Colloid Polym Sci (2004) 282: 782–792
DOI 10.1007/s00396-004-1126-z

ORIGINAL CONTRIBUTION

Bernd Ewen
Heide Götz
Ulrich Maschke

Structural and dynamic single chain behaviour in a binary blend of low molecular mass poly(siloxanes) as studied by small angle neutron scattering and neutron spin echo spectroscopy

Received: 27 January 2004
Accepted: 1 April 2004
Published online: 1 May 2004

Dedicated to Prof. Dr. Erhard W. Fischer on the occasion of the 75th anniversary of his birthday.

B. Ewen (✉) · H. Götz
Max-Planck-Institut für Polymerforschung,
Postfach 3148, D 55021 Mainz, Germany
E-mail: ewen@mpip-mainz.mpg.de

U. Maschke
Laboratoire de Chimie Macromoléculaire,
UPRESA CNRS No 8009,
Université des Sciences et Technologies de Lille, F 59655 Villeneuve d'Ascq, France

Present address: H. Götz
European Patent Office,
D 80335 Munich, Germany

Abstract Elastic and quasi elastic neutron scattering investigations, using the small angle neutron scattering (SANS) and neutron spin echo (NSE) techniques, respectively, were performed in order to study the static and dynamic single chain behaviour in a binary blend of low molecular mass deuterated poly(dimethylsiloxane) (d-PDMS) and protonated poly(ethylmethylsiloxane) (p-PEMS) at the critical composition ϕ_c. Since the single chain observation requires that only a small amount of one of both components is labelled, the d-PDMS/p-PEMS system was modified in such a way that the major part of the protonated PEMS component was replaced by the corresponding deuterated material. Although the de-mixing of the PEMS isotopes occurs far below the de-mixing of the PDMS/PEMS system the resulting chemically binary d-PDMS/d-PEMS/p-PEMS blend with the volume composition 0.5/0.425/0.075 is strictly speaking a ternary system. This complication had to be taken into account, in particular with respect to the correct evaluation of the SANS data.The careful analysis of the SANS curves allows one to determine all three thermodynamic interaction parameters with reasonable reliability and gives evidence that the radii of gyration agree with those, which were determined in corresponding isotopic PDMS and PEMS blends. This is in contrast to the observation on real binary PDMS/PEMS blends at ϕ_c, where the collective conformational properties exhibit a considerable chain expansion. The NSE data of the ternary system follow completely the predictions of the Rouse model, which describes the dynamics of a dense low molecular mass polymeric system in a single chain approximation. The experimental observations are also in contrast to the results of former NSE measurements on binary PDMS/PEMS blends, where a transition from Rouse behaviour at short times to a much weaker relaxation at longer times became obvious.The results of the static and dynamic single chain behaviour presented here confirm the results of a computer simulation on a low molecular mass binary blend at the critical concentration, where explicitly the pure single chain behaviour was probed and no indications for chain expansion and deviations from the Rouse dynamics were found.

Keywords Polymer blends · Neutron scattering · Single chain behaviour

Introduction

When the statics and dynamics of low molecular mass isotopic poly(dimethylsiloxane) (PDMS) and poly(ethylmethylsiloxane) (PEMS) blends were studied by small angle neutron scattering (SANS) and neutron spin echo (NSE) spectroscopy in the homogenous regime at the critical composition $\phi_c \cong 0.5$, it was found that the elastic and quasi elastic scattering intensity are well described on the basis of unperturbed chain dimensions and Rouse dynamics [1]. The same is true for corresponding systems, where the volume content of the protonated and deuterated material is shifted from equal distribution to a strong minority of one component. As is well known, this procedure increases the weight of the minor component in the elastic and quasi elastic scattering intensity and is commonly used to study the single chain behaviour of the diluted component. Contrary, in corresponding binary PDMS/PEMS blends at $\phi_c \cong 0.5$, where any of both components was completely deuterated whereas the other being protonated, strong deviations from the behaviour observed in isotopic blends occur [2]. These deviations manifest itself in a considerable increase of the radii of gyration and a cross over from Rouse dynamics at short times to a relaxation behaviour with a significantly weaker decline at longer times. Both effects fit to the outcome of a theoretical treatment presented some years ago [3, 4, 5], which predicts that chain expansion and chain localisation occur in the one phase regime of binary blends, when approaching the critical point. Due to the chain localisation the Rouse dynamics becomes restricted in space.

On the basis of these findings it is challenging to explore whether these deviations are a typical collective phenomenon or whether they are also apparent when predominantly the single chain behaviour is probed in these binary blends. With neutron scattering techniques in principle this can be done easily. One has to modify the sample in such a way that only a small amount of the originally completely protonated component remains as it is, whereas the rest is replaced by the corresponding deuterated material.

Although this modification seems to produce no serious alteration of the mixture—at least from a chemical point of view, physically the system has become much more complicated, since the binary blend is changed to a ternary system with three interaction parameters instead of one. With respect to the scattering this enhanced complexity is not reduced, when the scattering contrast between both deuterated components is zero or negligible compared to the both contributions from the protonated and the deuterated components.

In this paper we will present the results of SANS and NSE investigations on a low molecular mass d-PDMS/d-PEMS/p-PEMS ternary blend, the volume content of the different components being 0.5, 0.425 and 0.075, respectively, and show that the static and dynamic properties are completely different from the related d-PDMS/p-PEMS binary blend of volume composition 0.5/0.5. No indications for any chain expansion and chain localisation can be detected. These observations are in agreement with the results of a computer simulation on a binary blend [6], where explicitly the pure single chain behaviour was probed, and no deviations from unperturbed chain dimensions and spatially non-restricted Rouse dynamics could be observed.

Theoretical section

Theoretical background for the evaluation of the small angle neutron scattering (SANS) data

In the framework of the random phase approximation (RPA), extended to multi-component polymer mixtures [7, 8, 9], the coherent neutron scattering intensity I(Q) of an incompressible ternary blend, where the different components i = 1, 2, 3 are characterized by the volume content ϕ_i, the degree of polymerisation N_i and the molar volume v_i, can be written in a highly symmetric form as [9]

$$I(Q) = \frac{K_{12}S_3 + K_{23}S_1 + K_{31}S_2}{S_1S_2 + S_2S_3 + S_3S_1} \tag{1}$$

$$= I_{12}(Q) + I_{23}(Q) + I_{31}(Q) \tag{1a}$$

with

$$S_i = S_i(Q) = 1/S_i^0(Q) - \chi_i \text{ and } S_i^0(Q) = N_i v_i \phi_i P_i(Q) \; i = 1,2,3 \tag{2}$$

$Q = (4\pi/\lambda)\sin\theta$ is the magnitude of the scattering vector Q, with the wavelength of the scattering radiation λ, the scattering angle 2θ and

$$K_{ij} = K_{ji} = N_A\left(\frac{b_i}{v_i} - \frac{b_j}{v_j}\right)^2 \tag{3}$$

the scattering contrast between the components i and j (b_i scattering length, N_A Avogadro's number). $I_{ij}(Q) = I_{ji}(Q)$ are the partial scattering intensities resulting from the scattering contrast K_{ij}.

The thermodynamic interaction in pairs (Flory Huggins parameter) are put together as

$$\chi_i = \chi_{ij}\Big/(v_iv_j)^{1/2} + \chi_{ik}\Big/(v_iv_k)^{1/2} - \chi_{jk}\Big/(v_jv_k)^{1/2} \tag{4}$$

with

$$\chi_i + \chi_j = 2\chi_{ij}\Big/(v_iv_j)^{1/2} \tag{5}$$

$P_i(Q)$ is the Debye structure factor of a Gaussian coil

$$P_i(Z_i) = \frac{2}{Z_i^2}\left(e^{-Z_i} - 1 + Z_i\right) \tag{6}$$

with $Z_i = Q^2\left\langle R_{g,i}^2\right\rangle$ and $P_i(Q \to 0) = 1(\left\langle R_{g,i}^2\right\rangle = N_i\sigma_i^2/6$ mean square radius of gyration, σ_i^2 mean square segment length).

Equation (1) is equivalent with other formulae used in the literature [10, 11, 12, 13, 14] to calculate the neutron scattering intensity of incompressible ternary blends. However, the formula of Benoit, Benmouna and Wu [9] has the great advantage that the contributions of all three components enter explicitly in a similar manner, which makes it very clear.

In the case that there are no thermodynamic interactions present between the different components, Eq. (1) becomes very simple:

$$I_0 = (Q) = \frac{K_{12}S_1^0S_2^0 + K_{23}S_2^0S_3^0 + K_3S_3^0S_1^0}{S_1^0 + S_2^0 + S_3^0} \tag{7}$$

On the other hand, Eq. (1) leads directly to the well known RPA formula [15] for a related binary system with thermodynamic interactions, when components 2 and 3 are considered as being identical ($K_{12} = K_{13}$, $K_{23} = 0$; $S_2{}^0 = S_3{}^0$; $\chi_{12} = \chi_{13}$, $\chi_{23} = 0$ and $\phi_2 + \phi_3 = 1 - \phi_1$):

$$\frac{K_{12}}{I(Q)} = \frac{1}{S(Q)} = \frac{1}{\phi_1 v_1 S_1^0(Q)} + \frac{1}{(1-\phi_1)v_2 S_2^0(Q)} - \frac{2\chi_{12}}{(v_1v_2)^{1/2}} = S_1(Q) + S_2(Q) \tag{8}$$

where S(Q) is known as the structure factor of the binary blend.

For the ternary system the analogous relation for the partial structure factor $S_{12}(Q)$ is

$$\frac{1}{S_{12}(Q)} = \frac{K_{12}}{I_{12}(Q)} = S_1(Q) + S_2(Q) + S_1(Q)S_2(Q)/S_3(Q) \tag{9}$$

$S_{23}(Q)$ and $S_{31}(Q)$ are obtained by cyclic exchange of the indices and lead to similar expressions. The comparison between Eqs. (5) and (6) provides a good opportunity to see the influence of the additional third component on the scattering behaviour of both the others.

At the critical temperature T_c the total scattering intensity I(Q) is expected to diverge for $Q \to 0$ [12]. As a consequence the stability criterion can be immediately derived from Eq. (1):

$$S_1S_2 + S_2S_3 + S_3S_1 = 0 \tag{10}$$

or in detail:

$$\begin{aligned} &\frac{1}{S_1^0(0)}\frac{1}{S_2^0(0)} + \frac{1}{S_2^0(0)}\frac{1}{S_3^0(0)} + \frac{1}{S_3^0(0)}\frac{1}{S_1^0(0)} \\ &\quad = \chi_S \\ &\quad = \frac{(\chi_1+\chi_3)/S_2^0(0) + (\chi_2+\chi_3)/S_1^0(0)}{+(\chi_1+\chi_2)/S_3^0(0) - \chi_1\chi_2 - \chi_2\chi_3 - \chi_3\chi_1} \\ &\quad = \chi_{off} \end{aligned} \tag{11}$$

The stability limit (Eq. 11) is in agreement with the outcome of a thermodynamic treatment based on the Flory-Huggins lattice theory, where the difference of free energy of mixing ΔG per k_BT of the three component system is given by

$$\Delta G = \sum_{i=1}^{3} \phi_i \Big/ (v_iN_i)\ln\phi_i + \frac{1}{2}(\chi_1+\chi_2)\phi_1\phi_2 + \frac{1}{2}(\chi_2+\chi_3)\phi_2\phi_3 + \frac{1}{2}(\chi_3+\chi_1)\phi_3\phi_1 \tag{12}$$

and the spinodal line follows from [16]

$$\frac{\partial^2\Delta G}{\partial\phi_1^2}\frac{\partial^2\Delta G}{\partial\phi_2^2} - \left(\frac{\partial^2\Delta G}{\partial\phi_1\partial\phi_2}\right)^2 = 0 \tag{13}$$

Equation (13) is identical with Eq. (11), when the $S_i{}^0(0)$ are replaced by Eq. (2).

When the volume fraction ϕ_i of one of the different species in the ternary blend is small, one can see from Eqs. (1) and (7) that the scattering intensity is mainly determined by the single chain structure factor of the component with the small volume content. This effect becomes enhanced for systems where the scattering contrast between both components with the major content is zero or at least small compared to that of the other two.

Theoretical background for the evaluation of the neutron spin echo (NSE) data

Since the influence of the χ_{ij}-parameters becomes less important at spatial dimensions $Q\,R_g > 1$, which are probed by the NSE technique, the analysis of the NSE data can start from the assumption that in non-entangled polymer blends the internal relaxation is determined by the single chain Rouse behaviour at all compositions of the protonated and deuterated material as long as the degrees of polymerisation are almost the same.

The normalized dynamic structure factor (S(Q,t)/S(Q,0) for a single chain with Rouse dynamics [17] and superimposed centre of mass diffusion (diffusion coefficient D) is given by [18]

$$\frac{S(Q,t)}{S(Q,0)} = \exp\left\{-DQ^2t\right\}\int_0^\infty due^{-u} \times \exp\left\{-(\Omega_R t)^{1/2}h\left(u(\Omega_R t)^{-1/2}\right)\right\} \quad (14)$$

with

$$h(y) = \frac{2}{\pi}\int_o^\infty dx\frac{\cos xy}{x^2}\left(1-e^{-x^2}\right) \quad (15)$$

and the adjustable parameter

$$\Omega_R = \Omega_R(Q) = \frac{1}{12}\frac{k_BT}{\varsigma}\sigma^2Q^4 = \frac{1}{36}W\sigma^4Q^4 \quad (16)$$

where $W = 3\ k_BT/(\zeta\sigma^2)$ (ζ monomeric friction coefficient) is the elementary relaxation rate of the Rouse motion. W and D are related by

$$D = W\sigma^4\Big/\left(18\left\langle R_g^2\right\rangle\right) \quad (17)$$

For $D \to 0$ the dynamic structure factor for pure Rouse relaxation is a universal function of $(\Omega_R t)^{1/2}$. With finite D the same is true for $S_R(Q,t)/S_R(Q,0)$, which is defined as S(Q,t)/S(Q,0) divided by the centre of mass contribution $\exp\{-DQ^2t\}$.

The influence of the Flory-Huggins interaction on the internal dynamics of single chains can only be treated in the short time limit [19], where the characteristic frequency Ω(Q) is derived as the initial slope or the first cumulant of S(Q,t)

$$\Omega(Q) = -\lim_{t\to\infty}\frac{\partial}{\partial t}\ln S(Q,t) \quad (18)$$

In the framework of this approach $\Omega_R(Q,\chi_{12} \neq 0)$ is given by

$$\Omega_R(Q,\chi_{12} \neq 0) = \Omega_R(Q)\left(1-\phi_p(1-\phi_p)\chi_{12}12\Big/(Q\sigma)^2\right) \quad (19)$$

with $\Omega_R(Q)$ as introduced in Eq. (16).

Experimental section

Sample preparation and characterisation

Up to a molecular weight of about 50,000 g/mol narrowly distributed deuterated and protonated PEMS are obtained with nearly total conversion by anionic living ring-opening polymerization of the corresponding deuterated and protonated cyclic trimer in the solvent and promoter tetrahydrofurane (THF) with *sec*-butyl lithium as initiator. So the desired molecular weights were achieved with an accuracy better than 10% [20, 21]. The deuterated monomers were prepared in nine reaction steps starting from deuterated ethanol and methanol; the protonated monomers were synthesized from commercially available ethylmethyldichlorosilane [22].

Narrowly distributed protonated and deuterated PDMS were synthesized from the related protonated and deuterated cyclic trimers in two reaction steps [23]. First 10% of the monomers reacted in benzene with the initiator butyl lithium to form a prepolymer; then the rest of the monomers, dissolved in the solvent and promoter THF, was added. The protonated cyclic trimers were commercially available, the deuterated can be prepared in six reaction steps, starting from deuterated methanol.

The protonated and deuterated PDMS and PEMS polymers detailed in Table 1, carefully characterized by size exclusion chromatography (SEC) with toluene as solvent and PDMS or PEMS calibration curves, were used as components of the ternary blend d-PDMS/

Table 1 Characteristics of the deuterated and protonated PDMS and PEMS

	Label in ternary system	M_w/g mol^{-1}	M_w/M_n	N_w	T_g/K	η_0(300 K)/poise
p-PDMS	-	20,000	1.03	270	149	2.0
d-PDMS	1	19,700	1.04	250	148	
d-PEMS	2	21,500	1.07	225	141	
p-PEMS	3	23,700	1.04	270	142	4.4

M_w = mass average molar mass
M_n = number average molar mass
N_w = degree of polymerisation
T_g = glass transition temperature, as obtained from differential thermal analysis (DTA)
η_0 = Newtonian viscosity
The labels 1, 2, 3 are used as indices to identify the different components of the ternary blend

d-PEMS/p-PEMS (volume composition 0.5/0.425/0.075) to be studied by neutron scattering.

Neutron scattering

SANS The samples were kept under nitrogen in quartz cells (sample thickness: 1 mm) and mounted in brass cell holders. SEC before and after the SANS experiments showed no evidence of sample degradation. The experiments were performed with the instrument KWS II at the cold source of the research reactor FRJ-2 at the Forschungszentrum Jülich, Germany [24]. The wavelength λ of the neutrons amounted to $\lambda = 7.9$ Å; the wavelength width, transmitted by a helical slit selector, was $\delta\lambda/\lambda = 18\%$. The chosen distances between the two-dimensional He-detector and the samples were 2 m and 8 m, providing a usable span of scattering vector magnitudes in the range $0.007\ \text{Å}^{-1} < Q < 0.12\ \text{Å}^{-1}$. Measurements were performed at 462, 416, 379 and 369 K with an accuracy of ± 2 K, always in a descending sequence. The scattering data were corrected for empty cell scattering and scaled to absolute units by comparison to the scattering from a secondary standard sample (Lupolen). The latter had been calibrated at the same wavelength with a 0.1 mm thick, out-gassed and surface-polished vanadium single crystal. Corrections for multiple scattering and the effect of wavelength spread were found to be negligible. The scattering of the matrix samples d-PDMS, d-PEMS and p-PEMS were measured at 48 and 199 °C. After interpolation the scattering of the matrices were subtracted from the scattering intensity of each isotopic blend sample according to its volume fraction.

NSE The samples were kept under nitrogen in niobium containers (sample thickness: 2 mm) and a thermostat enclosure with 5 mm thick aluminium beam windows. Temperature control was better than 0.5 °C. SEC before and after the NSE experiments proved that no sample degradation occurred.

The experiments were performed with the NSE spectrometer at the cold source of the research reactor FRJ-2 at the Forschungszentrum Jülich, Germany [25]. The neutrons left the velocity selector with $\lambda = 8$ Å and $\delta\lambda/\lambda = 10\%$. The chosen scattering vectors $Q = 0.05$, 0.08, 0.10, 0.14 and 0.20 Å^{-1} allowed one to observe the segmental dynamics; the span of the Fourier times t was in the range $0.1 < t < 22$ ns. The experiments were performed at 200, 150 and 100 °C, always in a descending order. The coherent scattering of the deuterated matrices, determined for each temperature, as well as the background and empty cell scattering were subtracted from the measured intensities. Additionally, a correction for losses in polarisation was performed by division of the measured intensities through the resolution function of the spectrometer $S_{spec}(Q,t)$, the latter being determined from the elastic scattering of a magnesium oxide sample.

Results and discussion

As a representative example, in Fig. 1 the SANS data measured at $T = 462$ K are shown together with the result of fitting the theoretical scattering law of a ternary system (Eq. 1) to the experimental data. In addition some important details, which concern the related non interacting ternary blend as well as the contributions of

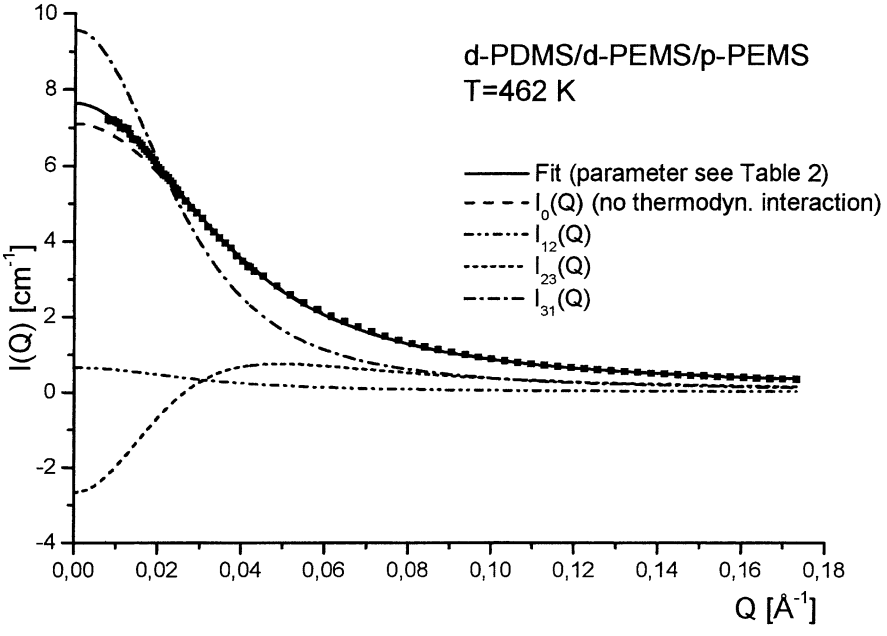

Fig. 1 SANS curve of the d-PDMS/d-PEMS/p-PEMS ternary blend at $T = 462$ K and fit of the experimental data with Eq. (1); partial scattering intensities I_{12}, I_{23} and I_{31} related to the three different scattering contrasts and scattering curve $I_0(Q)$ ignoring all thermodynamic interactions

Table 2 Input parameters (molar volumes v_i, radii of gyration $\left\langle R_g^2 \right\rangle_i^{1/2}$, neutron scattering contrasts K_{ij}) used for the fitting procedure and final values of the adjustable parameters (background correction, interaction parameters χ_{ij})

T	v_1	$v_2 = v_3$	$\left\langle R_g^2 \right\rangle_1^{1/2}$	$\left\langle R_g^2 \right\rangle_2^{1/2}$	K_{12}	K_{23}	K_{31}	Background correction	χ_{12}	χ_{23}	χ_{31}
					10^5	10^3	10^3		10^3	10^3	10^3
[K]	[cm^3/mol]	[cm^3/mol]	[Å]	[Å]	[mol/cm^4]	[mol/cm^4]	[mol/cm^4]	[cm^{-1}] (from $Q > 0.10$ Å^{-1})			
462	90.1	100.7	41.9	40.4	9.29	4.12	2.97	0.076	1.56 ± 2.1	-2.48 ± 0.8	8.34 ± 0.3
416	86.2	97.5	40.4	40.2	8.64	4.38	3.24	0.071	5.27 ± 0.8	-0.13 ± 0.5	9.25 ± 0.04
379	83.3	95.3	39.2	40.0	7.75	4.59	3.47	0.071	7.12 ± 0.3	0.27 ± 0.35	9.64 ± 0.04
369	82.5	94.7	38.9	39.7	7.55	4.66	3.55	0.056	6.91 ± 0.2	-0.98 ± 0.24	9.39 ± 0.03

each of the three scattering contrasts, are included. All the curves base on the parameters given in Table 2.

Comparing the experimental data and the curve, calculated according to Eq. (7) for the corresponding non interacting ternary system, one can see that the total thermodynamic interactions have no influence on the scattering curve at Q-values beyond 0.04–0.05 Å^{-1}. On the other hand the behaviour of the scattering curve at larger Q-values ($Q > 0.10$ Å^{-1}) requires either a reduce of the R_g below the values, observed in the related isotopic blend systems [1], or to add a small Q-independent background to compensate possible errors in the correction of the incoherent background. An increase of the R_g values, as found in the binary d-PDMS/p-PEMS and d-PEMS/p-PDMS blends [2] would make the discrepancies at large Q even more worse. Thus, a coil expansion beyond the ideal behaviour can be definitely excluded. As a consequence the R_g values of PDMS and PEMS [1] and this later Q-independent background correction, obtained at the different temperatures in the Q- range between 0.105 and 0.175 Å^{-1}, were used as fixed parameters for this and all the other fitting procedures and for the detail calculations shown in Fig. 1.

The contributions of the different K_{ij} to the total scattering intensity show that the part of both deuterated components ($I_{12}(Q)$) is not zero but significantly smaller than both other partial intensities and that the d-PDMS/p-PEMS ($I_{31}(Q)$) and the d-PEMS/ p-PEMS ($I_{23}(Q)$) parts have opposite signs at small Q-values. As can be seen from Eq. (2), the sign of $S_i(Q)$ depends directly on the sign of χ_i and on the scale of $1/S_i^0(Q)$ and χ_i. For $\chi_i < 0$ $S_i(Q)$ is always positive, whereas for $\chi_i > 0$ a change from $S_i(Q) < 0$ at small Q to $S_i(Q) > 0$ may occur depending on the scale of $1/S_i^0(Q)$ and χ_i.

The criteria for the final fixing of the three interaction parameters were both the quality of the fits and the physical plausibility of the numerical values, used for and created by the adjustments. In a first approximation $\chi_{13}(T)$ and $\chi_{23}(T)$ were taken from the related binary d-PDMS/p-PEMS [2] and isotopic d-PEMS/p-PEMS blends [1] of volume content 0.5/0.5, respectively, being aware that this choice may be imperfect due to a probable composition dependence [26, 27, 28]. As expected, when χ_{12} is used as the only adjustable parameter, the data description in the low Q-range is non-satisfying, in particular with respect to the scattering curves measured at 379 and 369 K. In addition the majority of the χ_{12}-values is negative, which is not reasonable when the χ-values derived from light scattering investigations on a related binary p-PDMS/p-PEMS blend [28] are taken as a reference.

To overcome this situation in the next steps a simultaneous variation of χ_{12} and χ_{13} or χ_{12} and χ_{23} was performed keeping only the third χ-parameter fixed as before. With χ_{13} fixed the situation is not improved. Except for the scattering curve for $T = 369$ K the fit produces for the three other scattering curves still stronger negative χ_{12}-values than before. The additional clear decrease of the χ_{23}-values is in contrast to theoretical predictions on the composition dependence of the χ-parameter [29] and related experimental observations on isotopic blends of UCST (upper critical solution temperature) type [14, 30]. On the other hand a general good data description becomes first possible, when χ_{23} is kept fixed instead of χ_{13}. The results of the adjustment fit nearly perfect to all four experimental scattering curves. This agreement can also be seen from the mean square deviations between the experimental and calculated scattering curves, which are considerably decreased compared to the both previous attempts described above. With respect to the adjusted χ_{12}- and χ_{13}-parameters the partially strong negative values of χ_{12} are shifted in the positive direction and the χ_{13}-values are generally increased compared to the findings from the corresponding d-PDMS/p-PEMS blend of 0.5/0.5 composition. This increase varies between 15 and 20% and seems to indicate a qualitatively similar composition dependence of the interaction parameter as observed in isotopic blends.

Taking the results of this fit together with the fixed χ_{23} as starting values, finally Eq. (1) was also fitted to the scattering curves using simultaneously all three χ_{ij} as adjustable parameters. It is not surprising that this produces the best agreement between the experimental and theoretical scattering curves. However the fit results can be taken as a later confirmation of the permissibility of this kind of proceeding.

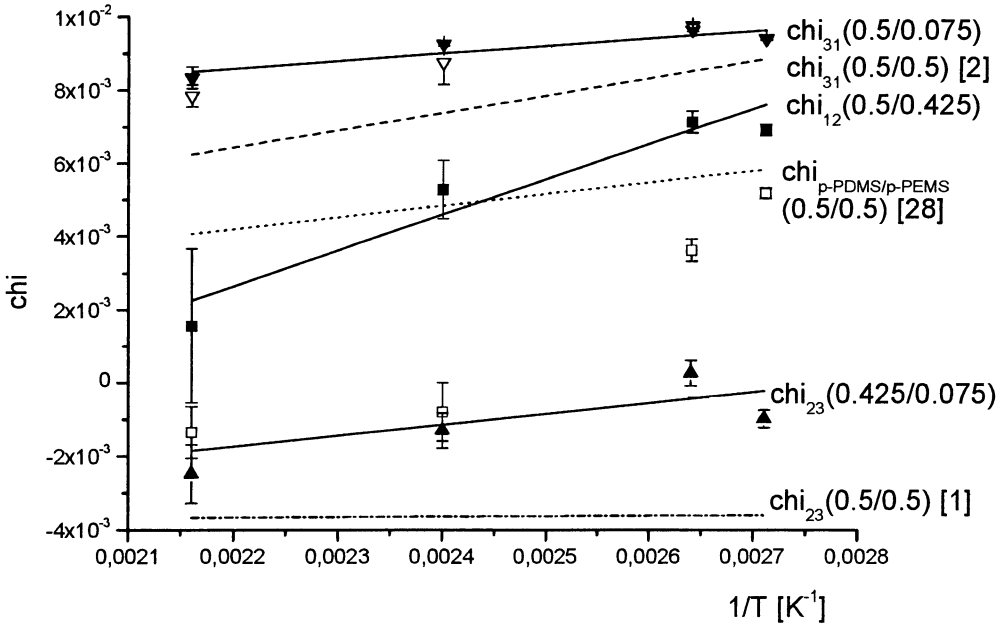

Fig. 2 χ-parameters (chi $\equiv \chi$), obtained from fitting Eq. (1) to the experimental SANS curves, as a function of the inverse absolute temperature T. For comparison the χ-values of the corresponding isotopic d-PEMS/p-PEMS and binary d-PDMS/p-PEMS blends [1, 2] and of a similar p-PDMS/p-PEMS blend [28] are also shown. The *open symbols* are the values for χ_{12} (□) and χ_{31} (*inverted open triangles*), which are obtained with χ_{23} fixed as derived from the isotopic d-PEMS/p-PEMS blend of the composition 0.5/0.5

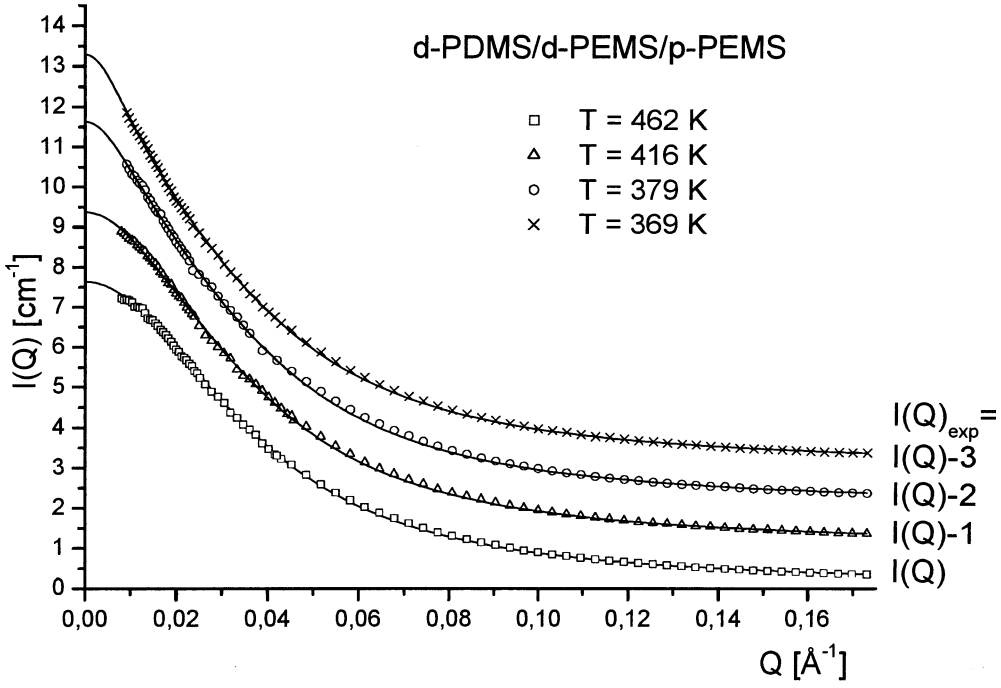

Fig. 3 SANS curves of a ternary d-PDMS/d-PEMS/p-PEMS blend of volume composition 0.5/0.425/0.075 at four different temperatures: experimental data and results of fitting Eq. (1) to the curves using simultaneously all three thermodynamic interaction parameters as adjustable. The fixed input parameters and the finally adjusted parameters are summarized in Table 2. For the sake of clarity the curves following one after the other are vertically shifted by 1 intensity unit

The temperature dependence of all the χ_{ij} follows the relation $\chi_{ij} = A + B/T$ with $B > 0$ as typical for UCST systems [31]; see Fig. 2. Compared to the related binary blends of equal volume content the χ_{23} as well as the χ_{13} are increased as expected for blends, where the different species have a strongly different volume content [29]. Most of the χ_{23} are < 0, in agreement with earlier findings on low molar mass isotopic blends, for which negative interaction parameters are characteristic [1, 32]. The magnitude of all χ_{13}-parameters is only slightly altered in comparison to the fits with fixed χ_{23}-values. Since the χ_{12}-values become very similar to the interaction parameters of a corresponding p-PDMS/p-PEMS blend [28], it seems to be reasonable to take the results of the three-parameter fits, which are collected in Table 2 and plotted in Fig. 2, as the basis for the data description presented here.

In Fig. 3 all experimental scattering curves, measured at temperatures between 462 and 369 K, are plotted

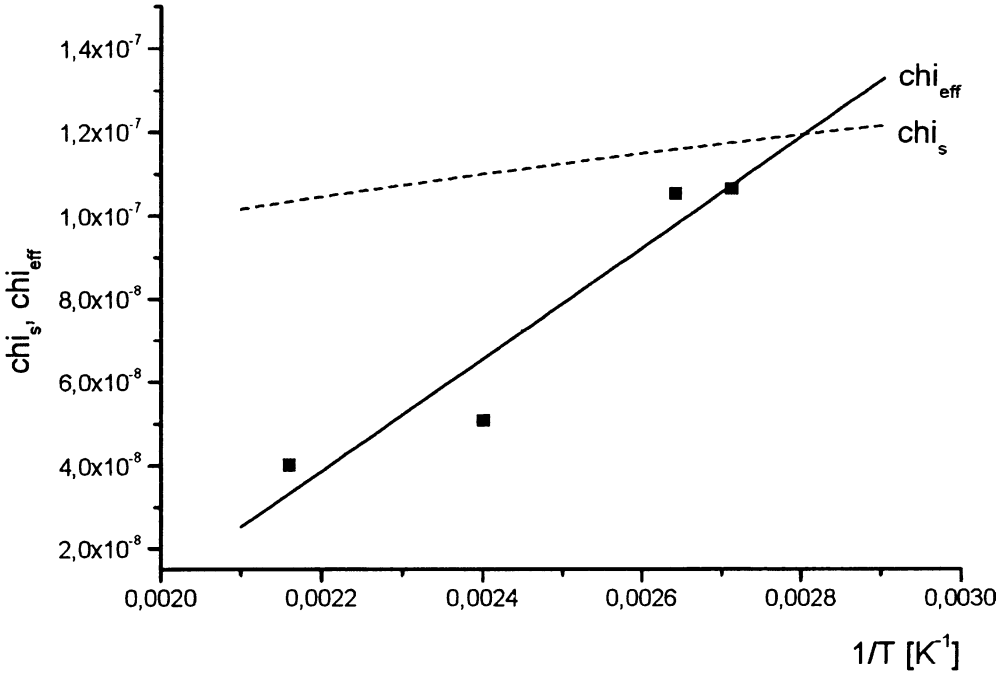

Fig. 4 χ_s and χ_{eff} (*filled squares*) (chi $\equiv \chi$) defined by Eq. (11) as dependent on the inverse absolute temperature 1/T. From the point of intersection of both lines the critical temperature $T_c = 365$ K is derived

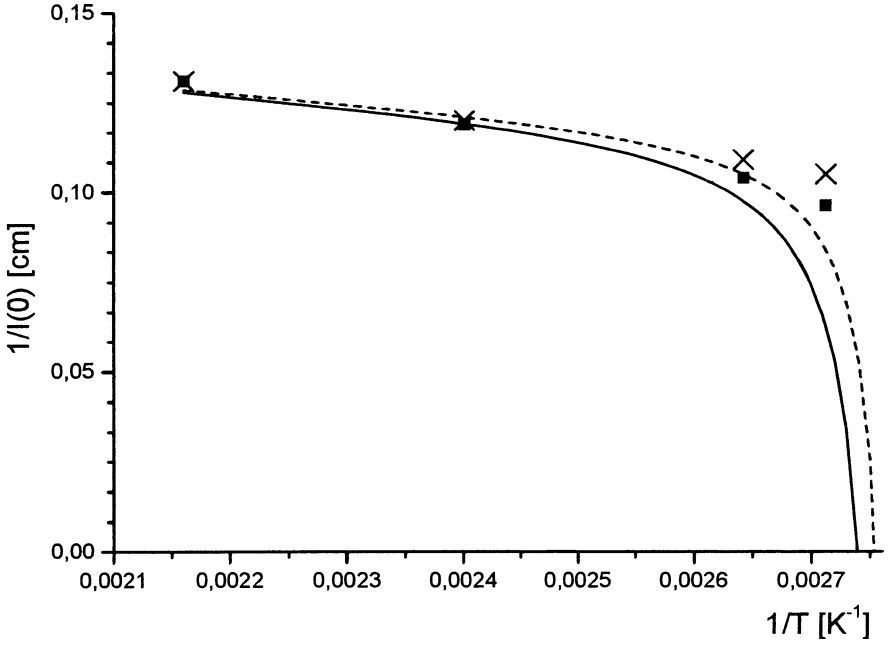

Fig. 5 Inverse scattering intensities of the ternary d-PDMS/d-PEMS/p-PEMS blend, extrapolated to $Q \rightarrow 0$, as dependent on the inverse absolute temperature 1/T. *Filled squares*, *crosses*: experimental data obtained from the fits (see Fig. 3) and Zimm plots (1/I(Q) vs Q^2), respectively. *Solid line*: 1/I(0) behaviour expected from Eq. (1) using the linear regression of the three adjusted interaction parameters as dependent on 1/T (see Fig. 2); *broken line*: 1/I(0) behaviour expected from Eq. (1) using the linear regression of the two adjusted interaction parameters χ_{12} and χ_{31} as before and changing the offset and the slope of the linear regression of χ_{23} by a factor 0.95

together with the outcome of the data fitting using Eq. (1). The agreement is continuously excellent. For each adjustment the three interaction parameters χ_{12}, χ_{23} and χ_{31} were varied simultaneously as outlined above, whereas the molar volumes v_i, the radii of gyration $\left\langle R_g^2 \right\rangle_i^{1/2}$, the scattering contrasts K_{ij} and the Q-independent background correction were taken as fixed input parameters. All the parameters are summarized in Table 2.

In Fig. 4 the χ_{eff} ,as defined in Eq. (8), is plotted vs 1/T. The corresponding extrapolation to χ_s leads to a T_c-value of 357 ± 4 K, which is in reasonable agreement with the findings of microscopic investigations [21], from which a critical temperature T_c of 361 ± 3 K is derived for this system. Independent of the confirmation of the

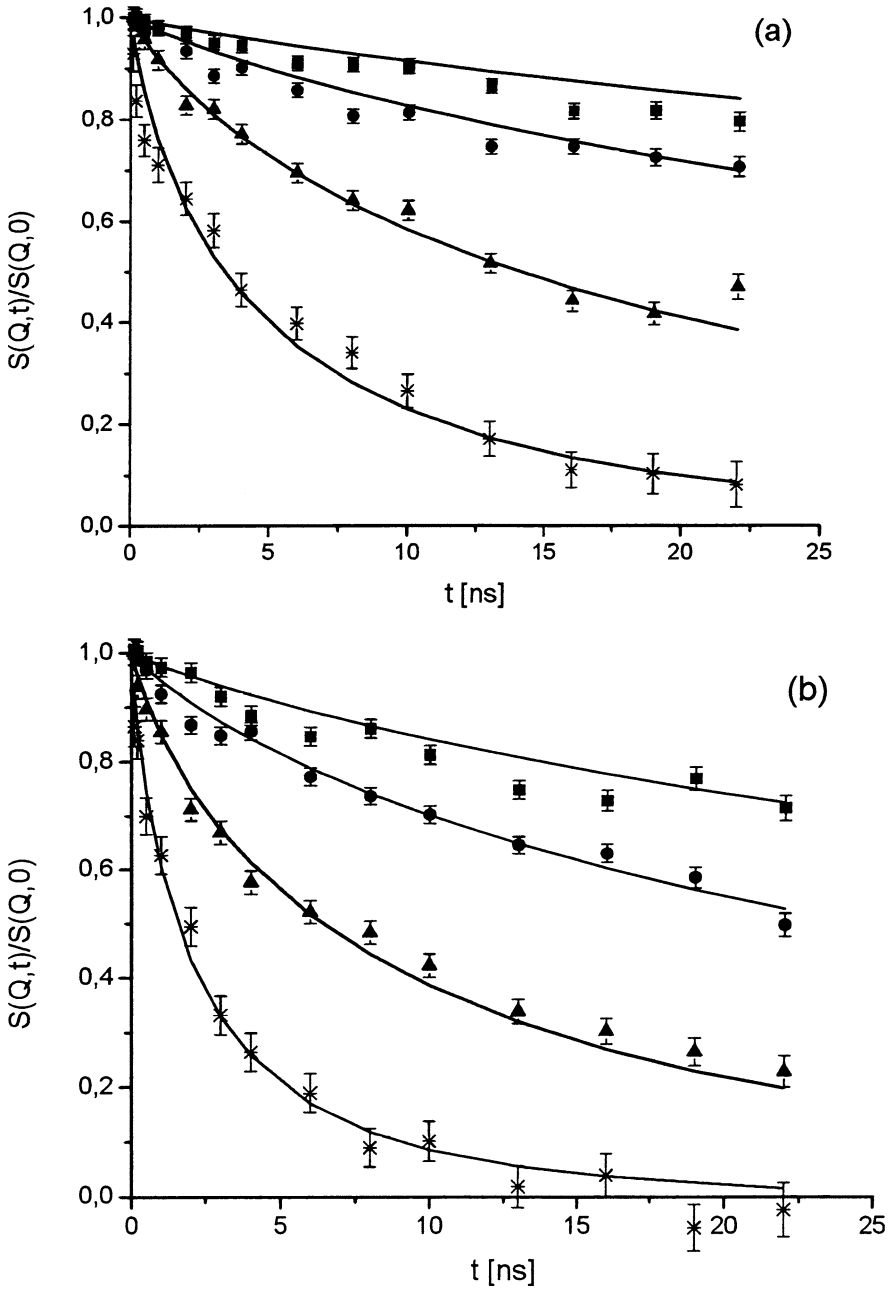

Fig. 6a,b NSE spectra of the ternary d-PDMS/d-PEMS/p-PEMS blend. The *solid lines* result from fitting the dynamic structure factor of the Rouse relaxation simultaneously to all spectra, using at a given temperature $W\sigma^4$ as the only adjustable parameter: **a** T = 373 K; **b** T = 423 K. *Filled squares* Q = 0.08 Å^{-1}; *filled circles* Q = 0.10 Å^{-1}; *filled triangles* Q = 0.14 Å^{-1}; *stars* Q = 0.20 Å^{-1}

T_c-value of this special composition it is interesting to realize that in a PDMS/PEMS blend of equal content of both polymers the T_c can be enormously shifted by an isotopic substitution, starting from $T_c = 339$ K for d-PDMS/d-PEMS over $T_c = 357$ or 361 K for d-PDMS/d-PEMS/p-PEMS (0.5/0.425/0.075) to $T_c = 403$ K for d-PDMS/p-PEMS [2, 21].

In the framework of the mean field approximation two component (isotopic or binary) polymer blends are characterized by an almost linear dependence between $1/I(Q \rightarrow 0,T)$ and $1/T$. The relation becomes completely linear if the structure factor is considered instead of the intensity. This fact provides a further simple possibility to determine T_c by extrapolating the inverse intensities or structure factors vs 0. As can be seen from Fig. 5, in the ternary system such a linear dependence does not exist and the determination of the critical temperature from the temperature dependence of the intensity at $Q \rightarrow 0$ requires measurements in the immediate vicinity of T_c. In the present case the expected $1/I(Q \rightarrow 0,T)$ behaviour was calculated using the linear regression of the three adjusted interaction parameters as dependent

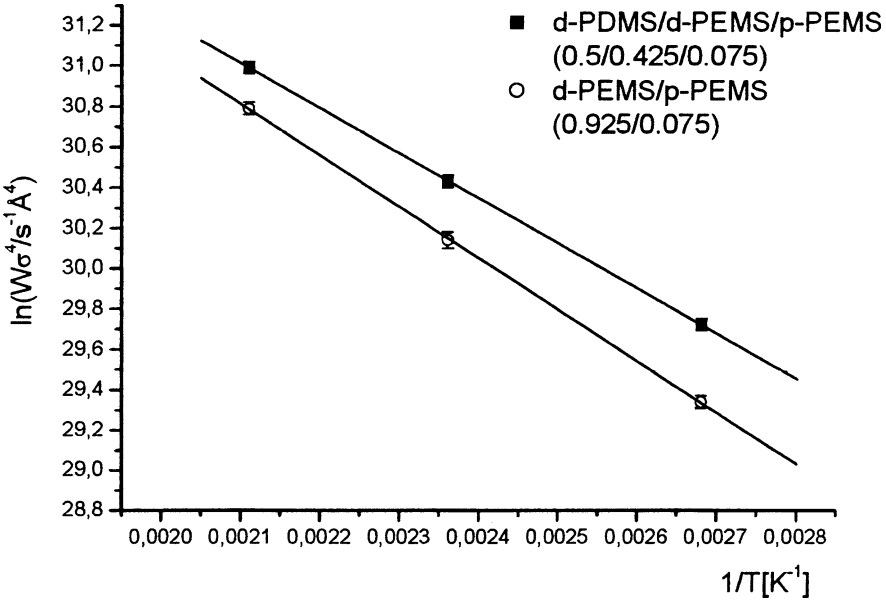

Fig. 7 Arrhenius plot of the Rouse rates $W\sigma^4$ of the single chain relaxation, obtained from an isotopic d-PEMS/p-PEMS and a ternary d-PDMS/ d-PEMS/p-PEMS blend

on 1/T (see Fig. 2) and is shown as solid line. This leads to $T_c = 365$ K. A better agreement with the four experimental data points is obtained, using for the calculation of 1/I(0) (broken line in Fig. 5) the linear regression of the two adjusted interaction parameters χ_{12} and χ_{31} as before and decreasing the offset and the slope of the linear regression of χ_{23} by only 5%. As a consequence T_c is shifted slightly downwards by 2 K.

As examples of the NSE measurements the spectra measured at 373 and 423 K and four Q-values between 0.08 and 0.20 $Å^{-1}$are plotted in Fig. 6. The solid lines result from a common fit of the four spectra the scattering law of the Rouse dynamics and superimposed centre of mass diffusion (see Eq. 11). Using R_g^2 as obtained by SANS on the related isotopic blends [1], for each of both temperatures $W\sigma^4$ is the only adjustable parameter. It is quite obvious that the data follow perfectly the predictions of the Rouse model, which describes the dynamics of the dense low molecular mass system by the single chain relaxation. This is not only true far away from the critical temperature T_c , but particularly also in the immediate vicinity of T_c.

In agreement with the Rouse behaviour master curves are obtained, when the scattering data reduced with respect to the centre of mass diffusion are plotted in the scaling representation, $Q^2\sigma^2(Wt)^{1/2}$being the scaling variable.

Due to the higher mobility of the PDMS component, which directly mirrors in the viscosities (see Table 1), the $W\sigma^4$ values in the d-PDMS/d-PEMS/p-PEMS blend are about 30% larger than those of a corresponding isotopic PEMS blend. From the temperature dependence of $W\sigma^4$ an activation energy $E_A = 18.6$ kJ/mol is derived, whereas for the d-PEMS/p-PEMS system with the same amount of protonated material $E_A = 20.3$ kJ/mol was obtained [21] (see Fig. 7). For a comparable p-PDMS/p-PEMS system the temperature dependence of the coefficient of interdiffusion in the regime, where the critical slowing down is not yet visible, is characterized by an activation energy of 18.6 kJ/mol, too, as gained from photon correlation spectroscopy [28].

Conclusion

When the single chain behaviour in a binary blend of low molecular mass poly(siloxanes) at the critical composition is probed by SANS and NSE techniques, one is first confronted with the fact that the chemically binary d-PDMS/d-PEMS/p-PEMS blend of the volume composition 0.5/0.425/0.075 is strictly speaking a ternary system.

The careful analysis of the SANS data, based on the application of a corresponding three component RPA formalism, allows one to determine all three thermodynamic interaction parameters with reasonable reliability and gives evidence that no chain expansion occurs as observed in a corresponding d-PDMS/p-PEMS blend of 0.5/0.5 volume content, where the collective behaviour is probed.

The NSE spectra agree in the whole experimentally accessible time window with the theoretical scattering law, calculated for the Rouse relaxation of single chains. This is in contrast to the observation of the collective dynamics in the just mentioned d-PDMS/p-PEMS system, which exhibits in the same time window a transition

from Rouse behaviour at short times to a much weaker relaxation at longer times.

The findings of the static and dynamic single chain behaviour confirm the results of a computer simulation on a low molecular mass binary blend at the critical concentration, which do not show any deviations, neither from unperturbed chain dimensions nor from the Rouse dynamics.

Moreover, from these investigations one may suppose that isotope exchange in a binary low molecular mass PDMS/PEMS blend with equal volume content of both components offers the possibility to shift the critical temperature T_c continuously in the limits of 339 K (d-PDMS/d-PEMS) and 403 K (d-PDMS/p-PEMS).

Acknowledgement The authors are grateful to G. Meier and to M. Monkenbusch (Forschungszentrum Jülich) for their assistance with respect to the SANS and NSE measurements and the data evaluation. They would also like to thank M. Benmouna for stimulating discussions. In particular B.E. and H.G. are indebted to the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF) for financial support in coarse of projects 03EW4MP1and 03-EW5MP2.

References

1. Götz H, Ewen B, Maschke U, Meier G, Monkenbusch M (2001) Macromol Chem Phys 202:3334
2. Götz H, Ewen B, Maschke U, Meier G, Monkenbusch M (2003) e-polymers 011
3. Brereton M, Vilgis TA (1989) J Phys France 50:245
4. Vilgis TA, Meier G (1994) J Phys I France 4:985
5. Vilgis TA (2000) Phys Rep 336:167
6. Müller M, Binder K (1996) J Phys II France 6:187
7. Benoit H, Benmouna M, Wu W (1990) Macromolecules 23:1511
8. Akcasu AZ, Tombakoglu M (1990) Macromolecules 23:607
9. Benoit H, Benmouna M, Wu W (1990) Macromolecules 23:1511
10. Mori K, Tanaka H, Hashimoto T(1987) Macromolecules 20:381
11. Ijichi Y, Hashimoto T (1988) Polym Commun 29:135
12. Hammouda B, Briber RM, Bauer BJ (1992) Polymer 33:1785
13. Reichart GC, Graessley WW, Register RA, Krishnamoorti R, Lohse DJ (1997) Macromolecules 30:3363
14. Balsara NP, Jonnálagadda SV, Lin CC, Han CC, Krishnamoorti R (1993) J Chem Phys 99:10011
15. de Gennes PG (1979) Scaling concepts in polymer physics. Cornell University Press, London
16. Sanchez IC (1982) Equation of state theories of polymer blends. In: Šolc K (ed) Polymer compatibility and incompatibility—principles and practices. Harwood Academic, Chur London New York
17. Rouse RP (1953) J Chem Phys 21:1272
18. de Gennes PG (1967) Physics (USA) 3:181
19. Akcazu Z, Benmouna M, Benoit H (1986) Polymer 27:1935
20. Maschke U, Wagner T, Coqueret X (1992) Makromol Chem 193:2453
21. Götz H (1999) PhD Thesis, Mainz
22. Götz H, Maschke U; Wagner T, Ritz S, Rosenauer C, Ewen B (1999) Des Monomers Polym 2:125
23. Götz H, Maschke U, Wagner T, Rosenauer C, Martin K, Ewen B (2000) Makromol Chem Phys 201:1311
24. Schwahn D, Meier G, Springer T (1991) J Appl Cryst 24:568
25. Monkenbusch M, Schätzler R, Richter D (1997) Phys Rev A 399:301
26. Shibayama M, Yang H, Stein RS, Han CC (1985) Macromolecules 18:2179
27. Araki T, Tran-Cong Q, Shibayama M (eds) (1998) Structure and properties of multiphase polymeric materials. Marcel Dekker, New York Basel Hong Kong
28. Momper B (1989) PhD Thesis, Mainz
29. Muthukumar M (1986) J Chem Phys 85:4722
30. Hopkinson I, Kiff FT, Richards RW, King SM, Munro H (1994) Polymer 35:1722
31. Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, Ithaca London
32. Beaucage G, Sukumaran S, Clarson SJ, Kent MS, Schaefer DW (1996) Macromolecules 29:8349