Molecular Dynamics Simulation of Nanoscale Distribution and Mobility of Water and Dimethylmethylphosphonate in Sulfonated Polystyrene

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The interest in a better understanding of the specific interactions of phosphor−organic compounds and water with sulfonated polystyrene (sPS) is motivated by the use of block copolymers as protective membranes against chemical warfare agents. Using classical molecular dynamics simulations, we explored the nanoscale segregation and diffusion of water and nerve gas simulant dimethylmethylphosphonate (DMMP) in sPS neutralized with calcium counterions at different sulfonation and hydration levels. The water content was varied from 15 to 54% of dry polymer weight, and the DMMP content was varied from 0 to 100 wt %. We found that, in the 40% sulfonated polystyrene, water forms well defined aggregates, which grow in size as the hydration increases, reaching ∼20 Å at the maximum water content. In the 100% sulfonated polystyrene, the overall structure of hydrated polymer is more uniform with smaller water aggregates. Diffusion of water at the same number of water molecules per sulfonate group is faster at a lower sulfonation level. The solvation of sPS in water−DMMP binary mixtures was found to differ substantially from Nafion, where DMMP forms a layer between the hydropholic and hydrophobic subphases. In sPS with divalent Ca^{2+} counterions, DMMP and water compete for the solvation of the sulfonate group. At high water and DMMP contents, the diffusion of DMMP turned out to be rather fast with a diffusion coefficient of ca. 30% of that of water. At the same time, water diffusion slows down as the DMMP concentration increases. This observation suggests that although sPS is permeable for both solvents, water and DMMP are partially segregated on the scale of 1−2 nm and have different pathways through the system. The nonuniform nanoscale distribution of water and DMMP in sPS is confirmed by analyses of different pair correlation functions. This feature may significantly affect the perm-selective properties of sPS-contained block copolymer membranes.

I. Introduction

The need for novel polymeric protective materials calls for a better understanding of the interactions of toxic industrial compounds and chemical warfare agents, in particular phosphoorganic compounds, with sulfonated polyelectrolyte membranes (PEMs), which are considered the most promising candidate materials for practical applications. Indeed, the protective membrane should work as a molecular sieve letting through water and blocking toxic compounds, which are soluble in water. This apparent contradiction may be resolved by using PEM composed of hydrophobic and hydrophilic (sulfonated) blocks, which self-assemble upon solvation, forming a perm-selective network of nanoscale hydrophilic channels. Typical examples of such perm-selective membranes are perfluorinated ionomers, such as Nafion, and block copolymers, such as sulfonated styrene−olefin triblock copolymers. Most experimental and simulation studies of sorption and diffusion of water and other chemicals in PEM concentrated on Nafion type membranes (reviews can be found in refs 1−3). It is established that hydrated Nafion undergoes a nanoscale segregation into a hydrophilic subphase formed by water, sulfonate side chains, and counterions and a hydrophobic subphase formed by the fluorocarbon backbone.[1]

This work focuses on sulfonated styrene−olefin block copolymers, in which the hydrophilic blocks are formed by

sulfonated polystyrene (sPS). The membrane hydrophilicity depends on the degree of sulfonation. The hydrophobic blocks can be represented by various polyolefins, such as polyethylene (PE), polypropylene (PP), polyisobutene (PIBL), and polybutadiene (PBD), as well as by quasi-random copolymers (PE−PBD, PE−PP, PE−PIBL, PE−PBD−PS). Block copolymers, including block ionomers,[4] tend to segregate into a variety of regular (such as cubic, hexagonal, lamellae, etc.) and irregular morphologies determined by the block length and solvent composition. In particular, distinct hexagonal and lamellae morphologies were observed in "parental" (nonsulfonated) polystyrene−polyolefin diblock and triblock copolymers.[5,6] Reports on nanoscale segregation of sulfonated triblock copolymers are scarce and sometimes conflicting. Kim et al.[5] reported a strong segregation in the sPS−(PE−PB)−PS copolymer system. Segregation was also concluded by Rivin and Schneider, who studied various sulfonated triblock copolymers with different block lengths and middle block composition.[7] Mauritz et al.[8] and Xu et al.[9] also observed segregation in sulfonated triblock copolymers. However, in their AFM study of the structure of triblock copolymers, Gromadzki et al.[10] observed uniform structures in sulfonated PE−PS diblock copolymers. Spherical micellar formations were observed at high hydration and referred to the regions with high concentration of sulfonic acid groups. It also remains unclear whether the hydrophilic subphase is homogeneous or segregated within itself. We are not aware of any direct investigations into this particular matter. Numerous papers report water sorption and diffusion in sPS of different sulfonation levels, mostly in

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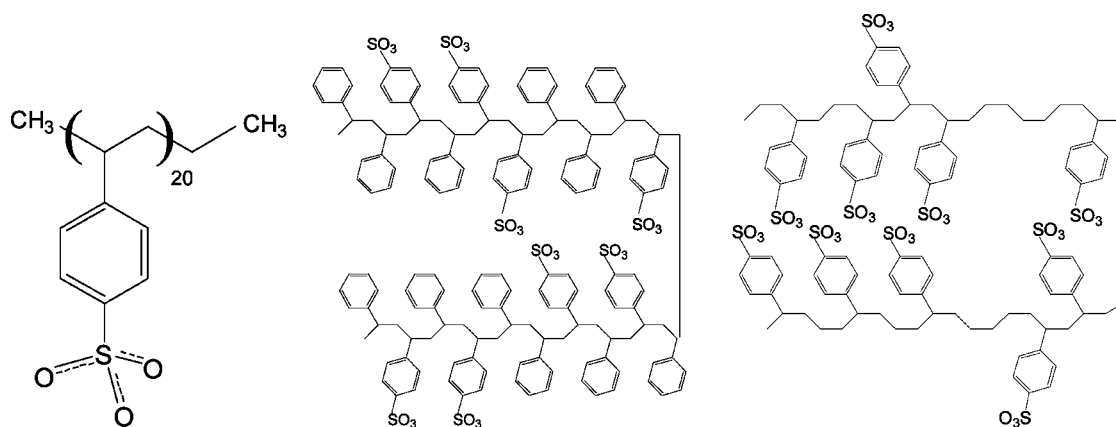
Figure 1. Polymer models used in this work: (left) 100% sulfonated polystyrene fragment; (middle) 40% sulfonated polystyrene fragment; (right) pseudorandom sulfonated ethylene–styrene copolymer fragment.

the acid form.[9,11–16] It was established that sPS acid becomes soluble in large quantities of water if the sulfonation level (that is, the ratio of the number of sulfonate groups to the number of benzene rings) exceeds 27%.[7] Water sorption in the polymer increases sharply with the sulfonation, reaching 350 wt % of the dry polymer weight for 100% sulfonated PS (one sulfonate group per phenyl ring). Different samples show significant variations in water sorption and diffusion coefficient, exhibiting dependence of the structure of the procedure of synthesis.

Even less information is available on cation substituted sPS and sPS–polyolefin block copolymers, which are of a greater interest for the protection-related applications. Schneider and Rivin[7] measured sorption and diffusion of water and DMMP in triblock copolymer membranes where the sPS endblocks were separated by hydrophobic blocks composed of polyisobutene, ethylene–butadiene, and ethylene–styrene pseudorandom co-polymers with H^+, Cs^+, and Ca^{2+} counterions. Sorption and diffusion of both water and DMMP in cation modified samples turned out to be lower than that in the acid form of the co-polymers. DMMP sorption and diffusion was strongly enhanced by sulfonation (PS only adsorbs 8 wt % DMMP under ambient conditions, while for 100% sulfonated PS, DMMP sorption reaches several hundred wt %) and the activity of water, though this tendency was not as pronounced as in Nafion membranes.[7] Molecular modeling studies of cation substituted sPS are also very limited. Hydration and water diffusion in water soluble sulfonated aromatic dendrimers grafted onto different backbone polymers including polystyrene was recently modeled by Jang and Goddard.[17] This system is somewhat similar to sPS in terms of functional groups present but differs substantially in skeleton structure and hydrophobicity. The authors considered large (7–8 nm) systems and analyzed polymer structuring and water diffusion in the hydrated polymers. The structure analysis showed inhomogeneity at the scale of about 20–35 Å. The mobility of water in sPS dendrimers was lower than that in Nafion at the same water content.

In this work, using molecular dynamics (MD) simulations, we explore the mechanisms of sorption and diffusion of water and DMMP in sPS of 40 and 100% sulfonation and in a pseudorandom copolymer of sPS and PE. Section II describes the systems and simulation details, and in sections III and IV, we analyze the local microstructure and diffusion, respectively.

II. Systems and Simulation Details

Sulfonated polystyrene was represented by short fragments (oligomers) of tactic PS composed of 20 monomers with some

of them sulfonated in the *para* position. These fragments were described in detail in ref 3. We studied sPS samples at two sulfonation levels, 100% sulfonation (sulfonate groups were attached to all phenyl rings) and 40% sulfonation, with only 8 sulfonate groups per 20 phenyls (Figure 1, left and middle), as well as one sample of random sPS–PE copolymer depicted in Figure 1 (right). The counterion was Ca^{2+} modeled as a charged Lennard-Jones sphere.[18]

The simulation procedure was similar to that employed in our previous works:[3,19,20] the oligomers, counterions, and solvent molecules were placed in a cubic box at very low density. Then, the system was gradually contracted in the course of constant pressure MD simulation performed at a pressure of $P = 100$ atm and temperature of $T = 303$ K (maintained by a simple velocity scaling). After the density of 0.9 g/cm³ was reached, the simulation proceeded at $P = 1$ atm and $T = 303$ K maintained with the Nose–Hoover thermostat.[21,22] System equilibration proceeded for 2 ns followed by an additional 3.8–6 ns of MD simulation, over which the system configuration was periodically saved to disk for further analyses. It is worth noting that, while the MC insertion of solvent molecules into the polymer matrix would be the best approach to mimic the experimental conditions of solvent sorption, a low probability of insertions into a dense glassy polymer makes this approach computationally expensive. The method of gradual contraction of the system in NPT MD simulation that we applied represents a reasonable approach to obtain configurations close to the equilibrium. During NPT MD simulation runs, we monitored the segregation process computing the variations of energy and volume, as well as the number of contacts between water oxy-gens. It appeared that the segregation structure did not change appreciably after the first 2 ps of the NPT MD trajectory.

The simulations of Nafion and other electrolytes published in the literature suggest that the time scale of several picoseconds is reasonable to study the segregation and self-diffusion of the solvents[17,23–25] in essentially static polymeric matrix. The effects of thermal fluctuations of the hydrophilic subphase on the solvent diffusion, that is, formation and break-up of bridges between hydrophilic aggregates over the simulation course found in our earlier work,[23] cannot be evaluated in this work due to the unsufficient length and time scales.

For sPS fragments, we employed the second-order classical forcefield constructed by us in ref 3. It is based on the TRAPPE forcefield of Wick et al.[26] with parameters for sulfonate groups fitted to the results of RHF/DFT minimization.[3] Water was presented by a rigid SPC/E model,[27] and the forcefield for

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DMMP was published in ref 28. The Newton equations of motion were integrated using the standard Verlet algorithm with a time step of 0.5 fs during the system contraction and 2 fs afterward for slow forces and a 0.2 fs time step for fast-fluctuating forces.[29] Long-range electrostatic forces were calculated using the Ewald summation.

III. Nanostructure and Water Dynamics in sPS: Dependence on the Hydration Level

The specifics of nanostructure formation and water dynamics of hydrated sPS with 40% sulfonation was studied by varying the water content from 15 to 54 wt % to the dry polymer weight. The limit of 54% was derived from the experimental data on water sorption in DAIS sulfonated PS−(PE−PB)−PS triblock copolymer membranes with the same counterion, assuming that water sorption in the hydrophobic phase is negligible.[7] In the case of sPS, 54 wt % water content would correspond to water humidity of 90% at room temperature, which is close to the membrane working conditions.

Since Nafion is a standard reference system for comparisons in experiments and simulation alike, it makes sense to evaluate the relative volumes of the hydrophilic and hydrophobic phases in sPS and Nafion. A water content of 15−54 wt % corresponds approximately to 3−11 water molecules per sulfonate group, which is also typical for cation modified Nafion membranes. However, the relative volume of the hydrophilic subphase is much larger than in Nafion of the equivalent weight of 1200 D, because the volume occupied by the skeleton fragment containing one sulfonate group in sPS at 40% sulfonation is nearly 2 times smaller than the monomer volume of Nafion. This factor may cause a substantial shift in the morphological and transport properties of sPS compared to Nafion and other perfluorinated systems, which were considered in previously published simulations (see ref 3 and references therein).

Another feature specific to this simulation work is the divalent counterion Ca^{2+}, which may significantly affect the system structure as compared with an alkali metal counterion, since two sulfonate groups are needed to neutralize one ion of calcium. Figure 2a shows radial distribution functions between the sulfur atoms in hydrated sPS at different hydration levels. At all hydration levels, these RDFs show distinct correlations at distances up to 15 Å. These correlations are similar at all hydration levels, although the relative significance of different peaks is altered as the hydration increases.

The correlations reveal the existence of typical patterns of mutual arrangements of sulfonate groups in the hydrated polymer. The intramolecular RDFs for the same systems are displayed in Figure 2b. The intramolecular RDF is the probability distribution of finding two atoms i and j of the same molecule at a certain distance from each other, while the *overall* RDF is the local concentration of atoms i at a certain distance r from atom j (not necessarily belonging to the same molecule as atom i) related to the average concentration of atoms i. Noteworthy, the peaks for the total and intramolecular RDFs do not coincide. Therefore, the typical patterns of the sulfonate group arrangement are not caused by the predominant conformations of the individual polymer chains but rather by mutual arrangements of different chains. The first peak of the overall RDFs at about 4.6 Å may correspond only to a configuration with two neighboring sulfonate groups neutralized by one counterion. As the hydration increases, these configurations lose importance, and this peak of the RDF disappears. In the other typical configuration, two sulfonate groups are located at the opposite sides of the same counterion, which is thus surrounded
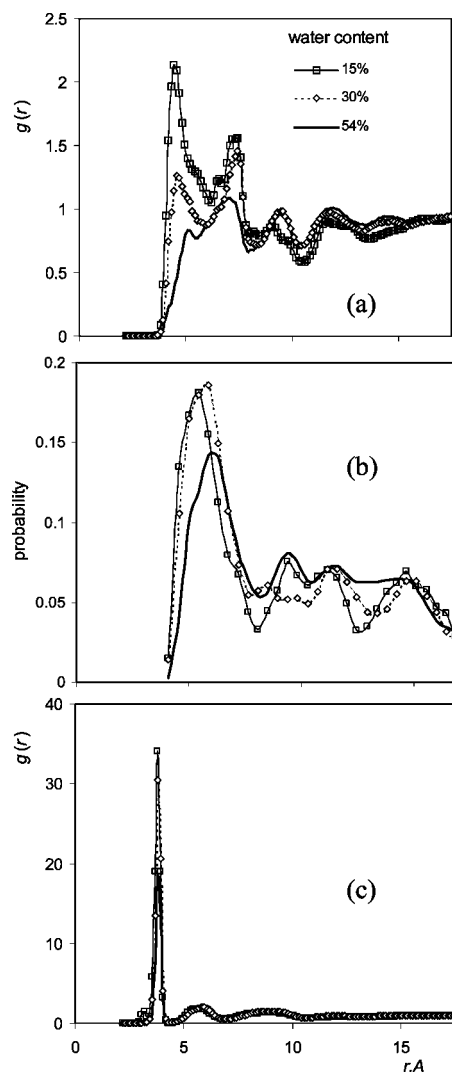
Figure 2. Radial distribution functions in hydrated sulfonated polystyrene at 40% sulfonation: (a) RDF between sPS sulfur atoms; (b) intramolecular sulfur−sulfur RDF; (c) sulfur−calcuim RDF. Different curves correspond to different hydration levels; see the legend in part a.

by six oxygen atoms (this arrangement corresponds to the second peak on the RDF at 7.4 Å in Figure 2a). At higher hydration levels, the share of these configurations decreases but remains significant. However, the fractions of fully hydrated calcium ions (completely surrounded by water and essentially separated from particular sulfonate anions) are small and do not exceed 10%, even at the maximum hydration. This means that the increase of hydration facilitates dissociation of $(-RSO_3)_2Ca$ quadrupole into $(-RSO_3Ca)^+ + (-RSO_3)^-$ ion pair with each of the ions covalently attached to the skeleton. The solvation of this system must therefore differ from that in our preceding work, where we studied short sPS fragments in large solvent volumes, thus allowing for the complete dissociation of Ca^{2+} cations.[3] The typical distances given here may not be exact because of an apparent deficiency of LJ models, but we believe that, in general, the forcefield employed adequately describes the molecular arrangements in these systems.

The nanostructure of hydrated sPS was characterized in terms of the solvent cluster size and hydrogen bonding, which was tracked using the geometrical criteria[30,31] given in the footnotes to Table 1. We assumed that the distance between the oxygens of neighboring water molecules in water clusters

TABLE 1: Systems Considered and Their Physical Properties

polymer[a]	water,[b] wt %	DMMP,[b] wt %	ρ, g/cm³	D_{H_2O}, 10^{-9} m/s²	$D_{Ca^{2+}}$, 10^{-9} m/s²	D_{DMMP}, 10^{-9} m/s²	n_{HB},[c] H₂O−H₂O	n_{HB},[c] H₂O−DMMP	n_{HB},[c] H₂O−O₃S	n_{HB},[c] total
sPS, 40%	15		1.180	0.030	0.0008[d]		0.74		0.91	1.65
sPS, 40%	30		1.177	0.21	0.0045		1.17		0.66	1.83
sPS, 40%	54	0	1.165	0.91	0.035		1.47		0.49	1.96
sPS, 40%	54	10	1.168	0.58	0.019	0.035	0.96	0.03	0.50	1.49
sPS, 40%	54	50	1.178	0.36	0.0096	0.041	1.40	0.13	0.45	1.98
sPS, 40%	54	100	1.188	0.19	0.0078	0.052	1.30	0.25	0.45	1.95
sPS, 100%	15		1.251	0.012	0.0006[d]		0.28		1.16	1.44
sPS, 100%	50		1.242	0.067	0.0007[d]		0.86		0.94	1.8
sPS-PE, 100%	39		1.208	0.109	0.0022		0.95		0.56	1.51

[a] Skeleton chemical structure and sulfonation level. See Figure 1. [b] Ratio of solvent weight to dry polymer weight. [c] Donated on average by one H₂O molecule; a hydrogen bond between two oxygens is considered established if the distance between the oxygens is less than 3.4 Å and the OHO angle exceeds 120°. [d] Self-diffusion coefficients were obtained from the mean square displacements (MSD) of solvent molecules and counterion; generally, the diffusion coefficients were calculated as $^1/_6$ of the slope of MSD dependence on time in 600−1300 ps intervals. Distinct linear dependence of the mean square displacements was observed in most systems. Exceptions are marked with *d*'s.
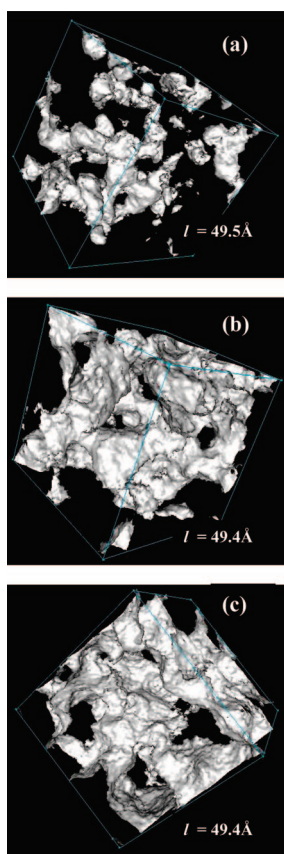
Figure 3. Snapshots of the hydrophilic subphase (water and counterions) in hydrated sulfonated polystyrene at 40% sulfonation level. Water content (to dry polymer weight): (a) 15%; (b) 30%; (c) 54%.

did not exceed 4 Å, which corresponds to first through of the RDF for the pure liquid. We found that, at 15% water content, water formed a network of channels of a quasi-cylindrical shape, about 9 Å in diameter (water cluster size was determined by inserting probe hard spheres into the polymer structure with water, sulfonate groups, and counterions removed). However, these channels did not span the whole system, and about 30% of all water molecules aggregated in small (less than four molecules) disconnected clusters (Figure 3a). Applying the geometrical criteria mentioned above, we found that water molecules donated 0.9 hydrogen bonds on average to sulfonate groups and only 0.75 bonds to other water molecules. Thus, almost every water molecule neighbors a sulfonate oxygen. The inhomogeneous distribution of water hinders the water mobility
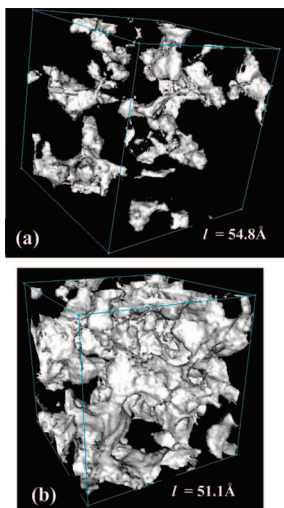
significantly: the self-diffusion coefficient of water determined from the mean square displacement was 2 orders of magnitude lower than that in the bulk water.[32,33]

As the hydration increases, the volume of the hydrophilic phase grows and it becomes continuous due to the coalescence of isolated clusters (Figure 3b,c). At the maximum hydration, the water diffusion coefficient reaches $^1/_3$ of that in the bulk water, and the counterion diffusion becomes visible. Most water molecules donate two hydrogen bonds, as in the bulk water. However, the segregation scale in sPS is substantially smaller than that in Nafion, where clusters of 30 Å and larger were found both in experiments and in simulations, even at a lower water content. At 54 wt % water, every other water molecule still donates a hydrogen bond to a sulfonate group, which means that the backbone conformation and the water distribution are largely correlated.

IV. Nanostructure and Water Dynamics in sPS: Dependence on the Backbone Structure and the Sulfonation Level

To reveal the influence of sulfonation level, we considered the same systems (water content of 15 and 50 wt %) in 100% sulfonated sPS. One has to keep in mind that the same relative water content at different sulfonation levels corresponds to different water activities. Therefore, it would be more accurate to compare the membrane properties at different sulfonation levels at the same water activity. However, we did not find the necessary data for cation substituted sPS in the literature, and the evaluation of the solvent chemical potential in segregated polymers via a simulation is a very complex task beyond the scope of this work. A cluster analysis showed that, at 100% sulfonation, more water molecules resided in small clusters containing less than four molecules and the hydrophilic subphase had more discontinuous inclusions (Figure 4a), resulting in a lower water diffusion coefficient and a much smaller number of water-to-water hydrogen bonds. From the comparison of diffusion coefficients for 100% sulfonated and 40% sulfonated samples, it appeared that, at the same number of water molecules per sulfonate group, the diffusion was faster at 40% sulfonation level.

Hydration in a pseudorandom copolymer (Figure 1, right) was studied only at 100% sulfonation and 39% water content. This water content corresponds to the 11 water molecules per sulfonate group; in this aspect, this system is comparable to sPS with a sulfonation level of 40% and a water content of 54 wt %. The ratio of styrene to ethylene monomer numbers

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Figure 4. Hydrophilic subphase of hydrated membranes: (a) sulfonated polystyrene 100% sulfonated at 15 wt % water content; (b) 1:1 ethylene−styrene copolymer 100% sulfonated at 39 wt % water content.

Figure 5. Radial distribution functions for the 40% sulfonated sPS−water−DMMP system: (a) sulfur−water oxygen RDF for 54% water, 50% DMMP content; (b) RDF between the root benzene carbon (the one attached to the aliphatic chain) and solvents represented by the phosphorus of DMMP and water oxygen at different DMMP contents.

generally determines the volume of the polymer per one sulfonate group. The skeleton flexibility differed also, as the neighboring sulfonate groups on the same chain were separated by larger distances compared to sPS at the sulfonation levels below 100%.

Figure 4b shows that segregation exists in pseudorandom copolymer also. Water in this system forms a continuous subphase, and water diffusion is slightly slower than in the corresponding 40% sulfonated sPS. Similar to the 40% to 100% sulfonation trend, this seems surprising because the relative volume of the hydrophilic subphase of the random copolymer was larger than that in 40% sPS. Thus, we have to conclude that the reduction of diffusivity reflects the dispersion of the hydrophilic subphase that is confirmed by a relative number of water−water and water−sulfonate hydrogen bonds.

V. Sorption and Mobility of DMMP in Hydrated sPS

In the sPS system with 40% sulfonation, we fixed the water content at 54% and varied the DMMP concentration from 10 to 100% of the dry polymer weight. The upper limit of this range approximately corresponds to the maximum DMMP sorption reported in ref 7. Solvation of sulfonate groups and counterions is demonstrated by RDFs shown in Figure 5. Similarly to the pure water solvent, most counterions are still associated with at least one sulfonate group. It is clear that the counterions are surrounded by both negatively charged water oxygens and the oxygens of DMMP bonded to the phosphorus atom, with a slight preference to water. On the S−O and S−P RDFs with all sulfonate groups counted, we observe a high first peak corresponding to the water molecules that form hydrogen bonds to sulfonate groups (Figure 5b). This peak is not prominent for DMMP, but it is clear that the sulfonate groups are not immersed in water, as was observed in our previous simulations of individual sPS fragments in larger solvent baths.[3] Our observation confirms the hypothesis made by Schneider and Rivin[34] about a competition between water and DMMP for the solvation of sulfonate groups in sPS in contrast to Nafion, where the sulfonate groups are predominantly solvated by water.[35] On the other hand, the RDFs between the phosphorus and benzene ring atoms (Figure 5b) undoubtedly confirm that DMMP prevails around the skeleton.
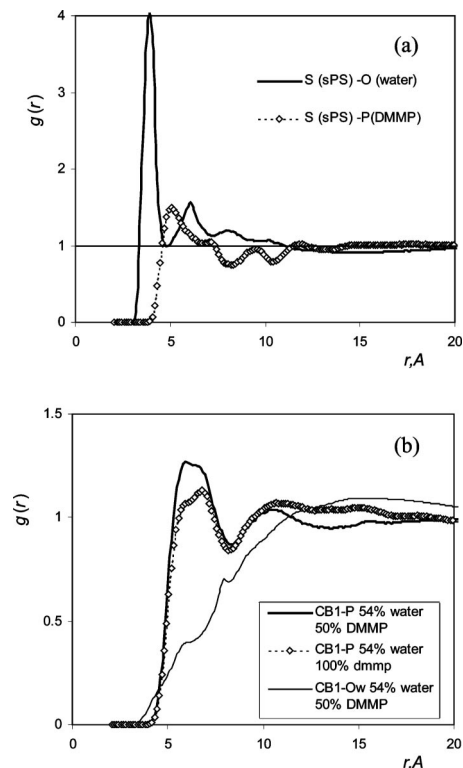
A cluster analysis of the sPS−water−DMMP samples shows that, in all systems, the mobile species (water, DMMP, and counterions) form a single continuous subphase. However, at higher DMMP concentrations (50 and 100 wt %), DMMP may be considered as creating a continuous subphase of its own (Figure 6). Therewith, the water diffusion coefficient steadily reduces with the increase of the DMMP content (and, respectively, the increase of the DMMP diffusion coefficient), despite the apparent increase of the cumulative volume occupied by the mobile species, which mix perfectly in the bulk (Table 1). These unforeseen observations indicate that water and DMMP have separate pathways through the system. Within the solvated sPS, DMMP molecules accept only 0.75 hydrogen bonds on average at DMMP contents of 50 and 100 wt % compared to 1.3−1.4 bonds accepted by water. This is in contrast to the bulk solution, where DMMP molecules accept 1.5−2 hydrogen bonds from water molecules on average, which is on par with water molecules.

In our previous simulation studies of nafion solvation with K$^+$ as a couterion, we observed a breakdown of a homogeneous water−DMMP solution placed in contact with model Nafion side chains, which acted like surfactants promoting the segregation of the mixture into aqueous and DMMP subphases.[35] Respectively, in hydrated Nafion, DMMP tended to be accumulated at the interface between hydrophilic and hydrophobic domains. In both simulations, the sulfonate groups and counterions were surrounded by water. Apparently, the solvation in hydrated sPS observed in this work is distinct from that in Nafion. A divalent counterion, a different segregation scale caused by a different volume of the hydrophobic fragments per sulfonate group, and a different flexibility of the skeleton, all of these factors may contribute to the difference in solvation.
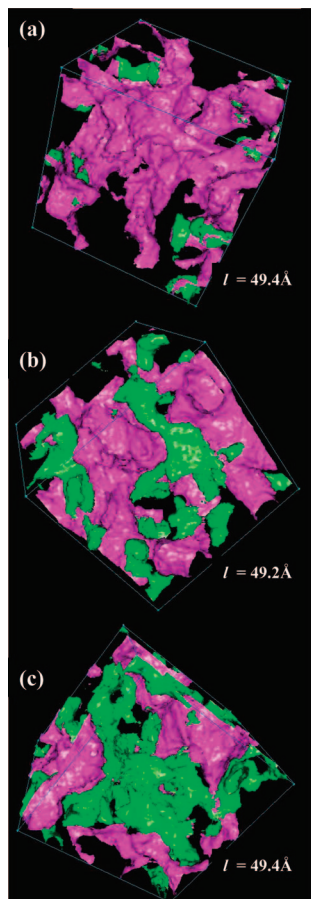
Figure 6. Snapshot of areas occupied by water (purple) and DMMP (green) sorbed in 40% sulfonated sPS: (a) 54% water (to dry polymer weight), 10% DMMP; (b) 54% water, 50% DMMP; (c) 54% water, 100% DMMP.

Conclusions

We have modeled water and DMMP sorbed in sulfonated polystyrene at sulfonation levels of 40 and 100%. Our simulations show that the systems undergo a nanoscale segregation, somewhat similar in nature to the nanosegregation in Nafion membranes,[35] however, on a substantially smaller scale of 1−2 nm. In hydrated sPS, the structure formation resembles that in Nafion; starting from isolated clusters, the hydrophilic suphase grows, coalesces, and becomes continuous, undergoing a percolation transition. Despite the smaller segregation scale in comparison to Nafion, the self-diffusion of water at high hydration is very fast: it reaches 30% of that in pure water. In the water−DMMP systems, we found that water and DMMP compete for the first solvation shell of the sulfonate group. This is a positive factor for the development of protective materials from sPS containing triblock copolymers: as water sorption prevails, phosphor−organic compound sorption is hindered. However, the ability of DMMP to interact effectively with both the skeleton (via van der Waals interactions) and water (via dipole−dipole interactions and hydrogen bonding) provides favorable conditions for DMMP sorption. Comparison of water

and DMMP diffusion shows the latter is very mobile at high hydration and DMMP content, and the dependence of the diffusion coefficients on the solvent concentrations suggests that water and DMMP have different pathways through the system. We may conclude that a special chemical modification of sPS containing triblock copolymers is required to reduce sorption of phosphor−organic compounds in the hydrophilic blocks of the membrane.

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