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Universal behavior of polymers in blends, solutions, and supercritical mixtures and implications for the validity of the random phase approximation

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Abstract

Blending (or mixing) of macromolecules is widely used to tailor the properties of polymeric materials and small-angle neutron scattering (SANS) has provided detailed information at the molecular level on the ability of different polymer species to mix or segregate at various thermodynamic conditions. For two decades, SANS data have been analyzed via the de Gennes "random phase approximation" (RPA) [P.-G. de Gennes, Scaling Concepts in Polymer Physics, second ed., Cornell University Press, Ithaca, London, 1979], which is based on the assumption that the dimensions of polymer chains remain unchanged on mixing for all concentrations and temperatures. Here we investigate the effect of temperature and concentration on the dimensions of macromolecules in blends using SANS and high-concentration labeling methods and construct a generic phase diagram, which specifies the range of validity of the RPA. Using scaling arguments, we demonstrate a parallel between the structure–property relationships in blends and solutions of polymers in small molecule solvents and reveal the impact of the chain length of the polymeric solvent on the phase behavior of polymer blends. The results offer new insights into the universality of the thermodynamic properties and structure of macromolecules in polymeric, liquid and supercritical solvents.
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Keywords: Polymer blends; Liquid–liquid equilibria; Critical state; Small-angle neutron scattering

1. Introduction

The scattering function from a single-phase incompressible polymer blend of components A and B was calculated by de Gennes based on the random phase approximation (RPA) [1]

$$S_{\mathrm{t}}^{-1}(Q) = S_{\mathrm{s,A}}^{-1}(Q) + S_{\mathrm{s,B}}^{-1}(Q) - 2\chi. \tag{1}$$

where $S_{\mathrm{t}}(Q)$ is the total scattering structure factor which embodies information on the total (both intra- and intermolecular) correlations between polymer segments and is related to the correlation length of

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the concentration fluctuations, ξ; $S_{s,i}(Q)$ the single-chain structure factor which contains information on the intramolecular correlations, and thus on the dimensions (e.g. the radius of gyration, R_g) of the polymer components; Q the scattering vector; and χ the Flory interaction parameter which reflects the nature of the local segment–segment interactions. The RPA (Eq. (1)) is based on the assumption that the dimensions of polymer chains remain unchanged on mixing and retain the unperturbed radius of gyration $R_g(\Theta)$ (as in amorphous state or in a polymer solution at the Θ point) at arbitrary temperatures and concentrations. However, recent theoretical and computer simulation results [2–7] have suggested that R_g may shrink or expand in various regions of the temperature–concentration phase diagram and there are several indications in the experimental literature to support this hypothesis [8–10]. In this paper we systematically explore the interrelation between R_g and the correlation length ξ in polymer blends using small-angle neutron scattering (SANS) and demonstrate the existence of the Θ lines in the phase diagrams of polymer blends, in addition to binodals and spinodals traditionally discussed in the literature. The occurrence of the Θ lines is used to delineate the range of validity of the RPA as well as to explore universal aspects of the polymer behavior in polymeric and small molecule Θ solvents.

2. Experimental

The coherent neutron scattering cross section, $I(Q)$, from an incompressible mixture of identical deuterated and protonated polymers (component A) in a polymeric solvent (component B) is given by [11]

$$I(Q, x) = K^* S_{s,A}(Q) + I_t(Q, x). \tag{2}$$

where $S_{s,A}(Q)$ is the single-chain structure factor, which contains information on the radius of gyration $R_{g,A}$ of the component A; $I_t(Q, x)$ the total intensity of scattering, which contains information on the correlation length ξ of the concentration fluctuations; x the mole fraction of deuterated chains relative to all chains of the component A, and $Q = 4\pi\lambda^{-1}\sin\theta$, is the scattering vector, where 2θ is the scattering angle and λ is the wavelength. The prefactor $K^* \sim (b_h - b_d)^2 x(1-x)$ is a function of scattering lengths of the deuterated (b_d) and protonated (b_h) monomers of component A.

For isotopic mixtures of poly(dimethyl siloxane) (PDMS) ($b_d = 6.33 \times 10^{-12}$ cm, $b_h = 0.086 \times 10^{-12}$ cm) and poly(ethyl methyl siloxane) (PEMS) ($b'_h = 0.003 \times 10^{-12}$ cm) studied in this work, there is no isotopic ratio, $0 < x < 1$, which eliminates $I_t(Q, x)$ completely, however one can minimize it contribution by choosing small x (e.g. $x = 0.1$). Therefore, we measure the intensity of scattering $I(Q, x = 0.1)$ from ternary mixtures ((0.1)PDMS-d + (0.9)PDMS-h)–PEMS at the critical concentration of PDMS defined as [7] $\phi_{C,A} = N_B^{1/2}/(N_A^{1/2} + N_B^{1/2})$ as well as the intensity of scattering $I_t(Q, x = 1, \Delta T)$ from a binary blend PDMS-d ($x = 1$)–PEMS at the same $\phi_{C,A}$. The single-chain scattering function $S_{s,A}(Q)$ is than obtained by weighed subtraction of the total scattering at the same temperature distance from the critical temperature of each blend via [12]

$$K^* S_{s,A} = I(Q, x = 0.1, \Delta T) - A^* I_t(Q, x = 1, \Delta T'). \tag{3}$$

The prefactor A^* is small (~0.0125 for $x = 0.1$) and thus the single-chain scattering is predominant far away from the critical temperature (large $\Delta T = T - T_C$), however, the effect of the correction for total scattering can become finite in the vicinity of T_C ($\Delta T \Rightarrow 0$) due to the divergence [12,13] $I_t(0) \sim (\Delta T)^{-1.24}$. The radius of gyration $R_g(\Delta T)$ of PDMS-d is determined by fitting $S_s(Q)$ to the

Debye function

$$S_D = \frac{2}{y^2}(y - 1 + e^{-y}), \quad y = Q^2 R_g^2. \tag{4}$$

Similarly, the correlation length ξ is obtained from $I_t(Q, x = 1)$ using the Ornstein–Zernike equation

$$I_t(Q) = \frac{I(0)}{1 + Q^2\xi^2}. \tag{5}$$

SANS experiments were carried out on the SANS facility at the Oak Ridge National Laboratory, USA, and KWS1 instrument at the IFF Forschungszentrum, Jülich, Germany. The range of scattering vectors was $0.005 < Q < 0.03\,\text{Å}^{-1}$. The temperature of the samples was controlled to better than ±0.2 and ±0.02 K in Oak Ridge and Jülich experiments, respectively. The critical temperatures of phase demixing of each sample were identified as a sharp maximum in the integral neutron count rate as a function of T. The data were corrected and placed on an absolute scale using standard procedures described elsewhere [14]. The structure factor $S_{s,A}$ was obtained from Eq. (3) and used to calculate R_g of PDMS-d at different temperatures. The correlation length $\xi(T)$ was obtained from Eq. (5).

PDMS-h, PDMS-d (M_W = 19,500 and 4900) and PEMS (M_W = 23,200) were synthesized and characterized at the Max Planck Institut für Polymer Forschung, Germany (courtesy of M. Stamm). PS-d (M_W = 246,000) and PVME (M_W = 196,000) were obtained from Polymer Laboratories (UK) and BASF Ludwigshafen (Germany), respectively. PS-d (M_W = 2620) and PPMS (M_W = 2530 and 37,000) were obtained from PSS-Mainz (Germany). The polydispersity index of all polymers was $M_W/M_N \leq 1.07$ with the only exception: PVME, $M_W/M_N \leq 2.5$. PDMS–PEMS and PS–PPMS blends were homogenized in situ in quartz cells by mechanical stirring at $T > T_C$. PS-d–PVME was prepared by dissolving the components in a common solvent toluene, evaporating the solvent at room temperature, and continuous drying under vacuum.

3. Results and discussion

The temperature variation of R_g and ξ in PDMS–PEMS blends is shown in Fig. 1, where the R_g of PDMS-d remains constant at all temperatures and the average radii, $R_g = 37 \pm 3$ and 20±2 Å agree with the corresponding unperturbed dimensions for PDMS ($R_g \approx 0.27 M_W^{1/2} \approx 34$ Å for M_W = 19,500 and 19 Å for M_W = 4900) [15]. To our knowledge, this is the first experimental determination of the R_g of one of the components of partially miscible polymer blends that confirms the validity of the RPA over a wide range of temperatures *including the critical region of phase demixing*. Our observations correlate well with high-concentration labeling measurements of R_g in miscible ($\chi < 0$) blends of polyethylene oxide and polymethyl methacrylate (PMMA) which reported unperturbed R_g of PMMA chains in the concentration range $0.3 \leq \phi_{PMMA} \leq 0.74$ [16]. At the same time, our results strongly contradict light scattering experiments [17], which revealed ∼200% variation of the chain dimensions above the critical temperature T_C of phase demixing in the blend PDMS-h (ϕ = 0.456)–PEMS. In contrast to the R_g, the correlation length (Fig. 1) varies strongly with temperature, diverging as $T \Rightarrow T_C$ ($\xi \gg R_g$), and leveling off ($\xi/R_g \sim 1.65 \pm 0.05$) for $T \gg T_C$. The observed variation of $\xi(T)/R_g$ in PDMS-d–PEMS blends (Fig. 1) is similar to that found in polymer solutions in poor organic solvents [18], which remain microscopically phase separated ($\xi \geq R_g$) at all temperatures. Similarly, PDMS-d and PEMS do not mix on the molecular level and thus PEMS behaves as a poor polymeric solvent for PDMS-d.

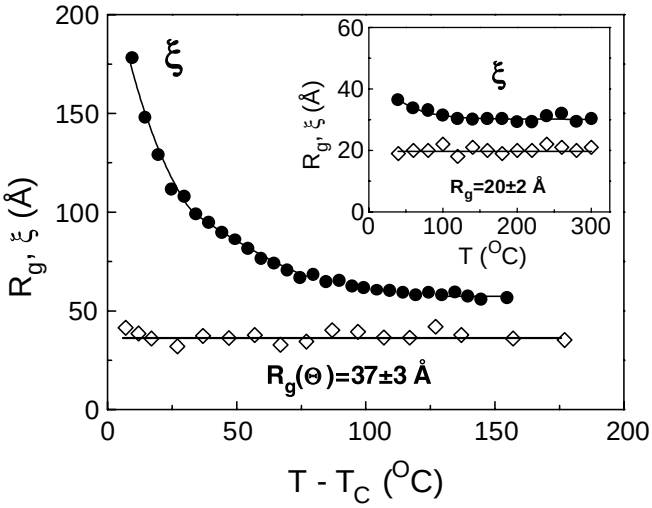

Fig. 1. The radius of gyration and the correlation length of PDMS-d ($M_W = 19{,}500$) and PDMS-d ($M_W = 4900$) (inset) in ((0.1)PDMS-d + (0.9)PDMS-h)–PVME ($M_W = 23{,}000$) blend at the critical concentration of PDMS $\phi = \phi_C = 0.51$ and $\phi = \phi_C = 0.31$, respectively. The figure demonstrates the constancy of R_g and thus validity of the RPA in concentrated polymer blends.

Polymer solutions in poor (non-Θ) solvents are believed to be incapable of reaching the Θ-condition at which the attractive intramolecular interactions are annulled by excluded effects. However, for the Θ-solvents, this condition can be reached at the Flory or Θ temperature at which two competing characteristic lengths (ξ and R_g) are related via: $\xi(\Theta) = R_g(\Theta)/\sqrt{3}$ for non-overlapping chains [12,13,18,19]. Here we extend this relation to polymer blends, which possess an additional characteristic length corresponding to the radius of gyration of the polymeric solvent. Expanding the Debye functions S_A, S_B (Eq. (1)) in the limit $Q \Rightarrow 0$ we obtain for the blend of non-interacting polymers at the Θ temperature ($\chi(T = \Theta) = 0$)

$$\xi_k(\Theta) = \frac{R_{g,k}(\Theta)}{\sqrt{3}}. \tag{6}$$

where $R^2_{g,k}(\Theta) = (1 + k)^{-1}(R^2_{g,A}(\Theta) + kR^2_{g,B}(\Theta))$ and $k = (\phi_A N_A v_A)/(\phi_B N_B v_B)$ is a factor which accounts for the cumulative asymmetry between the volume fraction ϕ, polymerization degree N, the monomer volume v of the polymers. We note that in the strong asymmetry limit ($k \Rightarrow 0, k \Rightarrow \infty$), as well as in the ideal symmetry limit ($k = 1$, $R_{g,A} = R_{g,B}$) the relation $\xi(\Theta) = R_g(\Theta)/\sqrt{3}$ for the Θ polymer solutions (single R_g) is recovered. Furthermore, using the mean field scaling law $\xi = \xi_{mf}\,|\tau|^{-(\nu=0.5)}$, where ξ_{mf} is the "mean field amplitude" with typical values 5/30 Å for polymer solutions and blends and $\tau = |T - T_C|/T$ is the reduced temperature, we obtain the relation between T_C, the amplitude ξ_{mf} and the Θ temperature:

$$\Theta = T_C \left\{ 1 \mp \left[\frac{\xi_{mf}}{\xi_k(\Theta)} \right]^2 \right\}^{-1}. \tag{7}$$

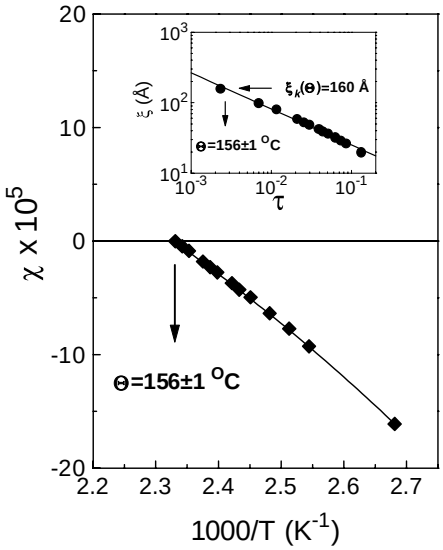

Fig. 2. The interaction parameter χ as a function of temperature for the PS-d ($M_W = 593{,}000$, $\phi = 0.4837$)–PVME ($M_W = 1{,}100{,}000$) (the data from [21]). The inset shows the correlation length ξ as a function of the reduced temperature τ. The Θ temperature of the blend is reached at $156 \pm 1\,^{\circ}$C, when $\chi = 0$ and or $\xi = \xi_k(\Theta) = 160$ Å.

where "−" and "+" correspond to UCST and lower critical solution temperature (LCST) blends, respectively.

We verify the validity of Eq. (7), by using the SANS data on $\xi(T)$ and $\chi(T)$ for LCST blends PS-d–PVME available in the literature [20,21]. As demonstrated in Fig. 2, for the blend PS-d ($M_W = 593{,}000$, $\phi = 0.4837$)–PVME ($M_W = 1{,}100{,}000$) the criteria $\chi = 0$ and $\xi_k(\Theta) = 160$ Å lead to the same lower Θ temperature $\Theta_L = 156 \pm 1\,^{\circ}$C, which confirms the equivalence of both methods for determining the Θ temperature. For the blend PS-d ($M_W = 246{,}000$)–PVME ($M_W = 201{,}000$) at the critical concentration $\phi_{\text{PS-d}} = 0.19$ studied in this work, we obtain from Eq. (7) $\Theta_L \cong 142\,^{\circ}$C, which is consistent with Θ_L values available in the literature as shown in Fig. 3. Similarly, the inset in Fig. 3 shows the upper Θ temperatures (Θ_U) for the UCST blend PS-d–PPMS calculated via Eq. (7) using the parameters ($\phi_{\text{PS-d}} = 0.16$, $T_C = 143\,^{\circ}$C, $\xi_{mf} = 14$ Å), ($\phi_{\text{PS-d}} = 0.31$, $T_C = 62.2\,^{\circ}$C, $\xi_{mf} = 10.4$ Å), ($\phi_{\text{PS-d}} = 0.48$, $T_C = -39.4\,^{\circ}$C, $\xi_{mf} = 6.7$ Å), obtained in this work as well as in our previous studies [22,23]. We note that both Θ_L and Θ_U are independent of N, but vary with the concentration of PS-d due to the perturbation of the segment–segment interactions caused by deuteration [24]. The effect of isotopic substitution is opposite in sign for UCST and LCST blends, respectively, with the former becoming less, and the latter more miscible as a function of $\phi_{\text{PS-d}}$. The magnitude of the effect is also significantly different for entropy-driven (LCST) and enthalpy-driven (UCST) phase demixing.

We believe the data presented in Fig. 3 to be the first demonstration of the existence of the Θ_U and Θ_L lines, which separate poor ($\chi > 0$) and good solvent ($\chi < 0$) domains in the phase diagrams of the LCST and UCST polymer blends. In the good solvent domain ($T < \Theta_L$, $T > \Theta_U$) excluded volume effects tend to expand R_g beyond the unperturbed dimensions. This effect is facilitated in strongly asymmetric blends ($k \Rightarrow 0$ or $k \Rightarrow \infty$), where individual chains of the dilute component are subject to minimal screening

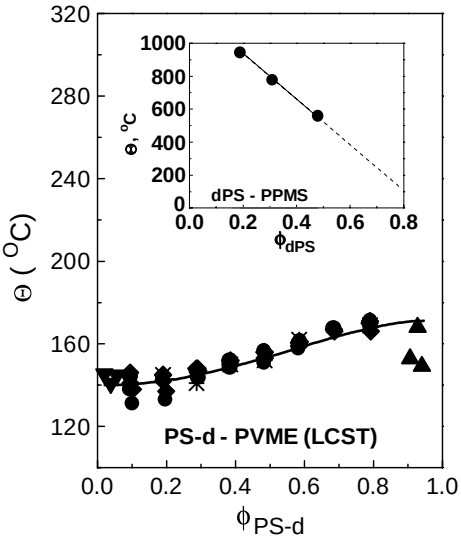

Fig. 3. Θ_L for the LCST blends PS-d–PVME obtained using the condition $\chi = 0$ (✳), [20] and (◆), [21] as well as the condition $\xi = \xi_k(\Theta)$ (●) for the same blends. (▼) and (▲) are Θ_L obtained for the dilute blends in [10,30], respectively. The inset shows Θ_U for the UCST blends PS-d–PPMS.

effects and expand due to a favorable interaction with the good polymeric solvent [9,10]. Conversely, in the poor solvent domain ($T > \Theta_L$, $T < \Theta_U$), the dominating attractive intramolecular interactions between the segments facilitate contraction of the dilute (minority) component [8]. At the same time, the majority species experience predominantly the environment of the same component and thus exhibit the unperturbed dimensions as in polymer melt at both $T \gg \Theta$ and $T \ll \Theta$ [3–7]. The deviation of R_g from unperturbed dimensions $R_g(\Theta)$ in strongly asymmetric blends restricts the applicability of the RPA to the regions shown schematically in the conceptual phase diagram of the UCST and LCST polymer blends (Fig. 4), which summarizes the available experimental observations as well as results of computer simulations.

It has long been appreciated that polymer blends, polymers solutions and binary mixtures of small molecule liquids (ordinary solutions) behave universally in the vicinity of the critical temperature where the diverging fluctuations ($\xi \Rightarrow \infty$) conceal the specific details of structure and intermolecular forces [22,25,26]. Current theories predict [27] that various systems may cross over from universal critical to non-universal mean field behavior in a different way depending on the availability of a specific supramolecular structure with the characteristic length scale ξ_D. The *first type* of crossover (small ξ_D) is controlled by the intermolecular forces and is observed, e.g. in ordinary solutions, where ξ_D corresponds to the molecular sizes (a) and $\xi \geq \xi_D$ even at $T \gg T_C$. The *second type* of crossover (large ξ_D) is defined by the competition between the characteristic length scales ξ and ξ_D and is observed, e.g. in polymer solutions in the Θ solvents where, $\xi \gg \xi_D \equiv R_g$ ($T \sim T_C$) but $\xi \ll R_g$ ($T \gg T_C$) [12,13,18,19]. The demonstration of the Θ points (Fig. 3) and the fact that polymer blends and solutions have the same characteristic length scale $R_{g,k}(\Theta)$ (Eq. (6)) suggests that the crossover in the Θ solvents and blends should be controlled by the ratio $\xi/R_{g,k}(\Theta)$.

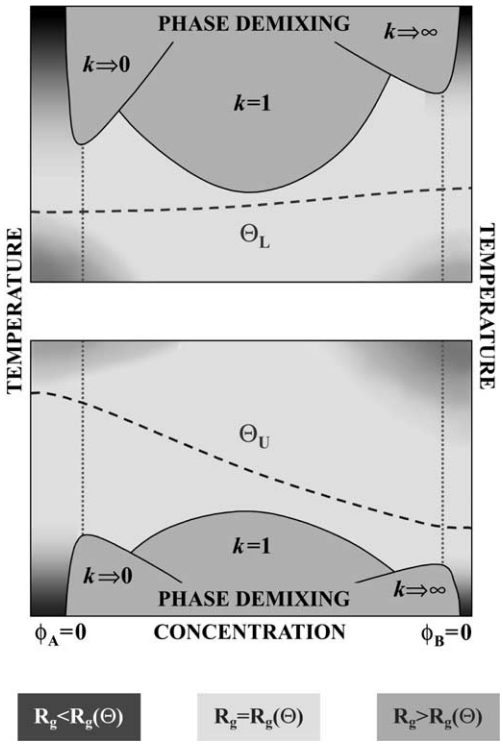

Fig. 4. Generic phase diagram of the UCST and LCST Θ polymer blends (one component deuterated). The vertical dotted lines correspond to the overlap concentration $\phi = \phi^*$ of the dilute polymer component. The RPA is valid in blue domains and breaks down in the strong asymmetry limit (dark blue and reddish domains) due to the swelling or shrinking of the polymer coils of the minority component.

We define the Ginzburg number for the Θ polymer blends as: $\tau_{\mathrm{Gi}} = |T - T_{\mathrm{X}}| / T$, where T_{X} is the crossover temperature at which the condition $\xi(T_{\mathrm{X}}) = R_{\mathrm{g},k}(\Theta)$ is met.[1] The asymptotic scaling law for the correlation length in the critical region $\xi = \xi_{\mathrm{cr}} |\tau|^{-(\nu=0.63)}$ in combination with $R_{\mathrm{g}}(\Theta) \sim N^{0.5}$ gives

$$\tau_{\mathrm{Gi}} = \left[\frac{\xi_{\mathrm{cr}}}{R_{\mathrm{g},k}(\Theta)} \right]^{1/0.63} \sim \langle N \rangle^{n=-0.794}, \tag{8}$$

where the average polymerization degree is [23] $\langle N \rangle = (\phi_{\mathrm{A}}/N_{\mathrm{B}} + \phi_{\mathrm{B}}/N_{\mathrm{A}})^{-1}$. Fig. 5 shows the Ginzburg numbers for the Θ polymer blends PS-d–PPMS and PS-d–PVME calculated using Eq. (8) with ξ_{cr} obtained in this study as well as determined previously [22,23]. As is seen in Fig. 5, the index $n = -0.73 \pm 0.07$ agrees within experimental error with $n = -0.79$ in Eq. (8). The suggested scaling relation for τ_{Gi} brings

[1] Strictly speaking, the crossover temperature T_{X} is uniquely defined only in the limit $k \Rightarrow 0$, $k \Rightarrow \infty$ (polymer solutions) or in the limit $k = 1$ (ideally symmetric polymer blends). For the intermediate values of k the crossover temperature develops into the *crossover interval* $T_{\mathrm{X1}} \leq T_{\mathrm{X}} \leq T_{\mathrm{X2}}$ corresponding to the condition $\xi_1(\Theta) = R_{\mathrm{g},1}(\Theta)/\sqrt{3} \leq \xi \leq \xi_2(\Theta) = R_{\mathrm{g},2}(\Theta)/\sqrt{3}$. The width of the crossover interval $\Delta T = |T_{\mathrm{X1}} - T_{\mathrm{X2}}|$ depends on the mismatch between the radii of gyration (or polymerization degree) of the components. Thus, in general the condition $\xi(T_{\mathrm{X}}) = R_{\mathrm{g},k}(\Theta)$ identifies the center of a broad crossover regime separating temperature ranges where mean field or critical fluctuation behavior is observed [28].

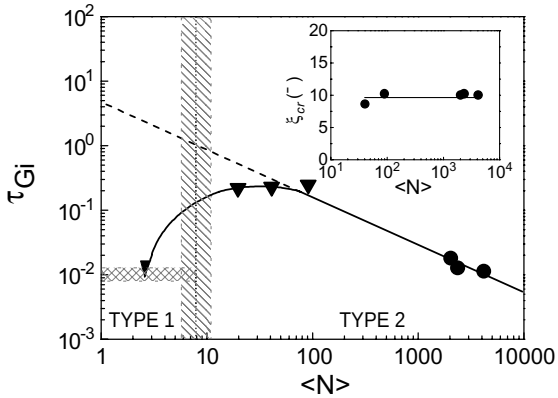

Fig. 5. Variation of the Ginzburg number vs. the average polymerization degree in the Θ polymer blends: (▼) PS-d–PPMS, (●) PS-d–PVME. Solid line corresponds to $n = -0.73 \pm 0.07$. The vertical dashed line ($\langle N \rangle = 8$, $\tau_{\mathrm{Gi}} \sim 1$) separates the ranges of $\langle N \rangle$ where the crossover of type 1 (ordinary solutions with $\tau_{\mathrm{Gi}} \sim 10^{-2}$) and type 2 ($\Theta$ polymer blends with τ_{Gi} described by Eq. (8)) are observed. The inset demonstrates that ξ_{cr} for the Θ blends PS-d–PPMS and PS-d–PVME is independent on $\langle N \rangle$.

the Ginzburg numbers of both UCST and LCST Θ blends on a single scale and describes the variation of τ_{Gi} over more than three orders of magnitude in $\langle N \rangle$.[2] The observed downturn of $\tau_{\mathrm{Gi}}(\langle N \rangle)$ for $\langle N \rangle \leq 40$ is a consequence of the inevitable transition from the crossover of type 2, which is characteristic of the Θ blends with large $\xi_{\mathrm{D}} \equiv R_{\mathrm{g},k}$ ($N \Rightarrow \infty$) to the crossover of type 1, typical for ordinary solutions with small $\xi_{\mathrm{D}} \equiv a$ ($N \Rightarrow 1$) and [27] $\tau_{\mathrm{Gi}} \sim 10^{-2}$. The "mid point" of the transition may be estimated from the condition $\tau_{\mathrm{Gi}} = 1$ (i.e. $\xi_k \cong \xi_{\mathrm{mf}}$) which gives $\langle N \rangle \approx 8$.

4. Conclusions

Our results show that polymer blends reproduce all main features of the temperature–concentration phase diagram [1] of polymers in small molecule organic solvents, along with their structural and thermodynamic behavior in the vicinity of the critical and Θ temperatures. Recently we have demonstrated that the Θ condition may also be induced in mixtures of polymers with supercritical fluids by varying temperature and or pressure [29]. Using the scaling temperature variable, $\tau* = (T - T_{\mathrm{C}})/(\Theta - T_{\mathrm{C}})$, which accounts for the temperature distance from both the Θ temperature and T_{C}, we represent the correlation length of the concentration fluctuations in the scaling form

$$\xi = \xi_k(\Theta)(\tau*)^{\nu*} \tag{9}$$

with the exponent $\nu^* = 0.5$ in the mean field domain ($T \Rightarrow \Theta$, $\tau^* \Rightarrow 1$) and $\nu^* = 0.63$ in the critical region ($T \Rightarrow T_{\mathrm{C}}$, $\tau^* \Rightarrow 1$), and ξ_k defined by Eq. (6). As is seen in Fig. 6, the correlation lengths $\xi/\xi_k(\Theta)$ (see Eq. (6)) of various Θ systems: both LCST and UCST polymer blends, polymer solutions, and mixtures of

[2] In one of the previous studies [23] an attempt was made to determine index n by fitting the data $\tau_{\mathrm{Gi}}(N)$ obtained for blends PS-d–PPMS and PDMS–PEMS. It is no wonder that the authors [23] came up with an unphysical value n ($=-2$) as they were fitting τ_{Gi} obtained for the Q blend PS-d–PPMS and the "poor solvent" type blend PDMS–PEMS, the Ginzburg number in which is governed by different physical reasons.

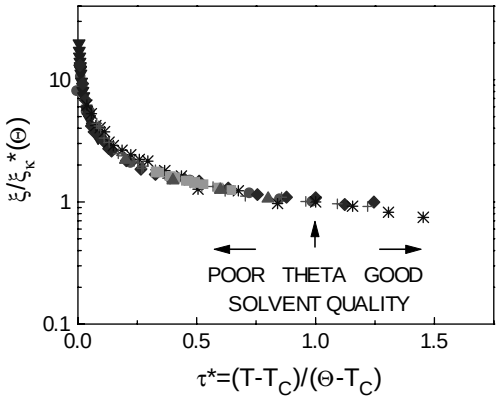

Fig. 6. Master curve for the correlation length in various systems, which exhibit the Θ temperatures in their phase diagrams. (Θ) Polymer blends: (■) PS-d ($M_W = 2620$)–PPMS ($M_W = 2530$) (this work), (▼) PS-d (37,000)–PPMS (2530) [22], (▲) PS-d ($M_W = 402{,}000$)–PVME ($M_W = 210{,}000$) [21]. Polymer solutions: (●) PS ($M_W = 22{,}000$)–methylcyclohexane-d [31], (◆) PDMS ($M_W = 47{,}000$)–bromobenzene-d [32]. Supercritical mixtures [29]: (✳) PDMS ($M_W = 79{,}000$)–supercritical carbon dioxide, (+) PDMS ($M_W = 22{,}000$)–supercritical carbon dioxide [29].

polymers with supercritical fluids collapse on a master curve in the wide range of the molecular weight 2500–400,000, Θ temperature 65–484 °C and the critical temperature −40 to 160 °C. We believe this to be the remarkable demonstration of the universality of the structure and thermodynamic properties of polymer molecules in the Θ polymeric, liquid and supercritical solvents [32].

The occurrence of the lower and upper Θ points as well as their significant variation with the concentration of a deuterated component in polymer blends may provide new insight and interpretation of some of the puzzling phenomena, such as variation of the interaction parameter χ with M_W and composition. The Θ state concept in polymer blends may also be constructive for rationalizing other important issues, e.g. the M_W-dependence of the Ginzburg number in polymer blends and the way they may cross over from the mean field to fluctuation regimes. We hope that this work will stimulate further experimental and theoretical efforts, in order to quantify universal and specific aspects of the polymer behavior in the regions of the phase diagram corresponding to the poor, Θ, and good polymeric solvents [33].

List of symbols

b_d	scattering length of deuterated monomer
b_h	scattering length of protonated monomer
$I_t(Q)$	total scattering intensity
k	asymmetry factor, $k = (\phi_A N_A \nu_A)/(\phi_B N_B \nu_B)$
M_W	weight average molecular weight
N	polymerization degree
Q	scattering vector
R_g	radius of gyration
S_D	Debye structure factor
S_s	single-chain structure factor
S_t	total structure factor

ΔT temperature deviation from the critical temperature, $\Delta T = |T - T_C|$
T_C critical temperature of phase demixing
T_X crossover temperature
v monomer volume
x mole fraction of deuterated polymer

Greek letters
θ scattering angle
Θ Flory or theta temperature
λ wave length
ν critical index of the correlation length
ξ correlation length of the concentration fluctuations
ξ_D supramolecular characteristic length
τ reduced temperature, $\tau = |T - T_C|/T$
τ_{Gi} Ginzburg number
τ^* de Gennes' reduced temperature, $\tau^* = (T - T_C)/(\Theta - T_C)$
ϕ_C critical concentration
χ Flory–Huggins interaction parameter

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