally; it is suppressed by strong thermal composition fluctuations as is seen by the parameter p in Eq. (14) which is not constant but singular near the critical temperature (Fig. 17).

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