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Self-Concentration and Interfacial Fluctuation Effects on the Local Segmental Dynamics of Nanostructured Diblock Copolymer Melts

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Even simple A−B diblock copolymers display a rich phase diagram in terms of various morphologies created upon spontaneous self-assembly into A- and B-block rich domains in the nanometer range. These ordered structures display a broad range of symmetries ranging from spherical, cylindrical, lamellar, to bicontinuous geometries.[1,2] For block copolymers with asymmetry, i.e., when the fraction of the A block, f_A, is low, highly curved surfaces are favored, leading to a variety of cylindrical micelles in hexagonal lattices or spherical micellar-like structure ordered in body/face centered cubic (bcc/fcc) lattices where the chains are effectively confined in two or three dimensions, respectively. By using more symmetric block copolymers, confinement in one dimension can be realized in a lamellar structure. This gives an interesting "dimensional" flexibility in the study of the confinement effects. In addition, very importantly, the effective confining "wall" can be varied selectively from *soft* to *hard* by using respectively a majority polymer block having a low or high glass transition temperature, T_g.

From a fundamental point of view it is interesting to understand how the component dynamics is affected in such segregated blend systems. This has been relatively little investigated in the past where previous studies have been mostly related to the more global mobility of the chains in self-diffusion experiments.[3,4] In contrast, the local structural α-relaxation associated with the glass transition has received much less attention. On the other hand, in miscible polymer blends, the α-relaxation has been a rather hot topic over the past years[5] where issues such as confinement,[6,7] self-concentration effects,[8−11] and thermally driven concentration fluctuations[12] have been extensively discussed. It is unclear, however, how or whether such effects will play a role on nanosegregated block copolymer melts.

A very useful technique in this respect is broad-band dielectric spectroscopy (BDS). This technique is particularly useful for polymers having a net dipole moment associated with the end-to-end vector such as poly(isoprene) (PI) with high cis-1,4 microstructure content. In this case both the global end-to-end chain orientation dynamics and the segmental α-relaxation[13] can be resolved simultaneously. So far for block copolymers, this technique has mainly been exploited in lamellar symmetric PI−poly(styrene) (PI−PS)[15−17] and poly(styrene)−poly(dimethylsiloxane) (PS−PDMS)[18] diblock copolymer in temperature ranges where the PS dynamics is effectively frozen and constitute a "hard" confinement of the PI or PDMS chains ($T < T_g^{PS}$), respectively. Here a strong slowing down and broadening of the normal mode relaxation have been found whereas only a slight effect has been detected for the α-relaxation. This has been interpreted as a combined effect of spatial confinement and change in configurational statistics.[15] On the other hand, in a neutron spin-echo study[19] of a lamellar diblock system an acceleration of the dynamics was observed and attributed to interfacial fluctuations. A dielectric study of PS−PI−PS triblock copolymer confined in a lamellar structure has also shown indirectly, via the dielectric strength, $\Delta\epsilon$, of the normal mode, that the phase boundaries are subject to fluctuations.[20]

In this communication we present a model for the α-relaxation in mesoscopically structured spherical and cylindrical diblock copolymer melts showing that the response relative to the homopolymer precursor can be quantitatively accounted for by considering chain connectivity (self-concentration) and interfacial fluctuation effects. The model has been applied to three highly asymmetric PI−PDMS diblock copolymers having a constant composition $f_{PI} \approx 0.16-0.18$ but different molecular weight. This system has a large dynamical contrast in terms of the glass transition temperature, $T_g^{PI} \approx 207$ K and $T_g^{PDMS} \approx 147$ K. A strong broadening and acceleration of both the normal mode and the local α-relaxation are found. We demonstrate that both the broadening and the shift of the α-relaxation can be quantitatively described by applying the model. Furthermore, this model allows obtaining detailed structural information about the interface which is not readily accessible even with highly sensitive scattering techniques.

Three model PI−PDMS block copolymers were prepared by anionic polymerization for the purpose: PI4−PDMS23, PI6−PDMS31, and PI9−PDMS50 (the numbers indicate the approximate molecular weight in kg/mol) (cis-1,4 content about 65%). As references, the actual precursor PI homopolymers for the diblocks were separated and individually characterized. The mesoscopical morphology of the diblock melts was characterized by SAXS using a Bruker AXS Nanostar instrument. The results show a hexagonally ordered cylindrical shape for the lowest molecular weight sample, PI4−PDMS23, while a somehow disordered crystal face-centered cubic (fcc) or body-centered cubic (bcc) like structure was found for the higher molecular weight. Details concerning synthesis and structure will be published in detail at a later stage and are here given as Supporting Information. The relevant information is given in Table 1. The complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ vs frequency was measured in a broad frequency range using a Novocontrol high-resolution dielectric analyzer (Alpha-S analyzer). The temperature was limited in the range 233−323 K in order to avoid effects from crystallization of PDMS (210−230 K) and chemical changes of PI. In a recent study,[21] we have found that the dielectric strength of PDMS is about 0.6. Even if this value is comparable to that of PI, the relaxation time of PDMS in the temperature range considered here is between 10^{-10} and 10^{-12} s, i.e., completely out of the current experimental window (10^{-6}−100 s). Hence, the dynamics of PI is strongly decoupled from that of PDMS and thereby can be independently analyzed. The central results from broad-band dielectric spectroscopy (BDS) are given in Figure 1. Here the full frequency dependence of the dielectric loss permittivity,

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Table 1. Characteristic Synthetical, Structural, and Dielectrical Properties of the Investigated Polymers

	$M_n^{PI\ a}$/g/mol	$M_n^{PDMS\ a}$/g/mol	f_{PI}^{b}	$\bar{N}^{c}$	phase[d]	R_c/Å	σ	$\Delta\epsilon_{HP}^{e}$	$\Delta\epsilon_{DB}^{e}$
PI4−PDMS23	4330	23 400	0.16	382	hexcyl	50	23 ± 4	0.188 ± 0.05	0.230 ± 0.05
PI6−PDMS31	6510	31 400	0.18	523	fcc/bcc	100	22 ± 5	0.196 ± 0.04	0.204 ± 0.05
PI9−PDMS50	9410	49 500	0.17	811	bcc	125	16 ± 3	0.194 ± 0.05	0.220 ± 0.06

[a] The polydispersity is about 1.02−1.04 and is given in detail in the Supporting Information. [b] Volume fraction based on the densities $d_{PI} = 0.91$ g/cm^3 and $d_{PDMS} = 0.97$ g/cm^3. [c] Total mean number of monomer units based on the average segmental volume, $\bar{v} = 75.6$ cm^3/mol. [d] Denotes the type of morphology: hexcyl = hexagonally ordered cylinders, fcc = spherically ordered face-centered cubic structure, and bcc = body-centered cubic structures. [e] Total dielectric strength of the homopolymer (HP) and diblock copolymer (DB) as determined from the fits.

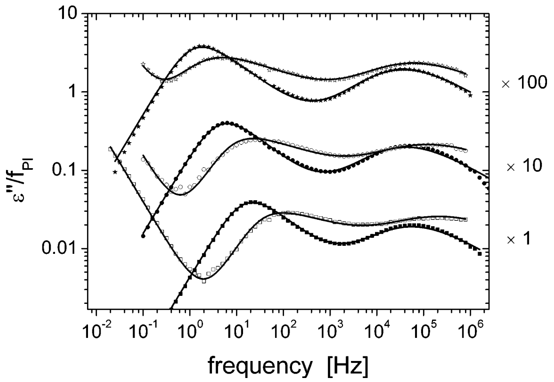

Figure 1. Dielectric loss permittivity as a function of frequency of the three diblock copolymer systems (open symbols) and the corresponding homopolymer references (filled symbols) at 243.15 K. Note that the data have been normalized to the volume fraction of PI (f_{PI}) and shifted by a constant factor: 1 (squares, PI4/PI4−PDMS23); 10 (circles, PI6/PI6−PDMS31); 100 (stars, PI9/PI9−PDMS50). The solid lines display fits to the models described in the text.

ϵ'', is given for each block copolymer and the corresponding precursor PI homopolymer at 243 K. Note that ϵ'' has been normalized to the actual volume fraction of PI, f_{PI}.

As seen, the spectra of the homopolymer display the typical feature of a well-defined peak at low frequencies manifesting the relaxation of the end-to-end vector (normal mode) and then at higher frequencies a broader relaxation characteristic of the more local structural α-relaxation. It is also worth remarking that the normal mode displays a strong shift toward lower frequencies with increasing molecular weight, M, reflecting the end-to-end vector relaxation which strongly depends on M as predicted by global Rouse/reptation like dynamics.[13] On the other hand, the α-relaxation does not change with molecular weight reflecting the fact that this process is sensitive only to the local scale.

Now comparing with the corresponding response from the block copolymer, we see that a general feature is a speed-up and a strong broadening of, surprisingly, both the normal mode process and the local segmental α-relaxation. This feature prevails at all temperatures investigated. It is natural to consider that such effects can be provoked by fluctuations of the interface between the nanosegregated PI and PDMS rich phases. This would lead to some degree of intermixing of the polymer segments of different kinds and consequently a modified effective heterogeneous local environment. Another possible effect that in principle could influence the dynamics is geometrical confinement (finite size effects). However, taking into account the relatively large size of the systems investigated (10−30 nm in diameter) as well as the results reported in recent literature (see, e.g., ref 14), we do not expect confinement effects to play an important role in the segmental dynamics of PI.

The effect of intermixing in immiscible polymer systems is in fact predicted from the theory of Helfand and Tagami (H−T) by the following density distribution function along the interface of a planar A/B polymer interface,[22] which we for a curved geometry write as

$$\phi(r) = 1/2[1 + \tanh((R_c - r)/\sigma)] \qquad (1)$$

where r is the distance from the center, R_c is the mean radius of the sphere/cylinder, and σ is the half-width of the interface related to the interaction parameter, χ, which in the H−T theory takes the form

$$\sigma_{HT} = 2\sqrt{\frac{{b_{PI}}^2 + {b_{PDMS}}^2}{12\chi}} \qquad (2)$$

where $b_{PI} = 6.4$ Å and $b_{PDMS} = 5.6$ Å are the respective Kuhn lengths and $\chi = 0.175$ in this case.[25] Inserting these values, we arrive at $\sigma_{HT} \approx 11$ Å, which indeed is on the order of length scales of which the α-relaxation should be affected and also implies that a significant portion of PI experiences some contact with PDMS segments. It should be noted that a later extension of this theory corrects for finite size effects and for the connectivity of the blocks and predicts[23] $w = w_{HT}(1 + 1.34/(\chi N))$, which gives corrected values between 13 and 12 Å from the lowest to highest molecular weight, respectively. In addition, classical capillary wave fluctuation theory would predict an additional broadening of the interface caused by random stochastic fluctuations. The mean-square amplitude of such a fluctuation can be calculated according to $\sigma_{CW}^2 \approx k_BT/(4\pi\gamma)\ \ln[l_{max}^2/l_{min}^2]$, where γ is the interfacial tension and $l_{min} = \sigma_{HT}$ and $l_{max} = R_c$ are the cutoff length scales.[24] Inserting the values of γ for the PI /PDMS two-phase homopolymer ($\gamma = 3.4$ mN/m)[25] system, we obtain values in the range of 5−7 Å. However, by using the values of the PI/PDMS system mixed with a PI−PDMS diblock copolymer with similar molecular weight ($\gamma = 0.5$ mN/m),[25] we obtain significantly larger values: 14−18 Å.

With these ideas in mind, we seek a quantitative model of the α-relaxation which will be an important ingredient to understand the characteristic of the more global dynamics, including the normal mode process. This will be subject of a future investigation.

Following the recent discussions of the dynamics of miscible polymer blends,[5] we can employ the ideas of self-concentration[8−10] and compositional concentration fluctuation effects.[12] The former concept states that since the α-relaxation is sensitive only to the local scale of some few nanometers, the effective concentration around the segment of one component is always greater than the bulk average value because of chain connectivity. In this case it is natural to consider the self-concentration modulated by interfacial fluctuations dictated by the mesoscopic density profile, $\phi(r)$, and the morphology of the system, giving a total local effective concentration:

$$\phi_{eff}(r) = \phi_{self} + (1 - \phi_{self})\phi(r) \qquad (3)$$

where $\phi_{\rm self}$ is the self-concentration of PI, which we take to be the value originally calculated by Lodge−McLeish: $\phi_{\rm self} = 0.45$.[9] The different concentration would imply different mobilities which can be accounted for by a effective Vogel temperature, $T_0^{\rm eff}(r)$, and can be calculated according to a simple Flory−Fox mixing rule of the pure components $T_0^{\rm PI}$ and $T_0^{\rm PDMS}$:[10]

$$1/T_0^{\rm eff}(r) = \phi_{\rm eff}(r)/T_0^{\rm PI} + (1 - \phi_{\rm eff}(r))/T_0^{\rm PDMS} \qquad (4)$$

where $T_0^{\rm PI}$ and $T_0^{\rm PDMS}$ are the Vogel temperatures of the pure components. The Vogel−Fulcher−Tamman equation then takes the form

$$\tau(r) = \tau_0 \exp(B/(T - T_0^{\rm eff}(r))) \qquad (5)$$

where the shortest time in the systems, τ_0, and the characteristic parameter, B, are taken as the values of the pure PI homopolymer component.

In this way the dielectric contribution of the α-process of the PI segments can be obtained from eqs 3−5 and integrating over the density profile, $\phi(r)$:

$$\epsilon(\omega)''_\alpha = \int_0^\infty C(r) HN(\omega,\tau(r))^{\rm HP} \phi(r)\,{\rm d}r \Big/ \int_0^\infty C(r)\phi(r)\,{\rm d}r \qquad (6)$$

where $C(r) = 2\pi r$ and $C(r) = 4\pi r^2$ are the usual geometrical factors for the volume element of cylinders and spheres, respectively. The general Havriliak−Negami function, $HN(\omega)$, is given by[13]

$$HN(\omega) = {\rm Im}\,\frac{-1}{(1 + (i\omega\tau)^\beta)^\gamma} \qquad (7)$$

where β and γ are the symmetrical and asymmetrical broadening parameters, respectively. In eq 6 they are assumed to be those of the pure PI precursor homopolymer. In order to model the whole dielectric spectrum, we chose to describe the homopolymer with a sum of two Havriliak−Negami functions characterizing the two relaxation contributions in addition to a general conductivity term:

$$\epsilon(\omega)'' = \Delta\epsilon[f_\alpha HN_\alpha(\omega) + (1 - f_\alpha) HN_N(\omega)] + C\omega^{-1} \qquad (8)$$

where f_α and $(1 - f_\alpha)$ are the fractions of the α and normal mode contributing to the total dielectric strength $\Delta\epsilon$.

As seen in Figure 1, this approach could fit the data of the homopolymer very effectively by setting the conductivity terms $C = 0$, $\beta_{\rm N}^{\rm HP} \approx 1$, and $\gamma_{\rm N}^{\rm HP} \approx 0.5$ for the normal mode relaxation and $\beta_\alpha \approx 0.64$ and $\gamma_\alpha \approx 0.57$ for the α-process.

In the analysis of the diblock copolymer blends used the following approach: while the HN function for the normal mode and a conductivity term was set as free, the α-relaxation contribution was calculated from eq 6 and inserted into eq 8 to replace $HN_\alpha(\omega)$. In the analysis, f_α was set fixed and equal to the homopolymer case, and all parameters describing the pure phases, $T_0^{\rm PDMS} = 130$ K, $T_0^{\rm PI} \approx 165$ K, $\phi_{\rm self} = 0.45$, τ_0, and B, were held fixed. In addition to the HN parameters of the normal mode relaxation, only $\Delta\epsilon$ and the width of the interface σ were allowed to vary.

As seen in Figure 1, this approach accounts for the data impressively well giving values of σ in the range of 16−23 Å. The corresponding radial density profiles extracted from the fits are given in Figure 2.

As seen from the plot, the interfacial region constitutes a significant portion of the chain environment, especially for the lowest molecular weight where PI chains experience a rather heterogeneous environment. We might speculate that the rather unexpected formation of cylinders for PI4−PDMS31 could be explained by large fluctuations—a feature which beyond the standard SCMFT (self-consistent mean field theory) approach. At this composition SCMFT predicts a spherical phase irrespective of the total molecular weight.[1,2]

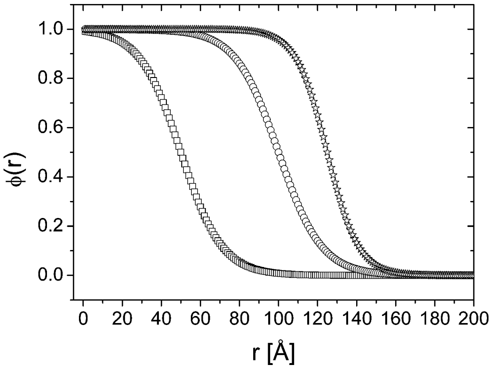

Figure 2. Extracted radial density profile calculated using the experimentally determined w from BDS and $R_{\rm c}$ from SAXS: PI4−PDMS23 (squares, $\sigma = 23$ Å, $R_{\rm c} = 50$ Å); PI6−PDMS31 (circles, $\sigma = 22$ Å, $R_{\rm c} = 100$ Å); PI9−PDMS50 (stars, $\sigma = 16$ Å, $R_{\rm c} = 125$ Å).

Concerning the σ values extracted from the fits (16−23 Å), the interfacial width is significantly bigger than the thermodynamical (HT) estimation alone (11−13 Å). As already mentioned above, this can be anticipated as the interfaces also are bound to fluctuate. Using the interfacial tension of the diblock copolymer to calculate $\sigma_{\rm CW}$ as discussed above and a Gaussian summation rule, we obtain $\sigma \approx (\sigma_{\rm CW}^2 + \sigma_{\rm HT}^2)^{1/2} = 19$−22 Å, which compares well with the experimental data. Nevertheless, we remark that the above calculation is strictly valid only for planar surfaces. In addition, we note that there are model assumptions that may influence the quantitative results, namely the Flory−Fox equation (eq 4), the constant value taken for the self-concentration, and the use of the Vogel−Fulcher parameters from the pure polymers. However, given the excellent consistency of the fits, further possible refinements will not be discussed at this point.

Finally, we comment on the acceleration of the normal mode which generally follow the same trend as the α-relaxation although the broadening is more pronounced as a high-frequency wing. It is clear that this can at least partly be explained by a change in the local environment also responsible for the strong effect on the α-process. A naive calculation using the average values of the monomeric friction coefficients of each component should give a factor of 2 faster dynamics, which is much smaller than observed (12−7) although a decrease and tendency in the shift factor toward 2 is seen at higher temperatures. However, at this point it is not clear how the interface dynamics itself will affect the chain motion which needs to be resolved in a more detailed experiment. We therefore leave this rather delicate issue as a future problem.

Summarizing, we have developed a simple structural model based on self-concentration considerations and finite interface density profiles in order to quantitatively describe the dielectric α-relaxation of diblock copolymers confined in mesoscopically structured phases. It is encouraging to see that BDS can give detailed structural information, such as interfacial widths, which generally is very difficult to obtain even from highly sensitive scattering techniques.

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Supporting Information Available: Details of synthesis and characterization of polymers as well as the structural SAXS results. This material is available free of charge via the Internet at http://pubs.acs.org.

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