Ternary mixture of homopolymer blend and diblock copolymer studied near the Lifshitz composition by small-angle neutron scattering

Kell Mortensen, a* Dietmar Schwahn, b Henrich Frielinghaus a and Kristoffer Almdal a

aCondensed Matter Physics & Chemistry department, Risø National Laboratory, Roskilde Denmark, b Inst. Festkörperforschung, Forschungszentrum Jülich, Germany. E-mail: kell.mortensen@risoe.dk

A ternary mixture of two homopolymers and the corresponding diblock copolymer represents a good model system to study critical phenomena near the mean field predicted Lifshitz point. The structure factor of concentration fluctuations is in this regime of the phase diagram described by a formula which independently accounts for the peak-position $q^*$, the scattering intensity at $q^*$, $S(q^*)$, and the forward scattering, $S(0)$. The susceptibility, which is given by the maximum value of either $S(0)$ or $S(q^*)$, shows markedly renormalized critical behavior with critical exponents significant larger than the 3d-Ising value relevant for simple binary blends.

1. Introduction

The characterization of different states of matter and the phase transitions between these states are 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 blends and in diblock copolymers.

In this paper we investigate the cross over regime from 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. By appropriate choice of molar sizes the ternary system has been made to fulfill 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 $V_{AB}$ for the diblock copolymer. The Flory-Huggins parameters $\Gamma$ must obey the condition $V_{AB}{\Gamma}_{ODT} \approx V_A{\Gamma}_A$, $V_B{\Gamma}_B$, $\Gamma_{ODT}$ representing the Flory-Huggins parameter of the diblock copolymer at the order-disorder transition and $\Gamma$, of the blend at the critical point. Within mean field approximation, the molar volumes must fulfill the ratio $V_{AB}/V_A = V_{AB}/V_B = 10.495/2 = 5$.

If homopolymers are added to a diblock copolymer in the ordered phase, the microdomain size might ideally increases continuously until the thermodynamic limit at $q^* = 0$ where the domains are of macroscopic size. In mean field theory the critical line of macrophase separation for homopolymer mixtures and the corresponding line of microphase separation in diblock copolymers meet at a multicritical point, the Lifshitz point (Broset a & Fredrickson, 1990; Holyst & Schick, 1992; Kielhorn & Muthukumar, 1997).

In the near vicinity of the critical point, however, fluctuation renormalized characteristics are different for homopolymer blends and diblock copolymers. The state of homopolymer blends is the 3d-Ising class (Schwahn et al., 1987), while that of diblock copolymers is the Bradsovskii type (Fredrickson & Helfand, 1987). The cross-over temperature from mean-field to renormalized states is given by the Ginzburg-criterion, which for homopolymer blends is predicted to scale with the degree of polymerization $N$ as $G = (T - T_c)/T_c \propto 1/N$, whereas the scaling for diblock copolymers is $G \propto 1/\sqrt{N}$. The critical behavior near the Lifshitz critical point is therefore expected to be highly complex and strongly influenced by thermal fluctuations.

In a recent study on a ternary system of relative high molar mass symmetric polyolefins composed of two homopolymers and the corresponding diblock copolymer: PE/PEP/PE-PEP, PE being polyethylene and PEP poly(ethylene propylene), mean field Lifshitz-like behavior was observed near the predicted isotropic Lifshitz critical point (Bates et al., 1995); the critical exponents of the susceptibility and correlation length were determined to be $\gamma = 1$ and $\nu = 0.25$, respectively, 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. Near 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 (Bates et al., 1997). An equivalent one-phase gap was observed between the microand macro-phase separated states in the more low-molar mass system of poly(ethyl ethylene) and poly(dimethyl siloxane), as shown in Fig 1 (see also Schwahn, Mortensen et al., 1999a & b). This system showed moreover, in the near vicinity of the mean field Lifshitz point, critical exponents that are significantly renormalized relative to both mean field and 3d-Ising behavior.

![Figure 1](image-url)

Figure 1: Phase diagram of ternary system of PEE/PDMS/PEE-PDMS, with fixed PEE/PDMS ratio: 0.516/0.484.

The present paper presents detailed experimental results on the structure factor of the poly(ethyl ethylene) and poly(dimethyl siloxane) system: PEE/PDMS/PEE-PDMS, measured close to the Lifshitz composition.

2. Experimental

The systems that have been studied are ternary mixtures of PEE and PDMS homopolymers and the corresponding PEE-PDMS diblock...
copolymer, PEE being the acronym for partially deuterated poly(ethyl ethylene), and PDMS the acronym for poly(dimethylsiloxane).

The similar sized PEE and PDMS homopolymers and the symmetric diblock copolymer PEE-PDMS were synthesized by anionic polymerization followed by catalytic hydrogenation (Almdal et al. 1996). The PEE-monomers were partly deuterated during the catalytic saturation, giving the monomer unit: C12D23H2. The degree of polymerization of the two homopolymers were close to be equal, while the symmetric diblock copolymer had a molar mass approximately 5 times larger, in the attempt to match the microphase separation temperature of the pure PEE-PDMS with the macrophase separation temperature of the pure homopolymer binary blend: \( N_{\text{PEE}} = 30.5, N_{\text{PDMS}} = 29.2 \) and \( N_{\text{PEE-PDMS}} = 168 \). The ratio of the molar volumes of the homopolymers relative to the diblock copolymer,

\[
\alpha = \frac{\sqrt{V_{\text{AB}}/V_{\text{PEE}}}}{V_{\text{AB}}/V_{\text{AB})), \quad i = A, B
\]  

is for this system, \( \alpha = 0.18 \). The Lifshitz critical value separating macro and microphase separation is given as \( \Phi_{c2} = 2\alpha^2/(1 + 2\alpha^2) \) (Broseta & Fredrickson, 1990; Fredrickson & Bates 1997).

The structure factor reflecting the thermal composition fluctuations was measured by small-angle neutron scattering in a number of mixtures of varying copolymer content \( \Phi_{\text{PEE-PDMS}} = \Phi \), keeping the ratio of the two homopolymer concentration constant equal the critical value: \( \Phi_{\text{PDMS}}/\Phi_{\text{PEE}} = 0.516/0.484 \). With the PEE monomers of the homopolymer and the block copolymer deuterated to the same degree, the measured structure factor, \( S(q) \), reflects thermal composition fluctuations with respect to the total PEE/PDMS-fractions. \( S(q) \) is therefore a measure of a scalar \( (m=1) \) order parameter represented by the local composition \( \phi = \phi(r) \).

In the present report we concentrate on the system with block copolymer concentration \( \Phi_{\text{PEE-PDMS}} = 10.9\% \), but extended studies will be reported elsewhere (Schwahn, Mortensen, Frielingshaus, Almdal, 1999a & b). The 10.9% sample is close to the experimental Lifshitz composition.

3. Results and Discussion

The basic thermodynamic features of systems near their consolute line are well described by the Landau expansion of the free energy:

\[
H = \frac{1}{2} \int d^4 r [c_2 (\nabla \phi)^2 + c_4 (\nabla^2 \phi)^2 + \tau \phi^2 + \sigma \phi^4 + u_6 \phi^6]  
\]  

with the order parameter \( \phi \) (Holyst & Schick, 1992). A principle effect of diblock copolymers solved with a homopolymer blend is a reduction of the surface energy which, according to the Hamiltonian (2), is described by a reduction of the parameter \( c_2 \). The \( c_2 \) parameter is positive at low copolymer content, becomes zero at the Lifshitz critical composition and is negative for large copolymer content.

The Hamiltonian (2) predicts composition fluctuations in the homogeneous (disordered) one-phase regime. These fluctuations are described by the structure factor \( S(q) \), which within the random phase approximation (Leibler, 1980), is giving as:

\[
S(q) = V_{AB}/[F(q) - 2\Gamma V_{AB}] 
\]  

where \( F(q) \) is the inverse form factor. The structure factor \( S(q) \) can be measured directly in a scattering experiment with \( q \) given by \( q = (4\pi/\lambda) \sin \theta \), \( \lambda \) being the wavelength of the used radiation, and \( \theta \) being half of the scattering angle.

\( S(q) \) can mean field approximation be expanded into powers of \( q^2 \), as

\[
S^{-1}(q) \approx S^{-1}(0) + \ell_2 q^2 + \ell_4 q^4 
\]  

with the coefficients given by of the parameters of the Hamiltonian (2). The first term of (4) is \( S^{-1}(0) = \tau \), which for compositions less than the Lifshitz value represents the susceptibility. The coefficients \( \ell_2 \) and \( \ell_4 \) are proportional to respectively \( c_2 \) and \( c_4 \) in the Hamiltonian (2), and can be determined in terms of the polymer parameters and composition (Kielhorn & Muthukumar, 1997)

\[
c_2 \sim \ell_2 = \left( \frac{R_q^2}{V} \right) \left[ 4\alpha^2 \left( 1 - \Phi_{AB} \right) - 2\Phi_{AB} \right] / \left[ 3\alpha^2 \left( 1 - \Phi_{AB} \right)^2 \right] 
\]  

\[
c_4 \sim \ell_4 = \left( \frac{R_q^2}{V} \right) \left[ \left( 1 - \Phi_{AB} \right)^2 (4\alpha^4 + 16\alpha^2 - 4\alpha + 4) - \left( 1 - \Phi_{AB} \right) (16\alpha^2 - 4\alpha + 8) + 4 \right] / \left[ 36(1 - \Phi_{AB})^3 \right] 
\]

At the Lifshitz composition \( c_2 = c_4 = 0 \) the characteristic meanfield behavior: \( S^{-1}(q) \propto q^2 \), clearly appear from (4).

3.1. Blend-like Compositions

For positive \( c_2 \)-values the structure factor \( S(q) \) as obtained from the Hamiltonian (2) has the basic characteristics of polymer blends, with \( S(q) \) maximum at \( q = 0 \), and with the susceptibility, \( \tau^{-1} \), correspondingly given by this \( S(q = 0) \) value:

\[
\tau = S^{-1}(q = 0) = 2(\Gamma - \Gamma) 
\]  

where \( \Gamma \) is the effective Flory-Huggins parameter and \( \Gamma \) represents the value at the critical point of phase separation. For dominating \( c_2 \) in (2) \( (\ell_2 \text{ term in (4))} \), \( S(q) \) approaches the common form of homopolymer blends:

\[
S^{-1}(q) = S^{-1}(0) + \ell_2 q^2 
\]  

At the critical temperature of macrophase separation \( T_c \) \((\Gamma = \Gamma_c)\), the susceptibility diverges, i.e. the inverse susceptibility \( \tau = S^{-1}(0) \) becomes zero. According to mean field theory, \( S^{-1} \) scales with \( T^{-\gamma} \), \( \gamma = 1 \). Including fluctuation renormalization, the critical exponent of the susceptibility increases to the 3d-Ising value \((\gamma = 1.24)\), but the form of \( S(q) \) as given in (8) remains a good approximation.

3.2. Diblock Copolymer-like Compositions

For negative \( c_2 \)-values the structure factor, \( S(q) \), has the basic characteristics of block copolymer melts with the maximum value of \( S(q) \) appearing at a finite \( q \)-value, \( q = q^* \). The formfactor \( F(q) \) in (3) can for \( c_2 \) dominating in (2) be calculated in terms of the partial structure factors \( S_{AA}, S_{BB} \) and \( S_{AB} \) describing the correlations between the monomers of type A and B (Leibler, 1980):

\[
F(q) = \frac{S_{AA}(q) + S_{BB}(q) + 2S_{AB}(q)}{S_{AA}(q)S_{BB}(q) - S_{AB}(q)} 
\]  

For unperturbed Gaussian chains (9) can be written in terms of molecular parameters via the generalized Debye-function:

\[
g_D(f, x) = (2/\lambda^2) \cdot \left[ f_x + \exp(-f_x) - 1 \right] 
\]  

with \( x = q^2 R_q^2 = q^2 N\sigma^2/6, \sigma \) being the statistical segment length of the copolymer, \( N \) the degree of polymerization, and \( R_q \) being the radius of gyration of the diblock copolymer. Inset into (9) gives:

\[
F(x) = g_D(1, x) / \left[ g_D(f, x)g_D(1 - f, x) - 1/4[g_D(1, f) - g_D(f, x) - g_D(1 - f, x)]^2 \right] 
\]  


K. Mortensen et al. 687
The susceptibility is in this diblock copolymer case given by the maximum value of the structure factor at \( q^* \). Within mean field theory of symmetric copolymers, \( S(q^*) \) diverges at the critical point \( T_c \). Below \( T_c \) the polymer system will microphase separate into a mesoscopic ordered lamellar structure.

In the fluctuation renormalized case, the structure factor can be approached a similar form as (3), but with a renormalized Flory-Huggins parameter given by

\[
\Gamma_{ren}^{VAB} = \Gamma^{VAB} - \tilde{c} \sqrt{S(q^*)}/V_{AB}
\]

(12)

where \( \tilde{c} \) is given by molecular parameters.

### 3.3. Structure Factor and Susceptibility near the Lifshitz Composition

With \( c_2 \approx 0 \) in the Hamiltonian (2) near the Lifshitz point, the forth order term of the gradient energy, \( c_4 \), becomes a leading factor in the free energy, giving rise to the mean field characteristic Lifshitz behavior of the structure factor, \( S(q) \sim q^4 \). Such behavior has been observed in a relative high molar mass ternary system of poly(ethylene propylene) and poly(ethyl ethylene) (Bates et al., 1995).

The expression for the structure factor of a three component mixture of a polymer blend and the corresponding diblock copolymer can within the random phase approximation be described by the same \( S(q) \) as given for pure block copolymers, (3) and (9), (Kielhorn & Muthukumar, 1997). 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 composition \( \Phi_A = \Phi_B \) and equal partial structure factors \( S_{AA} \) and \( S_{BB} \), \( S_{AB} = S_{BA} \)) and an AB diblock with volume \( V_{AB}, F(q) \) can be reduced to

\[
F(q)/V_{AB} = 2/[S_{AA}(q) - S_{AB}(q)]
\]

(13)

which in analogy with (11) can be written in terms of the generalized Debye function (10) (Kielhorn & Muthukumar)

\[
F(a) = 4/[1 - \Phi_{AB} |\alpha g_0(1, a\alpha) - \Phi_{AB} g_0(1, \alpha x/a)|]
\]

(14)

### 3.4. Effect of thermal fluctuations in blend/copolymer mixtures.

The structure factor of blend/diblock mixtures has been derived beyond the mean field approximation (Kielhorn & Muthukumar, 1997), using the Hartree approximation in the Bradzovskii formalism, equivalent to the procedure developed for pure diblock copolymer melts (Fredrickson & Helfand, 1987). The structure factor (3) & (14) was thereby parameterized into the simple form

\[
S^{-1}(q) = a/(b + q^2) + c + dq^2
\]

(15)

where the parameters, \( a, b, c, \) and \( d \) have been calculated assuming that the general shape of \( S(q) \) is unaltered compared to the mean field result (Kielhorn & Muthukumar, 1997). The parametrization of \( S(q) \) (15) with four parameters reflects the four characteristics:

\[
\begin{align*}
S^{-1}(0) &= a/b + c, \\
q^* &= \sqrt{a/d - b}^{1/2}, \\
S(q^*) &= \sqrt{d/a + \sqrt{da + c - db}},
\end{align*}
\]

(16)

and the width of the structure factor peak.

The structure factor of the 10.9% sample, as measured at temperatures in the range from 21-95°C is shown in Fig.2. The structure factor shows at low temperatures the characteristic behavior of diblock copolymers, i.e. \( S(q) \) has maximum at finite \( q^* \)-value, while at higher temperatures, \( S(q) \) shows the characteristics of homopolymer blends: \( S(q) \) maximum at \( q = 0 \). At even higher temperatures, the structure factor is again block copolymer like (for details, see Schwahn, Mortensen et al. 1999b). The curved Lifshitz line shown in the phase diagram in Fig.1 reflects this behavior. The experimental Lifshitz line is, in opposition to theoretical predictions, not constant in diblock copolymer content.

The structure factor \( S(q) \) is very well described by the Kielhorn-Muthukumar expression (15), as demonstrated by the solid lines giving the best fits. From these fits we obtain the parameters \( a, b, c \) and \( d \), and thereby the values of \( q^* \), \( S(0) \) and \( S(q^*) \). \( S(0) \) and \( S(q^*) \) are both shown in Fig.3, plotted versus inverse temperature.

**Figure 2**
Structure factor of PEE-PDMS/PEE-PDMS with composition \( \Phi_{PEE-PDMS}=10.9\% \). In this composition transitions from diblock to blend and from blend to diblock character is observed by increasing the temperature.

**Figure 3**
Susceptibilities \( S(0) \) and \( S(q^*) \) from fits to the experimental structure factor \( S(q) \) shown in Fig.2. The lines represents fits using the fluctuation renormalized scaling ansatz.
Crossing the Lifshitz temperature becomes clearly visible from the temperature behavior of the resulting $q^*$-values of the $S(q)$-peak, as shown in Fig. 4. At the Lifshitz temperature $q^*$ becomes zero. The behavior of $q^*$ near the Lifshitz line can approximately be described by a scaling law $q^* \propto |T - T_L|^{-\alpha}$ with an exponent $\alpha$ between 0.3 and 0.4 when approaching $T_L$ from both low and high temperatures. $q^*$ becomes relatively constant at low temperatures far from the Lifshitz line.

Both $S(0)$ and the $S(q^*)$ decrease continuously with temperature, but it clearly appears that at $T \approx 80^\circ$C ($T^{-1} \approx 2.83 \times 10^{-3}$K$^{-1}$), the susceptibility crosses over from being determined by $S(q^*)$ to $S(0)$, and again, somewhat less pronounced, at $T \approx 115^\circ$C ($T^{-1} \approx 2.58 \times 10^{-3}$K$^{-1}$), the susceptibility gets again determined by $S(q^*)$. This reflects the crossing of the Lifshitz line separating blend and copolymer like character.

The fluctuation renormalized susceptibility $S(q^*)$ is assumed to have the usual form (7):

$$S^{-1}(q^*) = 2[\Gamma_e - \Gamma_{ren}]$$

but with the renormalized Flory-Huggins parameter $\Gamma_{ren}$ that includes the effect of thermal fluctuations. The detailed form of $\Gamma_{ren}$ is given separately for the two cases, $\Phi > \Phi_{LL}$ and $\Phi < \Phi_{LL}$ corresponding to the susceptibility represented by respectively $S(q^*)$ at finite $q^*$ and $q^* \equiv 0$. Both $S(q = 0)$ and $S(q = q^*)$ have been fitted with the theoretical expressions according to (Kielhorn & Muthukumar, 1997). The corresponding fits are depicted as respectively solid and dashed lines in the figure. The $S(0)$-susceptibility is well described only 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.

4. Conclusions

Ternary mixtures of two homopolymers and the corresponding diblock copolymer represent a very good model system to study critical phenomena near the mean field predicted Lifshitz point. The structure factor as derived by Kielhorn and Muthukumar based on the random phase approximation on unperturbed chains, describes the experimental scattering function very well, and makes it possibly to derive the relevant parameters describing the system thermodynamics, e.g. the susceptibility $\tau^{-1}$, given by either $S(0)$ or $S(q^*)$, $(q^* > 0)$ depending on the composition relative to the Lifshitz value, $\Phi_L$. The temperature dependence of the susceptibilities are well described by the fluctuation renormalized parametrization, derived by Kielhorn and Muthukumar based on the Bradovskii formalism.

References