Correlation of Static and Dynamic Inhomogeneities in Polymer Mixtures: A Computer Simulation of Polyisoprene and Polystyrene

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ABSTRACT: Atomistic simulations of mixtures of oligomers of polyisoprene and polystyrene were performed over a range of compositions and temperatures. The influence of mixing on structure and dynamics was investigated. Increasing polystyrene concentration slows down the dynamics considerably. The inhomogeneities in the dynamics are correlated with the local neighborhood of segments. A local surplus of polystyrene leads to a slower than average local dynamics and vice versa. Static and dynamic inhomogeneities are correlated on the segment level. The local length scale to influence the dynamics is on the order of 0.8−1 nm. Moreover, we find strong end effects on the dynamics of both components.

I. Introduction

The dynamics of polymer mixtures is still some matter of debate, despite the many efforts devoted to solve this problem using experimental,[1−9] theoretical,[10] and computational[11−17] approaches. The problem becomes very apparent if the glass transition temperature of the constituents is distinctly different as is the case in binary mixtures of polystyrene and polyisoprene which will be the focus of this contribution. In the temperature range between the respective glass transitions or not too far above the higher glass transition temperature, the pure systems behave very differently. It is not clear whether individual chains at intermediate temperatures behave similarly to their dynamics in their pure environment or whether there is an average dynamics of the mixture. NMR experiments tend to support a strong difference in the dynamics of the constituents,[18−21] including a recent study on styrene−isoprene block copolymers.[22] However, there is an additional possibility that every individual chain or even segment has its own dynamics which can be influenced by a number of factors, including its chemical identity, the position along the chain-end segments are much more mobile than central segments, and additionally the local neighborhood.

It has been suggested that the inhomogeneities in the statics, i.e., the local concentration, are correlated with inhomogeneities in the dynamics, i.e., segmental relaxation times of individual segments.[8−10] Recently, Lodge and McLeish proposed a model that additionally bases on the effect of self-concentration;[10] every segment in a mixture of homopolymers has on average a neighborhood enriched in segments of the same type. This just stems from chain connectivity. There has been quite an experimental effort undertaken to substantiate this model, and the majority of results are supportive.[18−20,22] However, experimentally it is impossible to identify the dynamics of individual segments or elucidate the influence of the local neighborhood. In detailed computer simulations this is possible, and the present contribution performs this task for mixtures of polyisoprene with polystyrene. This mixture has been studied by dielectric spectroscopy[6,7] where mainly the phase behavior was addressed. For the short chain lengths to be discussed in the following, we can expect the system to be miscible at the temperatures under study. One experiment found a slow component in the dynamics of polyisoprene in the neighborhood of polystyrene.[6]

A recent simulation study of a model mixture of constituents only differing in dynamics showed that even with identical statical properties of the constituents the local neighborhood is relevant.[14] In that simulation the monomers of the different species differ only by their mass; still, the mixture behavior is not a linear combination of the pure systems.

II. Simulation Methods and Models

Mixtures of *cis*-1,4,-polyisoprene with isotactic as well as atactic polystyrene have been simulated by molecular dynamics using the YASP simulation package.[24] The polyisoprene simulation model comes from earlier simulations of *trans*-1,4,-polyisoprene[25−27] where only the stereochemistry at the double bond is changed from trans to cis. All other force-field parameters were directly transferred. The model is in detail described in refs 25 and 27 and therefore not repeated here. The polystyrene model was taken from a work on swelling of polystyrene in benzene[28] without further refinement. As the polystyrene model carries partial charges, a reaction field[29] for the electrostatic interactions was applied where the dielectric constant was set to $\epsilon_{RF} = 2.5$ irrespective of concentration. Monodisperse samples with 15 monomers per chain were simulated corresponding to molecular weights of 1.022 kg/mol for polyisoprene and 1.562 kg/mol for polystyrene. The time step in the simulation was 1 fs, except for the systems with at least 50% polystyrene at high temperature of 450 or 500 K where it was lowered to 0.5 fs. The systems containing isotactic polystyrene were started at densities about 60% of the expected density and then run at 500 K until the density was equilibrated. Then the temperature was ramped down to 300 K in 500 ps, except for the pure PS which was ramped in 1 ns. Afterward, a second equilibration period followed to allow density and energies to settle. The bond lengths were constrained using SHAKE.[30,31]

For the atactic polystyrene samples six different random stereochemistries were developed. The probability of meso-dyads in any position was 50%. All

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Table 1. Densities of Polyisoprene−Polystyrene Mixtures at Different Densities and for Different Stereochemistries of Polystyrene[a]

concn PI (%)	$\rho(I,300\text{ K})$	$\rho(I,500\text{ K})$	$\rho(I,380\text{ K})$	$\rho(I,450\text{ K})$	$\rho(A,450\text{ K})$
100	919	752		796	
80	947	800	899	842	842
66.7	967	829			873
50	(985)	867			908
33.3	1002	895			935
20	1008	921			957
0	1016	947		969	

[a] Except for the last column the data are for a mixture containing isotactic polystyrene (*I*); *A* denotes a mixture containing atactic polystyrene. Errors are on the order of 1%. Data in parentheses are not completely reliable.

simulations contain integer multiples of six polystyrene chains, so the stereochemistry was repeated as necessary; e.g., a system containing 24 PS chains contains four sets of the six different stereochemistries. The systems at 300 and 500 K have an isotactic polystyrene component, and at 450 K atactic PS was used; these systems were set up at 450 K at about 60% of the expected density and equilibrated until density and energies did not change any more. This latter system was chosen as experiments on a directly comparable mixture are under way.[32]

Seven different concentrations including the two pure polymers were simulated. The pure systems contain 48 chains each; the mixed systems contain 24 chains of the majority component and 6 or 12 chains of the minority component. The equimolar mixture contains 24 chains of either species. This corresponds to molar concentrations of 0%, 20%, 33.3%, 50%, 66.7%, 80%, and 100% of PI or PS, respectively. One of the concentrations (20% PS−80% PI) was chosen to investigate the influence of temperature, so simulations at 300, 380, 450, and 500 K were performed using isotactic PS.

The box lengths for the different systems turned out to be in the range of 3−5 nm depending on the number of chains. The different box lengths were coupled independently to ambient pressure (101.3 kPa) using the weak-coupling technique.[33,34] Also, temperature was controlled using this method. The correlation times are $\tau_t = 0.2$ ps for temperature and $\tau_p = 20$ ps for pressure.

We have to note that, unlike recent simulations on large-scale polyolefin mixtures using a united atom model,[17] we are not able to estimate the Flory−Huggins parameter ξ in this study. To that end, simulations on a much larger scale and longer times would be necessary. Additionally, we did not specifically optimize the unlike interactions but used Lorentz−Berthelot mixing rules.[29] This may affect the miscibility behavior. We are not aware of any studies calculating a Flory−Huggins parameter for an all-atom model.

III. Results

A. Statics and Thermodynamics. Before discussing the structure and dynamics of the mixture in detail, we have a look at the most easily accessible thermodynamic property, the density. It rises with increasing polystyrene concentration (cf. Table 1). The experimental density of 16-mers of polyisoprene at 298 K is 899 kg/m^3.[35] This shows that our PI model overestimates the density by only 1.6%. It is interesting to note that the stereochemistry for PI does not have an influence as 10-mers of *trans*-PI have the same density.[25] Experimental values for atactic PS at 413 K are 968 kg/m^3 and for isotactic PS at 523 K 897 kg/m^3.[35] These data are for chain lengths of 19.5 kg/mol and as they are at different temperatures it is difficult to compare. The comparison shows that we overestimate the PS density by less than 5% (comparing the simulation data at 500 K with the experimental data of 523 K). Assuming a constant thermal expansion coefficient, the extrapolated simulation value at 523 K arrives at 937 kg/m^3, which is 4% higher than in the experiments. Still, our densities are closer to experimental data than other simulations on pure polystyrene,[36] as most earlier work on polystyrene was performed in united-atom models.[37,38] To the best of our knowledge, detailed mixture simulations of this system have not yet been performed. Comparing data at 450 K and 80% PI, we do not find a difference in density using atactic or isotactic polystyrene. During cooldown from 500 to 300 K in the initial runs a clear change in slope of density with temperature has been seen for all PS dominated samples (not shown). This indicates the systems becoming glassy. The glass transition temperature of a pure polystyrene system in this molecular weight range is around 320 K.[39,40] With the limited range of temperatures simulated it is difficult to compare this to our results. The density data of Table 1 are converted to specific volumes and shown in Figure 1 for the pure constituents.

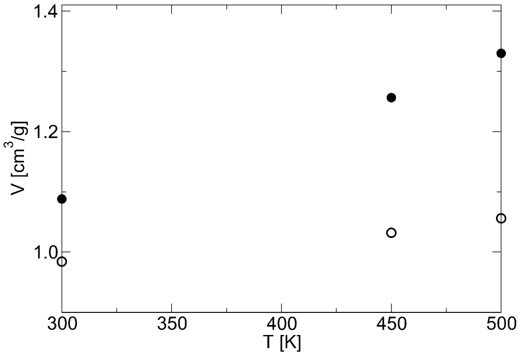

Figure 1. Specific volume of the pure components PI (filled circles) and PS (open circles) for the temperatures considered.

To elucidate the local structure, we recorded radial distribution functions of the mixtures. We restrict ourselves to systems including atactic polystyrene at 450 K. At this relatively high temperature we find very good equilibration. The simulations have been running for at least 2 ns each after the initial equilibration. Figure 2 shows partial radial distribution functions for concentrations of 20% PI, 50% PI, and 80% PI at given conditions. Subfigure a shows that the two chain types do not mix perfectly on the very local scale. There is a self-concentration effect visible. At close range the two types of chains are avoiding each other. Especially the polystyrene chains tend to cluster with each other (subfigure c). The different concentrations have only a weak influence on the structure of the mixture. We see at distance larger than 1.5 nm that the local fluctuations are averaged out. This means that any influence of local neighborhoods on the dynamics has to be on length scales of a few angstroms. The strong shoulders which dominate the self-radial distribution functions of the minority components at 20% concentration between 0.5 and 1.5 nm is due to the small number of chains. Here the self-concentration is over-proportionally important, as any given chain alone is a substantial fraction of the small overall system. For statistical reasons the interac-

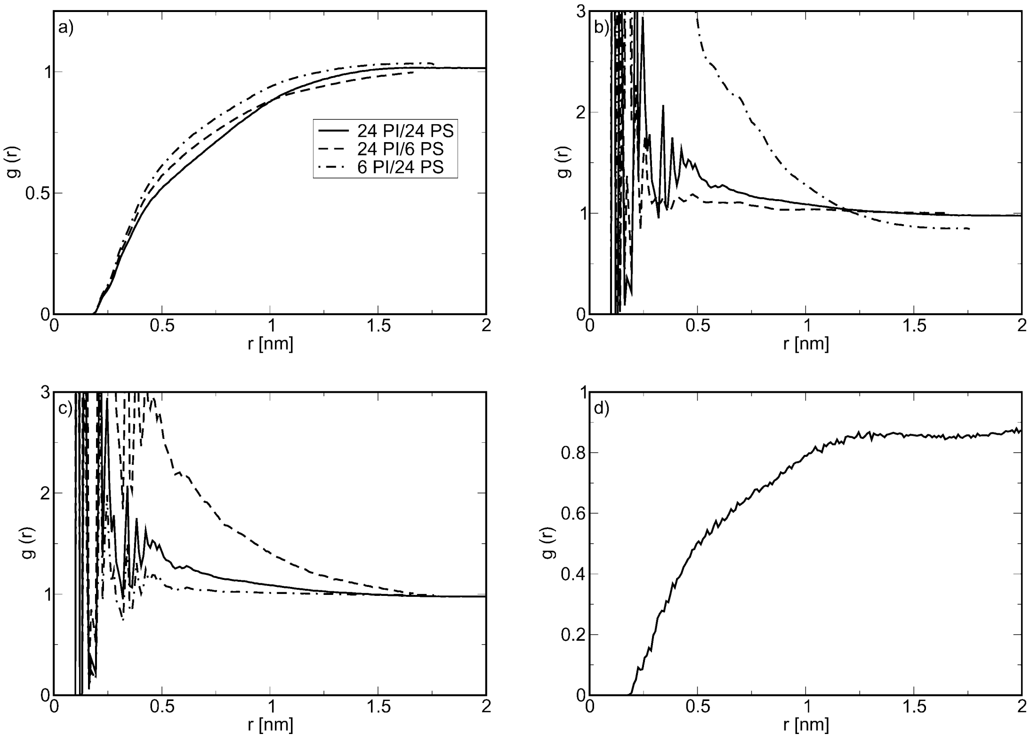

Figure 2. Partial radial distribution functions at 450 K for mixtures of atactic polystyrene in *cis*-polyisoprene. The legend of (a) applies to (b) and (c) as well. (a) Partial radial distribution function of PI with PS (b), PI with PI (c), PS with PS, and (d) PI with PI in 6 PI/24 PS where the pairs along the same chain are excluded. In (b) and (c) the local bonding peaks are not shown completely.

tions along the same chain have not been taken out. We clearly see bond peaks at very short distances. In subfigure d we show the partial radial distribution function of polyisoprene with itself in the system where there are only six PI chains. Here pairs along the same chain are not counted, the statistical error is quite high, but we still see a slight first neighbor peak at around 1.2 nm. This is not a self-concentration effect but depends on the mixing behavior. These results are in line with experiments suggesting that the blend is homogeneous on the length scales of the PI chains and weakly segregated on the monomer scale.[7] In atomistic simulations we cannot expect phase separation to occur due to the involved time scales.

B. Dynamics. The dynamics of polymers in the melt can be classified as global and segmental dynamics. Global dynamics includes the diffusion coefficient of whole chains as well as their reorientation. The diffusion of the chains cannot be reliably measured in simulations of the present length as the mean-square displacement of the center of mass is about 0.1 nm^2/ns (cf. Figure 4a), which is small compared to the end-to-end distance ($\langle\sqrt{\vec{R}^2_{\mathrm{e-e}}}\rangle_{\mathrm{PI}} = 1.57$ nm, $\langle\sqrt{\vec{R}^2_{\mathrm{e-e}}}\rangle_{\mathrm{PS}} = 1.86$ nm) or the box dimensions which are between 3 and 5 nm. Local or segmental dynamics can be characterized by reorientation of local vectors in the chain. All reorientation functions we will discuss are autocorrelation functions of second Legendre polynomials of the underlying vectors. They are defined as

$$C_2(t) = \langle P_2(\alpha(t))\rangle = \langle 0.5(3[\hat{u}(t)\ \hat{u}(0)]^2 - 1)\rangle \qquad (1)$$

with $\hat{u}$ being a unit vector. Averages are taken over all corresponding vectors and applying a running time average. The second Legendre polynomial is chosen because the integral over this correlation function relates to NMR experiments.[41] For global reorientation $\hat{u}$ is the direction of the end-to-end vector. For segmental dynamics it is the direction of the vector connecting the atoms we are interested in. The local vectors used in this work for polyisoprene and polystyrene are highlighted in Figure 3. End-to-end vectors are defined as vectors connecting the terminal carbons of the chains. We again restrict ourselves to the study of mixtures with atactic polystyrene at 450 K. Moreover, as the simulations become increasingly sluggish with increasing polystyrene concentration, systems with PS as majority component have not been analyzed for dynamic purposes.

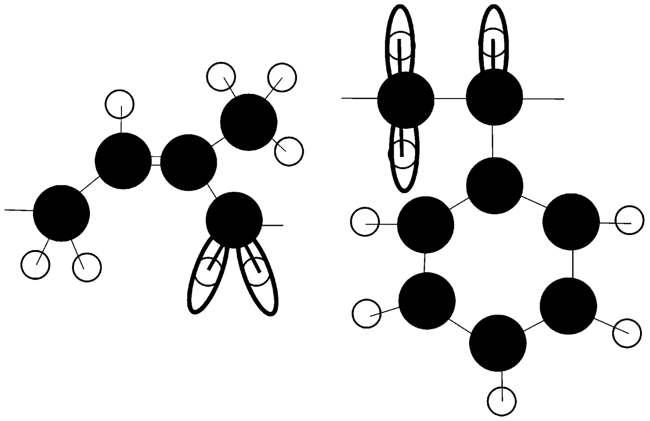

Figure 3. Monomers of *cis*-polyisoprene and of polystyrene. The vectors highlighted by a strong oval outline are used for calculation of segmental dynamics. Carbons are depicted as filled circles and hydrogens as smaller open circles.

Figure 4b shows reorientation correlation functions of the equimolar system (which is the slowest to be considered here). The correlation times of the local and global dynamics are found in Table 2. The global dynamics of polystyrene has not been elucidated as it is too slow for a simulation on the order of 3−5 ns.

Table 2. Reorientation of Local Segments of Polyisoprene and Polystyrene and Global Reorientation of Polyisoprene[a]

concn PI [%]	$A_{\mathrm{PI,loc}}$	$\tau_{\mathrm{PI,loc}}$ [ps]	$A_{\mathrm{PI,glob}}$	$\tau_{\mathrm{PI,glob}}$ [ps]	$A_{\mathrm{PS,loc}}$	$\tau_{\mathrm{PS,loc}}$[ps]	$\tau_{\mathrm{PI,loc}}$ [ps]	$\tau_{\mathrm{PI,glob}}$ [ps]	$\tau_{\mathrm{PS,loc}}$[ps]
100	0.30	56	0.60	529			21	340	
80	0.29	97	0.50	1153	0.47	1060	34	617 (1000)	632 (500)
66.7	0.32	138	0.71	1500	0.69	1191	49	1313 (1000)	983 (1000)
50	0.25	289	0.74	1810	0.68	1772	83	2200 (500)	1620 (600)

[a] The last three columns are results of a fit of the form $A\exp(-t/\tau)$ to the data. The remaining columns are data gained by numerical integration, if the numerical integration had to be extended by a fitting of the tail the time (in ps) up to which the numerical integration was performed is in parentheses. The errors for the local polyisoprene times are less than 5%; for polystyrene and the global reorientation of polyisoprene the errors are estimated around 20%.

Table 3. Definition of the Classifications Used To Determine the Radial Distribution Functions[a]

class PI (50−50)	t_{I} [ps]	$C_{\mathrm{I,min}}$	$C_{\mathrm{I,max}}$	class PS	t_{I} [ps]	$C_{\mathrm{I,min}}$	$C_{\mathrm{I,max}}$	class PI (pure)	t_{I} [ps]	$C_{\mathrm{I,min}}$	$C_{\mathrm{I,max}}$
very fast	50	0.0	0.08	very fast	500	0	0.15	very fast	50	0.0	0.08
fast	50	0.08	0.45	fast	500	0.15	0.75	fast	50	0.08	0.3
normal				normal				normal			
slow	250	0.2	0.5	slow	1000	0.8	0.92	slow	250	0.07	0.3
very slow	250	0.5	1	very slow	1000	0.92	1.0	very slow	250	0.3	1

[a] The "normal" category is defined as neither of the other. If due to noise in the function a correlation function matches formally the "fast" and "slow" class, it is assigned to the "fast" class.

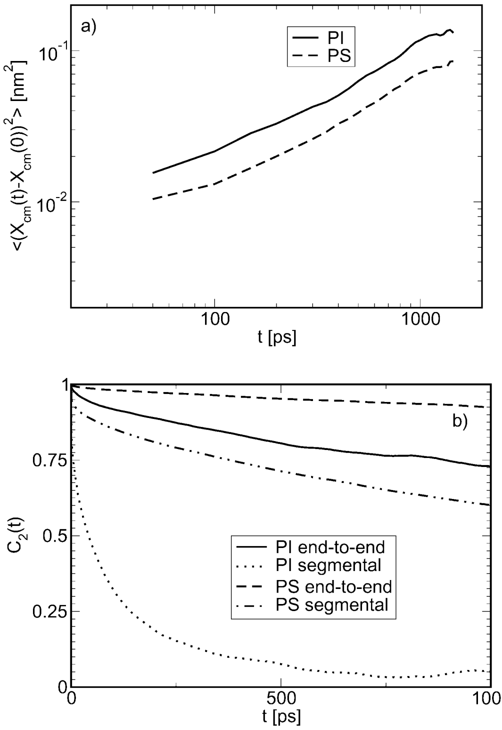

Figure 4. (a) Center-of-mass mean-square displacements and (b) global and segmental reorientation correlation functions for an equimolar system of polyisoprene and polystyrene at 450 K.

Reorientation times have been measured by numerical integration as well as by exponential fits. For large correlation times a pure numerical integration was impossible; only the initial decay was integrated numerically and the tail of the function was fitted exponentially, and this fit was integrated analytically.

For the segmental dynamics we see a two-stage process: an initial nonexponential decay and second exponential process at larger times. Any atom−atom vector can only relax until the connection to the chain backbone becomes relevant. For PI as well as for PS the local vectors we investigate connect backbone carbons to nearby hydrogens so that we can expect that these vectors, which are directly measurable in NMR experiments, truthfully represent the motion of chain segments. For polyisoprene the prefactor of the exponential, which is an inverse measure of the efficiency of the local process, is substantially lower than for polystyrene showing that the hydrogens in polystyrene have less local freedom. It is evident that PI has a much faster dynamics than PS irrespective of concentration. Increasing PS concentration leads to an overall slowdown of both components. Compared to experiments, we overestimate the slowing effect of polystyrene some degree.[32] The direct and detailed comparison to experimental data will be the topic of a subsequent publication.

C. Correlation between Local Statics and Dynamics. To understand the influence of the local surroundings on the dynamics of polymer segments, we correlate the statics with the dynamics. To this end, we focus on the equimolar system at 450 K containing atactic polystyrene. For this system we calculated all individual reorientation correlation functions for the C−H vectors described above, i.e., 720 correlation functions for either species. For PS only two of the three possible vectors per monomer were used. Then the PI and the PS vectors were classified into five classes: very fast, fast, normal, slow, and very slow. A reorientation correlation $C_2(t)$ is classified into a class I if the value at a given time t_{I} falls in a window $C_{\mathrm{I,min}} < C_2(t_{\mathrm{I}}) < C_{\mathrm{I,max}}$. Classifications involving correlation times were not possible due to the noise in the individual functions. The values for t_{I}, $C_{\mathrm{I,min}}$, and $C_{\mathrm{I,max}}$ for the individual classes are found in Table 3. The classes have been designated such that the slow, normal, and fast classes contain about about one-third of the vectors and very fast and very slow contain the slowest or fastest 3−5%. Then, partial radial distribution functions of the C−H pairs with all the PI or PS atoms in the system are calculated, and these distribution functions are averaged over the corresponding classes. This way, we can determine the average concentration of polyisoprene or polystyrene segments close to the segment under study. Because of the simulation length (2 ns), we did not consider vectors changing their dynamic class, which will be relevant on larger time scales. We find for the slow and very slow components a local increase of PS neighborhood and for the fast parts a PI dominated neighborhood. This shows that the individual neighborhood in the melt has an influence on the local dynamics behavior.

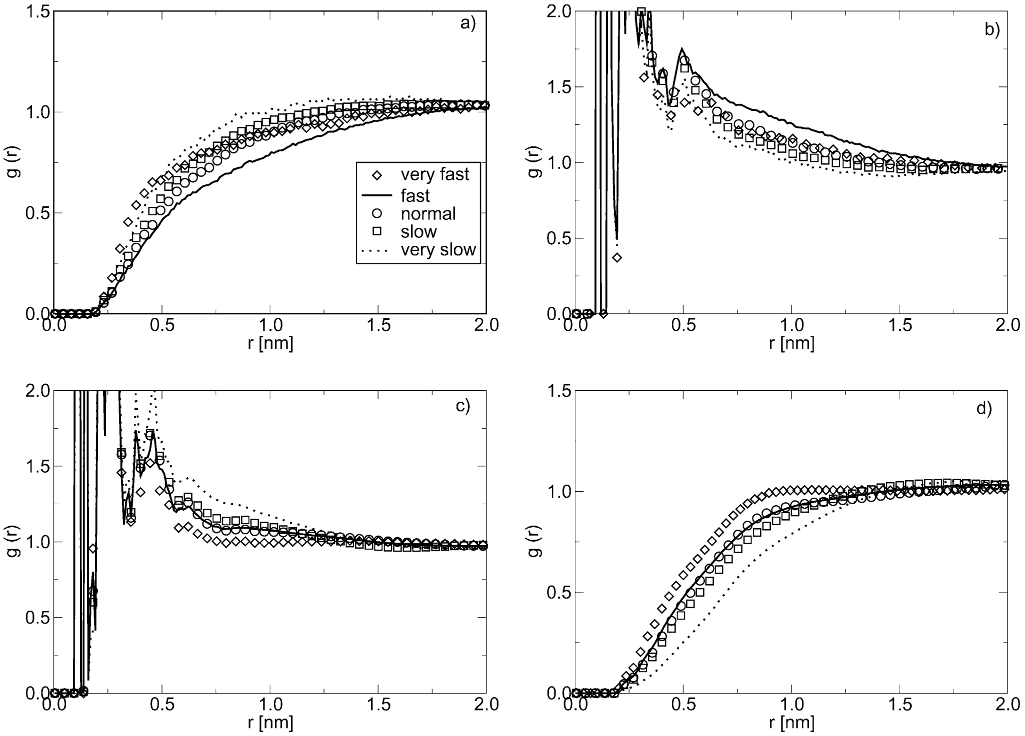

Figure 5. Partial radial distribution functions of the segments classified according to their dynamics: (a) PI segments with PS chains; (b) PI segments with PI chains; (c) PS segments with PS chains; (d) PS segments with PI chains The legend of (a) applies in all subfigures.

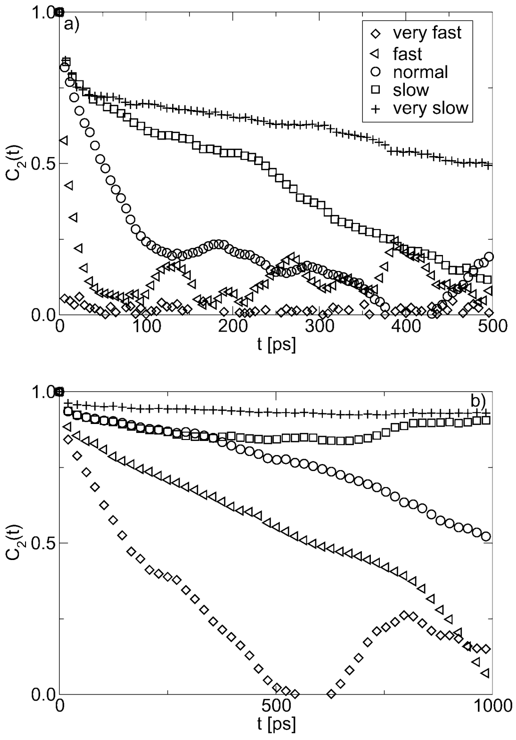

Figure 6. Exemplary segmental correlation functions which are designated to the five classes: (a) PI segment; (b) PS segments. The legend of (a) applies in both subfigures.

Figure 5 shows the results of the partial radial distribution functions, and Figure 6 shows for the different classes examples of the reorientation correlation functions. There is a clear distinction between fast and slow vectors. In the case of polystyrene chains the local environment is increasingly richer in polyisoprene chains with increasing mobility. It is noteworthy that for PS the average and the slow chains are almost indistinguishable. For polyisoprene segments the correlation of mobility and neighborhood is also evident. However, the fastest polyisoprene segments behave very peculiar. At very close distance these have a surplus of polystyrene in their neighborhood, and only at larger distances they behave similar to the fast class. It is not clear what triggers this effect; it may be connected to the fact that the very fast segments are mostly chain ends (see below), and chain ends are less prone to self-concentration than center segments. The local neighborhoods, which influence the dynamics of a segment, are in the region between 0.5 and 1.3 nm apart from the actual segment with the largest discrepancies at around 0.8 nm. This is the length scale of about 2−3 monomers, which is consistent with the Lodge/McLeish idea of the Kuhn length being the characteristic length scale for the dynamics. However, self-concentration alone cannot explain the wide variety of behaviors.

Figure 6 shows examples of segmental correlation functions in the different classes. Especially for PI we find dynamical inhomogeneities spanning around 2 orders of magnitude. The fastest polystyrene segments are about as mobile as the slowest polyisoprene segments. These results support the conclusion of early dielectric experiments which found a slow isoprene component in styrene-rich neighborhoods.[6]

It is clear that the neighborhood is not the only influence on the dynamics of a chain segment. Segments at the end of a chain are regularly faster than their counterparts in the chain center. Figure 7 shows the influence of the position along the chain on the dynamics of the individual segments in the equimolar mixture. Monomers number 1 and 15 are the end monomers. For both polymer species we find a marked influence of the position along the chain. Segments that are faster than average tend to be close to the end, and segments that are slower than average tend to be in the center. To

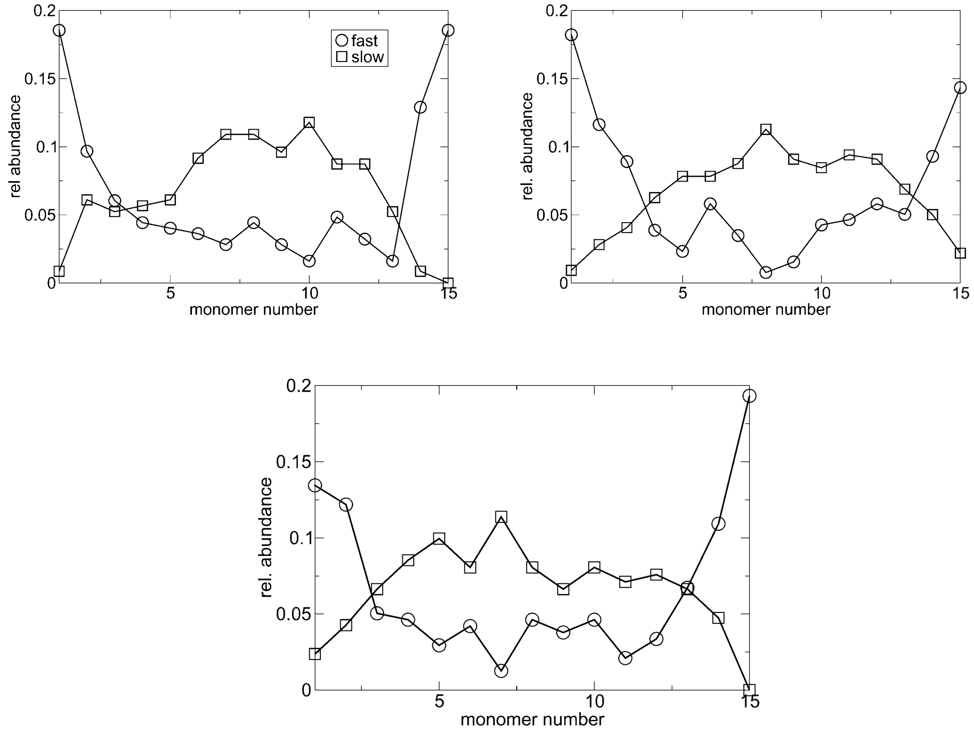

Figure 7. Influence of the position along the chain on the dynamics. The fast and slow in these figures include the fast and very fast classes, or slow and very slow classes, respectively. Upper left: polyisoprene in the 50:50 mixture. Upper right: polystyrene in the 50:50 mixture. Lower: pure polyisoprene.

estimate the relative importance of the different effects, we additionally analyzed the distribution of fast and slow segments in pure polyisoprene. To this end, the definition of the classes had to be adapted as the pure PI chains are clearly faster than the PI chains in the mixture (see right-hand columns in Table 3). The distribution is not very different from the PI in the mixture, but we see from the definition of the classes that both the fast and slow classes are slowed down in the presence of polystyrene. This end effect does not contradict the influence of the local neighborhood; it is a second effect, which must not be forgotten.

An additional question which we want to address is whether fast and slow segments cluster on fast or slow chains. To do so, we define the speed of a chain as the number of fast or very fast segments minus the number of slower than normal segments. Note that this definition is not connected to any dynamical property on the global scale; the speed of a chain is defined by the average of local segments. To be able to compare polystyrene and polyisoprene, we use two vectors per monomer in both cases. Consequently, chain speeds range from −30 to 30. In Figure 8 we see that most chains have a speed around 0, which means that either they are dominated by normal segments or the effects of fast and slow segments cancel. Polyisoprene chains appear to be slightly faster than polystyrene chains, but this stems from the fact that the different classes are not exactly the same size. As a matter of fact, the fast class is slightly larger than the slow class for PI, and the converse is true for PS. As there are only 24 chains of either type, it is difficult to judge the distribution, but we do not find any hint that there is clustering of fast or slow segments along chains.

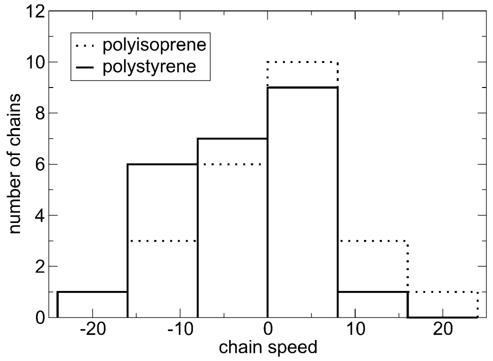

Figure 8. Histograms of (locally) fast and slow chains. The speed of a chain is the number of fast segments minus the number of slow segments. Note that here every monomer corresponds to two segments.

IV. Summary and Discussion

Our results clearly indicate a correlation of static and dynamic inhomogeneities in polymer melt mixtures consisting of chains with strongly different local dynamics. A local surplus of polyisoprene segments in the neighborhood tends to speed up a segment, and a local surplus of polystyrene segments tends to slow it down. This is true irrespective of polymer type. The dynamics of individual segments of the same chemistry can vary by 2 orders of magnitude. This very strong dynamic heterogeneity even leads to the effect that the fastest PS segments are as fast as the slowest PI segments in an equimolar mixture. These effects are on the segment level; we cannot find evidence for fast or slow chain segments clustering on certain chains. We see a self-concentration effect which is differently pronounced for fast and slow segments. The overall dynamics is slowed down by increasing polystyrene concentration.

Additionally the dynamics is strongly influenced by chain end effects. In chains of length 15 difficult it is difficult to extrapolate to the dynamics of long chains. Nonetheless, we could identify the position along the chain and the local neighborhood on the order of 1 nm as factors influencing the individual segmental dynamics.

Our results are in line with all the experiments on this system we are aware of. To understand these phenomena to greater extent, more local scale experiments would be necessary.

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