Evidence for chain shrinkage in binary polymer blends: Light scattering experiments and theory

W. Theobald
Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

A. Sans-Penninckx
L. L. B. Saclay, CEA, F-91191 Gif-sur-Yvette Cedex, France

G. Meier* and T. A. Vilgis*,†
Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

We report light-scattering experiments on the compatible binary polymer blend poly(ethylmethylsiloxane) PEMS ($N=223$) and poly(dimethylsiloxane) PDMS ($N=325$) with $\phi_{C,\text{PEMS}}=0.456$ in the one phase region. From the k dependence of the structure factor we obtain the effective segment length a_{eff}^2 for temperatures larger than the Ginzburg temperature, which shows a shrinkage if we approach the critical point in accordance with theoretical predictions. [S1063-651X(97)03105-X]

I. INTRODUCTION

Several years ago we predicted by using a mean field theory that individual chains in binary polymer blends show anomalous behavior [1–3]. When the phase separation is approached, it has been demonstrated that the individual chains shrink significantly. Such an effect has been observed in Monte Carlo simulations of polymer mixtures by Sariban and Binder [4]. At that time this behavior was not understandable. The random phase approximation (RPA) [5] suggests in its simplest version that the chains size is, however, not altered at all during all changes of temperature nor, hence also, when the critical point is approached. Moreover, in the original version of the RPA the radius of gyration is not even changed during the phase separation. This cannot be true, as the interactions experienced by an arbitrarily chosen individual chain in the binary polymer blend depend significantly on the density or composition fluctuations and their correlation length, i.e., the thermal distance from the critical point.

The chain size in dense interacting polymer systems such as melts, blends, and copolymer melts is determined by an effective potential that acts on the chain under consideration. To calculate the effective potential in the simple mean field theory, we suggested starting from the entire partition function and computing the effective partition function for an individual chain by integrating over all chains except one. This procedure yields an effective monomer-monomer potential that contains all information on the other chains and their thermodynamic behavior. Simple perturbation theory led to the conclusion that the individual chains shrink. These effects have so far been seen directly only in Monte Carlo simulations, as mentioned above.

To our knowledge there are no experimental data yet available, that support these statements measured at the critical composition in the vicinity of T_C. The first method of choice one may think of is to use small-angle neutron scattering on partially labeled samples, but measurements have not been analyzed in this respect up to now. In this paper we show that light scattering can indeed be used as an alternative to determine the effective chain size during temperature changes, especially when the phase separation is approached and large-scale fluctuations are present. It is indeed shown experimentally below that the chains shrink as predicted even by the simple mean field model. Extensions of the theory to nonclassical effect yield good agreement with the light scattering experiments.

For realistic ''melt'' systems, however, mean field theory is not sufficient close to the critical point, i.e., a certain region near the Ginzburg temperature [6], and more refined methods have to be used. In the theoretical part of this paper we use an ''effective renormalization'' that replaces the Gaussian propagator of the mean field theory by the correct correlation function at the critical point involving nonclassical exponents. This procedure yields interesting predictions near the critical point and in the critical region that are combined with the mean field predictions outside the critical regime. It is therefore tempting to postulate chain shrinking above the Ginzburg temperature, where other effects happen in the critical region.

The crucial step of understanding the physical behavior of tagged chains in mixtures can be seen by the following simple intuitive picture. Assume a partially miscible polymer A-B blend, say, in the one phase regime, i.e., where the correlation length is very small. The effective interaction experienced by an A chain is the average of all the interactions present, i.e., AA and AB interactions. When the correlation length is increased, e.g., by increasing the (Flory) interaction parameter (or decreasing the temperature), the blend starts to phase separate on scales of the correlation length. Based on these ideas a corresponding droplet picture has been developed in the general theory of phase transitions [7]. Whenever the correlation length is smaller than the average chain size, very interesting effects on individual chains can be expected. It is this regime when the chains start to shrink that the effective interaction potential becomes smaller and smaller by local phase separation on the scale of the correlation length. We have used this idea to postulate a ''weak local-

———
*Corresponding author.
†Electronic address: VILGIS@MPIP-MAINZ.MPG.DE

ization'' of individual chains within that temperature region [8]. The natural size of the correlation length, and the droplets when that maximum effect is reached, compare to the size of the chain. Physically this means that whenever the correlation length is of the order of the individual chain size the blend is already phase separated on the level of the radius of gyration. The chains filling these spatial regions characterized by $\xi \simeq R_G$ now experience mainly AA interactions, and thus take their natural melt dimension. Below that temperature (at larger correlation length) the process on the level of the chain size is then less important, and a macrophase separation takes place. It is natural to expect this temperature given by $\xi(T) \propto (\chi_0 - \chi_F)^{-1/2} = a N^{1/2}$ close to the Ginzburg temperature of the mixture.

In this paper we present light scattering experiments which support these ideas. At first glimpse, neutron scattering seems to be the most appropriate method to study this. However, as shown in the Appendix, we would have to choose an A-B mixture where only a small part of, say, A is deuterated, which is then looked upon to determine the form factor. It turns out that for such a procedure (see the Appendix), for every temperature, a different, small, fraction of deuterated chains is needed. In this paper we use light scattering instead, and a special way of data treatment is introduced below.

The paper is organized as follows. In Sec. II A we remind the reader of the simple mean field theory already derived in [1–3] for the sake of convenience. This theory is, however, generalized to the critical regime with an effective renormalized (critical) correlation function in Sec. II B. There our effective Gaussian model is used, but with the exact form of the critical correlation function. In Sec. III A, we formulate the experimentally relevant quantities from the scattering function, and compute the effective size of the chain near criticality. In Sec. III B we provide a crossover analysis with respect to the mean field to Ising transition which is important to truly discriminate between these two opposing regions. In Sec. IV we provide information on the sample and other experimental details. We finally discuss results and draw conclusions in Sec. V.

II. THEORETICAL RESULTS

A. Perturbation approach—a reminder

The behavior of single chains in a binary mixture of polymers has been investigated recently in mean field theory. We repeat the main results for convenience. It is useful to consider the Edwards Hamiltonian [9] for the tagged A chain in the blend in the form

$$\beta H = \frac{3}{2a^2} \int_0^N ds \left(\frac{\partial \mathbf{R}^A(s)}{\partial s} \right)^2$$
$$+ \int_0^N ds \int_0^N ds' \beta U_{\text{eff}}(\mathbf{R}^A(s) - \mathbf{R}^A(s')). \quad (2.1)$$

a^2 is in the bare mean square length of the statistical Kuhn segment, N the degree of polymerization of both species (symmetric blend), and $\mathbf{R}^A(s)$ the chain (contour) variable.

The Fourier transform of the effective interaction potential $U_{\text{eff}}(\mathbf{k})$ has been shown to be of the following form [1–3] for an incompressible blend

$$U_{\text{eff}}^{AA}(\mathbf{k}) = \frac{1}{S_A^0(\mathbf{k})} \frac{[1/S_B^0(\mathbf{k})] - 2\chi_F}{[1/S_A^0(\mathbf{k})] + [1/S_B^0(\mathbf{k})] - 2\chi_F}. \quad (2.2)$$

$S_A^0(\mathbf{k})$ and $S_B^0(\mathbf{k})$ are the wave-vector-dependent bare structure factors of species A and B, and χ_F the usual Flory-Huggins interaction parameter.

From these already known results the radius of gyration of the tagged chain has been computed by perturbation theory. This procedure led to the general expression

$$\langle R^2 \rangle = Na^2 \left(1 + \frac{12}{\pi^2 a^4} \int_0^\infty dk \frac{1}{k^2} U_{\text{eff}}(\mathbf{k}) \right), \quad (2.3)$$

where an ''effective'' segment length a_{eff}^2 can be defined as

$$a_{\text{eff}}^2 = a^2 \left(1 + \frac{12}{\pi^2 a^4} \int_0^\infty dk \frac{1}{k^2} U_{\text{eff}}(\mathbf{k}) \right). \quad (2.4)$$

The disadvantage of the above formulation is that it holds only above the Ginzburg temperature when the mean field theory is expected to be valid. Nevertheless, Eq. (2.4) is later on shown to be useful at certain temperatures, i.e., in special regimes of the Flory-Huggins interaction parameter χ_F. For these latter reasons it is convenient to rewrite it by use of the temperature dependence of the Flory χ_F parameter, i.e., $\chi_F = (\chi_A/T) + \chi_B$. In this notation, for the temperature dependence of the effective segment length, we find

$$a_{\text{eff}}^2 = \alpha \frac{1 - (2T_{\text{MF}}/T)}{(1 - (T_{\text{MF}}/T))^{1/2}}, \quad (2.5)$$

where the positive proportionality constant α will be determined below in Sec. IV. The mean-field critical temperature T_{MF} is given by the identification

$$\chi_0 = \frac{2}{N} \equiv \frac{\chi_A}{T_{\text{MF}}} + \chi_B \equiv \chi_{F(T_{\text{MF}})} \quad (2.6)$$

for symmetric blends.

B. Results beyond mean field

It is desirable to study the conformational behavior of the tagged chains beyond the mean field theory. This is definitely not a simple task. The difficulty can be seen as follows: The mean field Hamiltonian for two tagged chains interacting with themselves and the (critical) medium can be written as follows [9,10]:

$$H = \frac{3}{2l^2} \int_0^N \left(\frac{\partial \mathbf{R}_A}{\partial s} \right)^2 ds + \frac{3}{2l^2} \int_0^N \left(\frac{\partial \mathbf{R}_B}{\partial s} \right)^2 ds$$

$$+ i \int_0^N ds \ \phi_A(\mathbf{R}_A(s)) + i \int_0^N ds \ \phi_B(\mathbf{R}_B(s))$$

$$+ \tfrac{1}{2} \sum_k \vec{\rho}_k \vec{V} \vec{\rho}_{-k} - i \sum_n \vec{\phi}_k \vec{\rho}_{-k} + \ln \prod_{k,\sigma} \delta$$

$$\times \left(\phi_{\mathbf{k}}^\sigma - \sum_{\alpha=1}^n \int_0^N \exp(-i\mathbf{k} \cdot \mathbf{R}_\alpha^\sigma(s)) \right) \quad (2.7)$$

where the $\vec{\phi}_{\mathbf{k}} = (\phi_{\mathbf{k}}^A, \phi_{\mathbf{k}}^B)$ fields are auxiliary fields whose correlation functions $\langle \phi_{\mathbf{k}}^\sigma \phi_{-\mathbf{k}}^\tau \rangle = U^{\sigma\tau}(\mathbf{k})$ are the effective monomer potentials, e.g., given in Eq. (2.2) in the Gaussian approximation. The logarithmic term in Eq. (2.7) can be systematically expanded [10]. It is easy to show that (in the Gaussian approximation) the effective potential between species A and B is given by the general expression [3]

$$U^{\sigma\tau}(\mathbf{k}) = \langle \phi_{\mathbf{k}}^\sigma \phi_{-\mathbf{k}}^\tau \rangle = \{ (\vec{S}^0 + V^{-1})^{-1} \}_{\sigma\tau}^{-1}. \quad (2.8)$$

The latter equation can be rewritten simply by matrix algebra as

$$U^{\sigma\tau}(k) = [\vec{S}(\vec{S}_0^{-1} + \vec{V}) \vec{V}^{-1}]_{\sigma\tau}^{-1} = (V(S_0^{-1} + V)^{-1} S_0^{-1})_{\sigma\tau}. \quad (2.9)$$

Near criticality the Gaussian approximation is invalid, and the higher-order terms of Eq. (2.7) have to be taken into account. This procedure is not simple, as higher-order terms appear, but can be performed by renormalization group methods. For the purpose of this paper a simplified approximate approach is presented. To do this it is important to realize that the Gaussian propagator of the density field is given by

$$\langle \vec{\rho}_{\mathbf{k}} \vec{\rho}_{-\mathbf{k}} \rangle_G = (\vec{S}_0^{-1}(\mathbf{k}) + \vec{V})^{-1}. \quad (2.10)$$

It is therefore tempting to replace the Gaussian value for $\langle \vec{\rho} \cdot \vec{\rho} \rangle$ by the exact one $\langle \vec{\rho}_{\mathbf{k}} \vec{\rho}_{-\mathbf{k}} \rangle \equiv \vec{S}(\mathbf{k})$ [11]. This yields, instead of Eq. (2.9), the general expression for the tagged chain potential matrix

$$\vec{U}(\mathbf{k}) = \vec{V} \cdot \vec{S}^{-1}(\mathbf{k}) \vec{S}_0^{-1}(\mathbf{k}), \quad (2.11)$$

which can be evaluated in the limit of incompressibility, i.e., $V_{\sigma\tau} = V + \varepsilon_{\sigma\tau}$, $V \rightarrow \infty$. The incompressible limit of $\vec{S}(\mathbf{k})$ replaces the mean field structure factor

$$S(\mathbf{k}) = \frac{1}{2(\chi_0 - \chi_F) + \frac{1}{12} a^2 k^2} \quad (2.12a)$$

by the critical structure factor

$$S(\mathbf{k}) = \frac{B}{k^{2-\eta}}. \quad (2.12b)$$

B in a critical amplitude, and η the corresponding critical exponent of the correlation function near the critical point.

As polymer blends fall into the Ising universality class, $\eta = 0.039$ [7]. Note that the procedure of replacing Eq. (2.12a) by Eq. (2.12b) corresponds to the use of rather than the correct $\phi^4(\mathbf{x})$ theory for the polymer mixture, an effective (renormalized) Gaussian [11], i.e.,

$$\int d^d x \ \frac{a^2}{12} |\nabla \rho|^2 + (\chi_0 - \chi_F) \rho^2(\mathbf{x}) + \lambda \rho^4(\mathbf{x})$$

$$\rightarrow \int \rho(\mathbf{x}) |\mathbf{x} - \mathbf{x}'|^{d-2+\eta} \rho(\mathbf{x}') d^d x d^d x'. \quad (2.13)$$

This procedure yields effective potentials which contain the renormalized propagator, i.e., they are given by

$$U_{AA}(\mathbf{k}) = \frac{B}{S_A^0(\mathbf{k})} \frac{[1/S_B^0(\mathbf{k})] - 2\chi_F}{k^{2-\eta}}. \quad (2.14)$$

The tagged A chain has therefore the effective Hamiltonian

$$H = \frac{3}{2l^2} \int_0^N ds \left(\frac{\partial \mathbf{R}_A}{\partial s} \right)^2$$

$$+ \tfrac{1}{2} \int_0^N ds \int_0^N ds' \ U_{AA}(\mathbf{R}_A(s) - \mathbf{R}_A(s')), \quad (2.15)$$

where $U_{AA}(\mathbf{r})$ is the Fourier transform of $U_{AA}(\mathbf{k})$.

It is now easy to show that the perturbation calculation [see Eqs. (2.8) and (2.4)] can be carried out for the potential given by Eq. (2.14). Obviously the integral has an infrared and ultraviolet divergence. Both are here simply removed by a cutoff. The short range cutoff (large values of the wave vector $\mathbf{k}$) is assumed to be the Kuhn step length a of the polymer; i.e., $k_{\max} \sim 1/a$.

The long wavelength cutoff $k_{\min}$ is slightly more complicated. If it is chosen to be $k_{\min} \sim 1/(a^2 N)$ we consider scales inside the considered polymer coil. The first order perturbation yields in this case

$$R^2 = a^2 N \left\{ 1 + g \left(1 - \frac{2T_{\mathrm{MF}}}{T} \right) \left(\frac{1}{a^{3-\eta}} - \frac{1}{N^{3-\eta}} \right) + O(N^{-5}) \right\}, \quad (2.16)$$

where g is a constant. Therefore the additional contribution is not important and can be neglected: At the critical point the chain is almost Gaussian. Moreover inside the coil the mean field theory Eqs. (2.3) and (2.5) is recovered.

The other and more interesting possibility is to choose the cutoff to be of the order of the correlation length, i.e., $k_{\min} \sim \xi^{-1}$ in order to investigate the statistics outside of the coil. The leading contribution therefore is given by

$$R^2 = a^2 N \left\{ 1 + \hat{g} \left(\frac{2T_{\mathrm{MF}}}{T} - 1 \right) (\xi^{-(3-\eta)} - a^{-(3-\eta)}) + O(\xi^{-5}) \right\}, \quad (2.17)$$

or, neglecting irrelevant details,

$$R^2 = a^2 N \left\{ 1 + g \left(\frac{2T_{\mathrm{MF}}}{T} - 1 \right) |T - T_C|^{\nu(3-\eta)} \right\}, \quad (2.18)$$

where $T_C \neq T_{MF}$ is the real critical temperature of the system. We note that the additional contribution vanishes at the critical point T_C. These results can easily be interpreted in a droplet picture, and we will return to this point in the discussion at the end of this paper in Sec. V.

III. DATA TREATMENT

Since it turns out to be important to discriminate truly the various possible regions of thermal distance to T_C, in Sec. III A we will first present the necessary framework to extract the effective segment length a from the experimental $S(\mathbf{k})$ vs $\mathbf{k}$ curves. In Sec. III B the crossover analysis (between Ising and mean fields) is presented, which is basically needed to separate the pure Ising zone from the entire set of data.

A. Determination of the effective segment length a

In the framework of the random phase approximation the static structure factor of an incompressible polymer blend is given by [12,13]

$$S(\mathbf{k})^{-1} = S(\mathbf{k})_{n.i.}^{-1} + V(\mathbf{k}), \qquad (3.1)$$

where $S(\mathbf{k})_{n.i.} = S^0(\mathbf{k})$ is the noninteracting part of the structure factor, and $V(\mathbf{k})$ is the Fourier transform of the interactions. For $S(\mathbf{k})_{n.i.}$ we write, according to de Gennes [5], for a binary blend,

$$S(\mathbf{k})_{n.i.}^{-1} = [S_A^0(\mathbf{k})]^{-1} + [S_B^0(\mathbf{k})]^{-1}, \qquad (3.2)$$

with $\phi_A + \phi_B = 1$ are the volume fractions, and $S_{A,B}^0(\mathbf{k})$ is the unperturbed single chain form factors of the respective polymers. In the Gaussian approximation, and further using the Zimm expansion, we can write, thereby identifying $V(\mathbf{k}) \simeq -2\chi_F$ with χ_F being the Flory-Huggins interaction parameter, for $S(\mathbf{k})^{-1}$,

$$S(\mathbf{k})^{-1} = [\phi_A N_A]^{-1} + [\phi_B N_B]^{-1} - 2\chi_F + \frac{a^2}{18\phi_A \phi_B} k^2, \qquad (3.3)$$

with N_A and N_B being the number of statistical segments per chain and a the statistical segment length that is taken to be equal for both species. From Eq. (3.3) the scattered intensity in forward direction ($\mathbf{k} = \mathbf{0}$) is immediately given as ($S(\mathbf{k} = \mathbf{0}) \equiv S(\mathbf{0})$)

$$S(\mathbf{0})^{-1} = [\phi_A N_A]^{-1} + [\phi_B N_B]^{-1} - 2\chi_F. \qquad (3.4)$$

Equation (3.3) then becomes

$$S(\mathbf{k})^{-1} = S(\mathbf{0})^{-1} + \frac{a^2}{18\phi_A \phi_B} k^2. \qquad (3.5)$$

Equation (3.5) is our working equation to extract a from the angular dependence of the scattered intensity. For the conversion of the intensity into $S(\mathbf{k})$; see [14]. The segment length a is related to the radius of gyration $R_g^2 = \frac{1}{6} N a^2$ for Gaussian coils.

χ_0, the value of χ_F at the spinodal, is given by Eq (2.6); hence from Eq. (3.5) we obtain

$$S(\mathbf{k})^{-1} = 2(\chi_0 - \chi_F(T)) + O(k^2), \qquad (3.6)$$

which can be rewritten for $\mathbf{k} = \mathbf{0}$ into

$$S(\mathbf{0}) = \frac{1}{2\chi_0} \left(1 - \frac{\chi}{\chi_0} \right)^{-1}, \qquad (3.7)$$

or equivalently, using the standard empiric formula for the Flory-Huggins interaction parameter $\chi = \chi_F = (\chi_A/T) + \chi_B$ for convenience. $\varepsilon = (T - T_{MF})/T$ is the reduced temperature, and the zero wave vector structure factor is then written as

$$S(\mathbf{0}) = \frac{T_{MF}}{2\chi_A} \left(\frac{T - T_{MF}}{T} \right)^{-1} = \text{const} \times \varepsilon^{-\gamma}. \qquad (3.8)$$

Equation (3.8) yields the mean-field exponent $\gamma = 1$ for the temperature variation of the susceptibility.

Furthermore, we may rewrite Eq. (3.5) into

$$S(\mathbf{k})^{-1} = S(\mathbf{0})^{-1}(1 + \xi^2 k^2), \qquad (3.9)$$

where we have defined the correlation length ξ of critical fluctuations. Equation (3.9) leads to

$$\xi = \left(\frac{\chi_0}{\chi_A} T_{MF} \right)^{1/2} \sqrt{2N} \frac{a}{6} \left(\frac{T - T_{MF}}{T} \right)^{-1/2} = \text{const} \times \varepsilon^{-\nu}, \qquad (3.10)$$

where $\nu = 1/2$ is the mean field value for the temperature variation of the correlation length. Equation (3.9) has the well known Ornstein-Zernike (OZ) form. Its Fourier transform yields the space correlation function $G(\mathbf{r})$ which decays exponentially with r^{-1} as

$$G(\mathbf{r}) = \frac{B}{r^{d-2}} \exp \left(-\frac{r}{\xi} \right), \qquad (3.11)$$

with B being the amplitude and d the space dimension. It is well known that close to the critical point the mean field theory fails due to its neglect of fluctuations, but a scaling and renormalization group analysis leads to the correct refinement of Eq. (3.11) via

$$G(\mathbf{r}) = \frac{B'}{r^{d-2+\eta}}, \qquad (3.12)$$

where η is the universal critical exponent with $\eta = 0.039$ for the three dimensional case ($d = 3$) [7]. This latter equation corresponds to an expression for the structure factor, which can be presented by use of an unknown scaling function $g(k\xi)$,

$$S(\mathbf{k})^{-1} = S(\mathbf{0})^{-1} g(k\xi). \qquad (3.13)$$

For the scaling function $g(k\xi)$ the analytical expression given by Fisher and Burford [15] was used for values of $k\xi$ up to 4, by Tracy and McCoy [16], who found that the OZ approximation [Eq. (3.9)] gives a good representation of the data within the experimental accuracy. In the regime for $\varepsilon > Gi$ a straightforward determination of a is simply accomplished by dividing Eq. (3.8) and the square of Eq. (3.10). In the fluctuation dominated regime; however (Ising-like), the

polymer topology is unimportant. Thus using the scaling relation $(2-\eta)\nu=\gamma$ [7] with the Ising critical exponents $\nu=0.63$ and $\gamma=1.24$, from Eq. (3.13) together with Eq. (3.9), for the universal ratio of the critical amplitudes, we obtain

$$A = \frac{\xi_0^2}{S_0(0)} \left(\frac{T-T_c}{T}\right)^{-\nu\eta}, \qquad (3.14)$$

where ξ_0 and $S_0(0)$ are the amplitudes of the correlation length and susceptibility in the Ising regime, respectively. Note that here now the Ising critical temperature T_C enters. In the regime where Eq (3.14) is valid, T_{MF} does not make sense.

B. Crossover between the mean field and Ising regimes

Mean field theory on the one hand and three-dimensional Ising behavior on the other hand are the two opposing limiting cases in the behavior of the blends considered here. The proper criterion what separates these cases can be derived from the Ginzburg criterion (Ginzburg number Gi) [5–7]. The Ginzburg-Wilson formulation of the free energy ΔG that describes the second-order phase transition is given by [7]

$$\frac{\Delta F}{kT} = \int d^3r \left[\frac{1}{2!} a_0 \varepsilon \psi^2(\mathbf{r}) + \frac{1}{4!} u_0 \psi^4(\mathbf{r}) + \tfrac{1}{2} c_0(\nabla\psi(\mathbf{r}))^2 \right], \qquad (3.15)$$

with $\varepsilon=1-T_{MF}/T$ being the reduced temperature and the order parameter $\psi(\mathbf{r})=\rho(\mathbf{r})-\rho_c$. The bare constants a_0, u_0, and $c_0=a_0\xi_0^2$ were, i.e., specified by Hair et al. [18] for the case of polymer blends. The general definition of the Ginzburg number Gi in the light of the above coefficients is [17]

$$\mathrm{Gi} = \frac{1}{32\pi^4} \frac{u_0^2}{a_0^4 \xi_0^6 N_A^2}. \qquad (3.16)$$

The Ginzburg criterion states that mean field theory will be valid only at temperatures where $\varepsilon \gg \varepsilon_{\mathrm{crossover}}$, $\varepsilon^* = (T^*-T_C)/T$ is related to the crossover temperature T^*, which marks the deviation from the high-T mean field line in a $S^{-1}(0)$ vs $1/T$ plot; see, e.g., Ref. [25]. It can be in the one phase region (disordered state) directly obtained from Eq. (3.15) via the condition $\frac{1}{4} u_0 \langle\psi^4\rangle \ll \frac{1}{2} a_0 \varepsilon^2 \langle\psi^2\rangle$. Using a crossover function which is an explicit solution to first order in the perturbation parameter $\varepsilon=4-d$, based on a renormalization group analysis, Meier et al. [19] were able to combine the two limiting cases, namely the mean field ($\varepsilon \gg \mathrm{Gi}$) and the three-dimensional Ising regime ($\varepsilon \ll \mathrm{Gi}$) which takes over close to T_c. The crossover function reads [20]

$$\hat\varepsilon = [1 + 2333\hat{S}(0)^{\Delta/\gamma}]^{(\gamma-1)/\Delta}[\hat{S}(0)^{-1}$$
$$+ (1 + 2333\hat{S}(0)^{\Delta/\gamma})]^{-\gamma/\Delta} \qquad (3.17)$$

where $\hat\varepsilon=\varepsilon/\mathrm{Gi}$ and $\hat{S}(0)=a_0\mathrm{Gi}S(0)$. The critical exponents are naturally those for the 3D Ising cases $\Delta=0,51$ and $\gamma=1.24$. In the two limiting cases from Eq. (3.17), $\varepsilon \ll \mathrm{Gi}$, the Ising regime is recovered and, for $\varepsilon \gg \mathrm{Gi}$, the mean field regime. Note, however, that Eq. (3.17) is valid only for

$S(k=0)$ and not for $S(k)$. From a fit of Eq. (3.17) to the experimental data, the parameters a_0 and Gi can be obtained, thus enabling us now to discriminate between mean field and Ising regimes with respect to the temperature difference from T_C. Below we present data on the blend investigated in this paper that will also show this behavior.

IV. EXPERIMENT

In this study we used a binary mixture of poly(ethylmethylsiloxane) PEMS ($N=225$) with poly(dimethylsiloxane) PMDS ($N=325$). The polymers were synthesized by anionic ring opening polymerization of methylcyclotrisiloxane and triethyl-trimethyl-cyclotrisiloxane yielding PDMS and PEMS, respectively, by a procedure described elsewhere [22]. The typical polydispersity u of the samples, as obtained by GPC, was $u=1.06$. The critical volume fraction of PEMS was $\phi_{C,\mathrm{PEMS}}=0.465$, in good agreement with the expectation $\phi_{C,\mathrm{PEMS}}=N_{\mathrm{PDMS}}^{1/2}/(N_{\mathrm{PDMS}}^{1/2}+N_{\mathrm{PEMS}}^{1/2})$. The critical (Ising) temperature amounts to $T_c=301.90\pm0.01$ K. The critical temperature found here is in agreement with the data presented previously [14], thereby taking into account the experimentally determined T dependence of χ_0 [22]. Light scattering measurements were performed with a dust free, sealed sample in optical quality, which was obtained after filtration through a 0.22 μm Millipore filter into glass cylinders of 1/2″ outside diameter. The light source was an argon ion laser (Spectra Physics 2000) operating at $\lambda=488$ nm. Static and dynamic light scattering data was accomplished by an ALV goniometer using an ALV 5000 correlator system (ALV Langen, Germany). The exact details of the experimental conditions together with those parts of the results which are not a matter of the purely conformational aspects together with the analysis of the dynamic scattering function are published separately [23].

V. RESULTS AND DISCUSSION

A. Discussion of the effective a^2 with respect to the Ising and mean-field behaviors

Figure 1 displays the major result of the study: The dependence of a^2, the squared effective segment length obtained from Eq. (3.5), as a function of temperature. A strong drop of a^2 with decreasing temperature can be seen. First of all, this figure can be divided into two parts with respect to temperature on the basis of the crossover function formalism [Eq. (3.17)]. This gives a Ginzburg number (Gi$=6.88 \times10^{-3}$, in agreement with Gi numbers published previously [19,21], which can be converted into temperature and the known a_0 according to Hair et al. [18] and Meier et al. [19] The position of T_{Ginzburg} is indicated by an arrow on the temperature axis, and corresponds to $T=304$ K. Data points below are naturally in the regime $\varepsilon \ll \mathrm{Gi}$ and only the ratio of critical amplitudes can be deduced as already outlined in the proceeding sections; thus Eq. (3.14) must be valid. The weak divergence of A is in very good agreement with the expected value for $\eta\nu=0.024$ and implies $\eta=0.038\pm0.002$, thereby using $\nu=0.62\pm0.01$, which was obtained from an Eq. (3.10)-type of analysis [23].
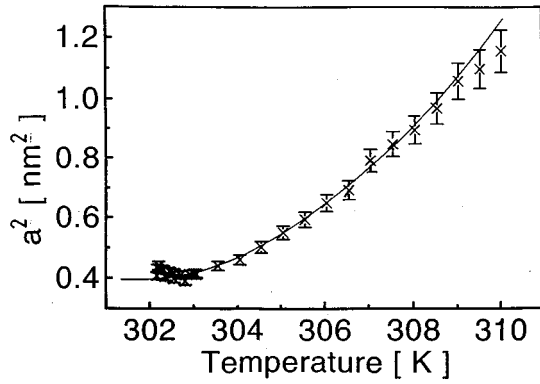
FIG. 1. The square of the effective segment length a_{eff}^2 obtained via Eq. (3.5) as a function of T. Indicated by arrows is the Ginzburg temperature as obtained by a fit of the susceptibility data by Eq. (3.17), and the temperature where the effective potential [Eq. (2.2)] changes sign. The former one marks the crossover between pure Ising and MF behavior, and the latter one is related to the recently developed localization picture (Ref. [8]). The full line is a fit of Eq. (2.5) together with Eq. (5.1) on the basis of a perturbation approach [1–3]. Clearly, this picture is only adequate for $\varepsilon \gg$ Gi; specifically it fits only to $U_{eff}=0$.

B. Fitting a model function to a^2 for $\varepsilon > \varepsilon_{\text{Ginzburg}}$

Having analyzed the data for $\varepsilon \ll$ Gi, we first apply the perturbation solution to our data [1–3]. As outlined in the theoretical reminder, Eq. (2.5) is the result for the temperature dependence of the effective segment length in the framework of Refs. [1–3]. The proportionality constant α in Eq. (2.5) is given by [24–26]

$$\alpha = \frac{36\sqrt{2}V_{\text{mon}}}{\pi N^{2/3}\alpha^3} R_{g,0}^2. \quad (5.1)$$

We are able to calculate the proportionality constant α with $V_{\text{mon}}=1.325 \times 10^{-22}$ cm^3 [14] and typically $a=1$ nm (see Fig. 1) being $\alpha=0.13$. A fit of Eq. (2.5) to the data for $\varepsilon >$ Gi yields the curve which goes through the data points in that indicated temperature range as is depicted in Fig. 1. The fitted parameters are $\alpha=0.20\pm0.02$ and the unperturbed segment length $a_0(R_{g,0}^2 = \frac{1}{6}Na_0^2)$ being $a_0 = 1.53\pm0.08$ nm. This value is higher than the one reported for PDMS by Aharoni [26] ($a_0=1.08$ nm), values for PEMS are not known. However, preliminary measurements by Momper [22] indicated that values for a_0 beyond $a_0=1.2$ nm are possible. By fitting Eq. (2.5) to the data, also the mean field critical temperature enters, with amounts to be $T_{\text{MF}}=302.2$ K. This value was obtained by plotting the reciprocal structure factor versus the inverse temperature and extrapolate it to $S(0)^{-1}=0$ to find T_{MF}. This procedure is meaningful only for high molecular weight blends like those here, as was outlined recently [21].

In a recent paper, Vilgis and Meier [8] put forward a variational treatment to predict a weak localization of chains, at temperatures when the correlation length is of the order of the chain dimensions. This is supported by the droplet picture [7], which is well established in the physics of critical phenomena, where the localization is most pronounced when the size of the chains is of the order of a critical droplet. The corresponding value of χ_F for that situation is given by [27]

$$\chi_F = \frac{1}{N}, \quad (5.2)$$

which is precisely the value when the potential Eq. (2.2) changes sign. In order to rationalize our result further we adopt the above picture and treat in Eq. (2.2) the bare structure factor through the Padé approximation $S_A^0(\mathbf{k}) = S_B^0(\mathbf{k}) = N/(1 + \frac{1}{12}Na^2k^2)$. For $\mathbf{k}=\mathbf{0}$ (valid for light scattering experiments) from Eq. (2.2) we then obtain, for the effective potential for symmetric blends,

$$U_{eff} \propto \frac{1}{N} \frac{\chi_0 - 2\chi_F}{2(\chi_0 - \chi_F)}. \quad (5.3)$$

This can be rearranged using $\xi^{-2} \propto 2(\chi_0 - \chi_F)$ into

$$U_{eff} = N^{-1}(1 - \chi_0\xi^2), \quad (5.4)$$

which, in view of the above discussed droplet picture, for the position where the effective potential is zero, the condition provides

$$\xi^2 = \frac{N}{2}, \quad (5.5)$$

yielding $\xi \simeq \sqrt{3}R_g = 180$ Å using $a_0 = 1.53$ nm. The temperature where ξ exceeds that given value in Fig. 1 is at $T = 305.7$ K, which is close to the value of the Ginzburg temperature, a result that could be expected intuitively. We have indicated that temperature T by $U_{eff}=0$ in Fig. 1. However, this further marks the limits of the simple perturbation theory which is brought forward by Eq. (2.2). Therefore we went a step further and applied Eq. (2.18), which is valid beyond the mean field picture. We assume this treatment to be valid down to the minimum in a_{eff}^2 (Fig. 1) being located at a value of $a_{eff}^2 \approx 4$ nm^2, and which is given by roughly the position of T_{Ginzburg}. As we had seen, for $\varepsilon \ll$ Gi, a completely different physics, where the polymer topology is unimportant, comes into play. Hence, for T's even lower, the pure Ising case is a perfect representation of our data (see [23]). Rewriting Eq. (2.18) into the following form gives

$$a_{eff}^2 = a_{\min}^2\left\{I + C\left(\frac{2T_{\text{MF}}}{T} - 1\right)(T - T_C)^{\nu(3-\eta)}\right\}. \quad (5.6)$$

If we use $a_{eff}^2=4$ nm^2, $T_{\text{MF}}=302.2$ K, $T_C=301.9$ K, and $\nu(3-\eta)=1.814$, we are able to obtain a (one parameter) fit to the data which is indicated in Fig. 2. Thereby the value of the constant C was found to be $C=0.05$. Thus we conclude that from our study the following physical sensible picture emerges: The crossover from MF to Ising is given by the Ginzburg temperture. This temperature differs from the classical MF estimate for the width of the critical region as outlined by Joanny [28], as has been shown by Refs. [19], [21] based on Ref. [20]. Our study adds another temperature that is important on the level of tagged chains. This $T_{u\,eff=0}$ is given by the value when the correlation length $\xi(T)$ compares with the values of the size of the polymer chains, and corresponds to the zero of the effective interaction potential [Eq. (2.2)]. It is natural that the latter temperature is very
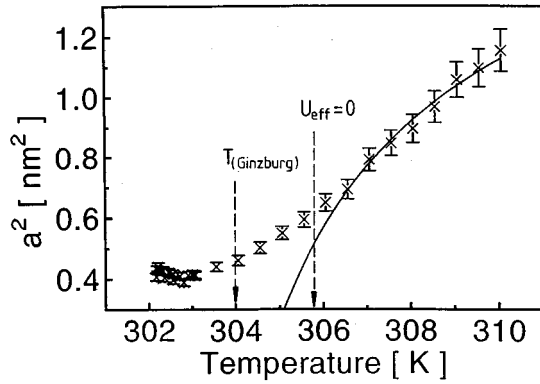
FIG. 2. The same data as in Fig. 1. The full line is a fit of Eq. (5.6) to the data. In the picture of the effective renormalized correlation function, the chain dimensions remain finite at T_C. Evidently, this result describes the data around $\varepsilon \gtrsim$Gi with deviations for $\varepsilon \gg$Gi.

close to the Ginzburg temperature. The last point is consistent with our recent ''localization model'' [8].

In the past, peculiar scattering results from polymer blends [29] have been interpreted as being due to a k-dependent χ parameter. In the framework of Khokhlov and Erukhimovich's treatment [30] this is likely related to glass point effects when local structural phenomena such as difference in stiffness, dynamics of side groups, etc., matter. The polymer blend under the present consideration may be chosen as a model system where these effects are absent. This has been proven also in a recent study on the interdiffusion dynamics [31].

Finally, we would comment on recent neutron results by Briber, Bauer, and Hammouda [32] on d-PS–PVME blends. They report also chain shrinkage to a much lesser extent for mixtures which are off-critical in the concentrations and, even more important, not close to T_C. Their data were analyzed with the RPA, although the blend is very asymmetric and the application of the RPA is questionable [33]. However, the results reported there cannot be compared with our data nor with our theoretical predictions, since they are taken in the wrong (ε, N) phase space. For a further quantitative justification of this, see the Appendix. One may further argue that the pure thermal expansion may also be an effect which one has to take into account here. That is erroneous as the rotational isomeric state (RIS) model reflects only purely configurational properties of isolated chains, and coupling to critical density fluctuations are not taken into account. Consequently, RIS effects can be neglected.

APPENDIX: SINGLE CHAIN CONFORMATION AND NEUTRON SCATTERING

The determination of the effective tagged chain conformation of a chain of species A can be obtained alternatively by small-angle neutron scattering. To do this, a fraction of A chains is labeled. The static scattering intensity is then given by

$$I(\mathbf{q}) = f(1-f)(a_D - a_H)^2 S_A(\mathbf{q})$$
$$+ (fa_D + (1-f)a_H - b)^2 S_{AA}(\mathbf{q})$$
$$+ (\text{incoherent part}), \qquad (A1)$$

where a_D and a_H are the scattering lengths of deuterium and hydrogen, respectively, b in the scattering length of the B species $S_A(\mathbf{q})$ is the single chain structure factor of the A chains, and $S_{AA}(\mathbf{q})$ the divergent collective structure factor of the blend. Thus

$$S_A(\mathbf{q}) = \phi_A \sum_{i,j} \langle \exp\{i\mathbf{q} \cdot (\mathbf{r}_i^A - \mathbf{r}_j^A)\} \rangle,$$

$$S_{AA}(\mathbf{q}) = \sum_{\substack{\alpha\beta \\ i,j}} \langle \exp\{i\mathbf{q} \cdot (\mathbf{r}_i^\alpha - \mathbf{r}_i^\beta)\} \rangle.$$

The difficulty now is that the divergent part $S_{AA}(\mathbf{q})$ dominates $I(\mathbf{q})$ close to the phase transition, and it is difficult to extract $S_A(\mathbf{q})$.

The only way to obtain $S_A(\mathbf{q})$ in a reliable way is to choose

$$fa_D + (1-f)a_H - b = 0.$$

This condition is, in general, difficult to satisfy, and there are direct measurements of $S_A(\mathbf{q})$.

[1] M. G. Brereton and T. A Vilgis, J. Phys. (Paris) **50**, 245 (1989).

[2] T. A. Vilgis and R. Borsali, Macromolecules **23**, 3172 (1990).

[3] T. A. Vilgis and P. Haronska, Acta Polym. **45**, 160 (1994).

[4] A. Sariban and K. Binder, Macromolecules **21**, 711 (1988).

[5] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).

[6] V. L. Ginzburg, Sov. Phys. Solid State **2**, 1824 (1960).

[7] *Phase Transitions and Critical Phenomena*, edited by C. Domb and E. Green (Academic, New York, 1976), Vols. 5a and 6.

[8] T. A. Vilgis, G. Meier, J. Phys. (France) I **4**, 985 (1994).

[9] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).

[10] T. Otha and K. Kawasaki, Macromolecules **19**, 2621 (1988).

[11] T. A. Vilgis, A. Sans, and G. Jannink, J. Phys. (France) II **3**, 1779 (1993).

[12] H. Benoit, M. Benmouna, and W. Wu, Macromolecules **23**, 1511 (1990).

[13] T. A. Vilgis, M. Benmouna, and H. Benoit, Macromolecules **24**, 4481 (1991).

[14] G. Meier, B. Momper, and E. W. Fischer, J. Chem. Phys. **97**, 5884 (1992).

[15] M. E. Fischer and R. G. Burford, Phys. Rev. **156**, 583 (1967).

[16] C. A. Tracy and M. M. McCoy, Phys. Rev. B **12**, 368 (1975).

[17] S. Janβen, D. Schwahn, and T. Springer, Phys. Rev. Lett. **68**, 3180 (1992).

[18] D. W. Hair, E. K. Hobbie, A. I. Nakatani, and C. C. Han, J. Chem. Phys. **96**, 9133 (1992).

[19] G. Meier, D. Schwahn, K. Mortensen, and S. Janβen, Europhys. Lett. **22**, 577 (1993).

[20] M. A. Anisimov, S. B. Kiselev, J. V. Sengers, and S. Tang, Physica A **188**, 487 (1992).

[21] D. Schwahn, G. Meier, K. Mortensen, and S. Janβen, J. Phys. (France) II **4**, 37 (1994).

[22] B. Momper, Ph.D. thesis, University of Mainz, 1989.

[23] W. Theobald and G. Meier, Phys. Rev. E **51**, 5776 (1995).

[24] E. K. Hobbie, L. Reed, C. C. Huang, and C. C. Han, Phys. Rev. E **48**, 1579 (1993).

[25] F. S. Bates, J. Rosedale, P. Stepanek, T. P. Lodge, P. Wiltzine, G. H. Fredrickson, and R. P. Hjelm, Phys. Rev. Lett. **65**, 1893 (1990).

[26] S. M. Aharoni, Macromolecules **19**, 426 (1986).

[27] Here we give the correct relation. Please be aware of the misprinted Eq. (9) in our Ref. [8].

[28] J. F. Joanny, J. Phys. A **11**, 117 (1978).

[29] M. G. Brereton, E. W. Fischer, C. Herkt-Maetzky, and K. Mortensen, J. Chem. Phys. **87**, 6144 (1987).

[30] A. R. Khokhlov and I. Y. Erukhimovich, Macromolecules **26**, 7403 (1993).

[31] G. Meier, G. Fytas, B. Momper, and G. Fleischer, Macromolecules **26**, 5310 (1993).

[32] R. M. Briber, B. J. Bauer, B. Hammouda, J. Chem. Phys. **101**, 2592 (1994).

[33] K. Binder, Adv. Polym. Sci. **112**, 181 (1994).