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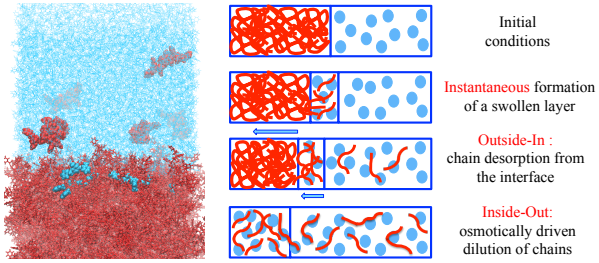

The immediate formation of an interfacial layer allows for chains detachment from a glassy polymer before the osmotic swelling starts.

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How does low-molecular-weight polystyrene dissolve: osmotic swelling vs. surface dissolution

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ABSTRACT By means of multiscale hierarchical modeling we study the real time evolution of low-molecular-weight polystyrene, below the glass transition temperature, in contact with its solvent, toluene. We observe two concurrent phenomena taking place: (1) the solvent diffuses into the polymer by a Case II mechanism, leading to osmotic driven swelling and progressive chain dilution (inside-out mechanism); (2) polymer chains are solvated, detach from the interface and move into the solvent before the film is completely swollen (outside-in mechanism). From our simulations we conclude that, below the entanglement length, a thin swollen layer, also observed in previous experiments, forms almost instantaneously, which allows for the outside-in mechanism to start a few tens of nanoseconds after polymer-solvent initial contact. After this initial transient time the two mechanisms are concurrent. We furthermore observe that the presence of the solvent significantly enhance the mobility of the polymer chains of the surface layer, but only in the direction parallel to the interface.

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Polymer dissolution and the penetration of solvents in glassy polymers have been of interest for many years[1, 2]. Many industrial applications, like nanolithography, membrane based separations, plastic recycling and drug delivery, rely for their performance and optimization on a deep knowledge of the mechanisms involved in polymer swelling and dissolution[3-6]. When a solvent reservoir gets in contact with a polymer matrix, two distinct processes occur: the solvent diffuses in the polymer matrix and the polymer chains near the solid-liquid interface get solvated. The diffusion of the solvent and the consequent formation of a swollen layer favor detachment of the chains from the surface. Cases exist, however, where the interfacial layer does not swell and the polymer cracks. The solvent penetration into the glassy matrix exhibits significant deviations from the classical Fickian diffusion, where the mass uptake of the solvent by the polymer is proportional to the square root of time. In the so-called *Case II* diffusion[7] the mass uptake is linear in time and the rate of solvent transport is determined by the relaxation time of the chains.

Recent studies have shown how a deep understanding in the processes involved in polymer dissolution can be relevant for wetting properties. Even if much is understood about the wetting of nonsoluble substrates, much is still to be understood in the case of soluble substrates. Dupas et al. have recently shown that the rates of the solvent transfer into the substrate determines the wetting dynamics of the solvent, water, on the soluble polymeric substrate, low molecular weight maltodextrins[8]. The glassy polymer substrate may undergo a glass transition, which dramatically reduces the wetting contact angle[9]. In the case of toluene droplets spreading on polystyrene (note that toluene is a solvent for polystyrene) a finite contact angle is observed at the end of the spreading process, instead of the formation of thin liquid film[10]. The dissolution of polystyrene chains may offer an explanation. The solvated chains increase the viscosity of the toluene drops and this eventually causes the three-phase contact line to stop spreading.

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The major role in the diffusion-dissolution process is played by the surface dynamics. Experimental studies showed that in thin polymeric films the surface has an enhanced mobility compared to the bulk region[11, 12], with Fakhraai and Forrest being the first to quantitatively characterize the surface relaxation time of polystyrene films[13, 14]. A thin layer of liquid-like material is present at the free surface of glassy, low-molecular weight polymer films, with reduced viscosity of the chains. The surface dynamics is affected by the molecular weight of the polymer and by the preparation methodology of the film, in particular by the quality of the solvent and its concentration[15]. Furthermore there is still an open-debate in the literature whether the glass transition temperature (T_g) of thin films depends on the thickness of the film[16].

Due to the experimental difficulties, swelling of thin films with liquid penetrants is rarely investigated. Hori et al.[17] studied the diffusion of methanol in polymethylmethacrylate thin films. The diffusion coefficients at the surface of the thin films are higher than in the bulk, hinting at a surface layer with enhanced mobility. Ugur and coworkers[18] analyzed the dependency of the dissolution coefficients of polystyrene in cyclohexane-toluene mixtures. The dissolution is highly influenced by the polydispersity of the systems and decreases with increasing molecular weight. Ogieglo et al.[19, 20] studied the swelling of ultra-thin polystyrene films by n-hexane. The experimental findings suggest that immediately after first contact with the solvent an approximately 14 nm thick surface layer gets swollen. After the interfacial swelling, the diffusion front velocity perpendicular to the surface does not significantly vary. These findings suggest an increased chain mobility or a decreased viscosity at the surface of the polymer films. The same group[21] has very recently examined the differences between a glass transition induced by temperature variation or by sorption of small molecules. The temperature-induced dilation is

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smaller than the local matrix deformation due to the uptake of the penetrant, which may actuate more relaxation processes at the surface, resulting in a different macromolecular dynamics.

The molecular level details of a polymer surface are accessible also by computer simulations. Fully atomistic simulations are however limited to nanometer and nanosecond length and time scales, respectively and are often strongly influenced by the initial setup of the simulation box, in particular if the material is glassy. The pioneering atomistic simulations by Mansfield and Theodorou showed an enhancement in the mobility of the chains in the vicinity of the free surface of glassy atactic polystyrene[22]. The dynamical interfacial thickness was found to be approximately 1.5 nm. The enhanced mobility of the surface has been more recently investigated also with bead-spring models[23-25]. In these simulations the focus is on generic effects due to the presence of the polymers rather than on specific interactions between chemical groups. While the effect of the presence of a solid surface on chain conformations have been studied at atomistic level[26], studies of the effect of a liquid surface onto the polymer matrix are not so widespread. Previous simulations have analyzed the effect the plasticization of the polymer induced by a solvent in the case of benzene and PS[27] and PMMA with THF[28] and of intrinsic microporous polymers with nitrogen[29]. These studies rely however on pre-swollen bulk system and therefore cannot access interfacial properties. An extensive simulation study of the interfacial effects of gas sorption on polyimide films has been recently reported by Neyertz and Brown[30, 31]. They report that the swelling is due to local relaxations of the matrix rather than to larger changes in the structures, with the glassy chain mobility remaining restricted. The diffusion coefficient of the gas is directly related to the mobility of the matrix.

In this report, we investigate with full atomistic simulations the first phase of swelling of low-molecular-weight polystyrene (PS) induced by toluene (TOL), a well-known solvent for

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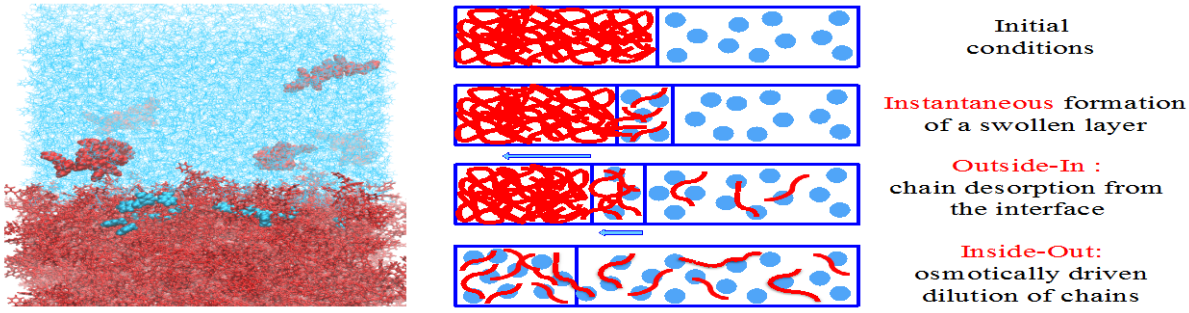
polystyrene. We overcome the intrinsic difficulties of obtaining an equilibrated atomistically detailed polymer surface structure with a hierarchical simulation approach. Based on a transferable coarse-grained model for polystyrene[32] we have efficiently equilibrated polystyrene chain conformations and chain packing at the surface at a temperature slightly above the glass transition temperature and on time scales up to approximately 25 μs[33]. With an inverse-mapping procedure[34] that reintroduces the atomistic degrees of freedom in the equilibrated coarse-grained polymer configurations we then obtained a detailed atomic-scale picture of the glassy polymer surface characteristics.



"**Figure 1.** Left: Simulation box after 60 ns atomistic molecular dynamics simulation. Polystyrene chains are shown in red, toluene molecules in blue. Highlighted are the solvated polystyrene molecules and the toluene molecules that diffused in the polymer matrix. Right: Schematic description of the sequence of phenomena taking place. The simulation box on the left represents the atomistic snapshot of the Outside-In mechanism."

This surface has then been put in contact with a toluene reservoir. It is worth pointing out that the system size of 10 nm x 10 nm x 30 nm corresponds to approximately 400,000 atoms, a size that

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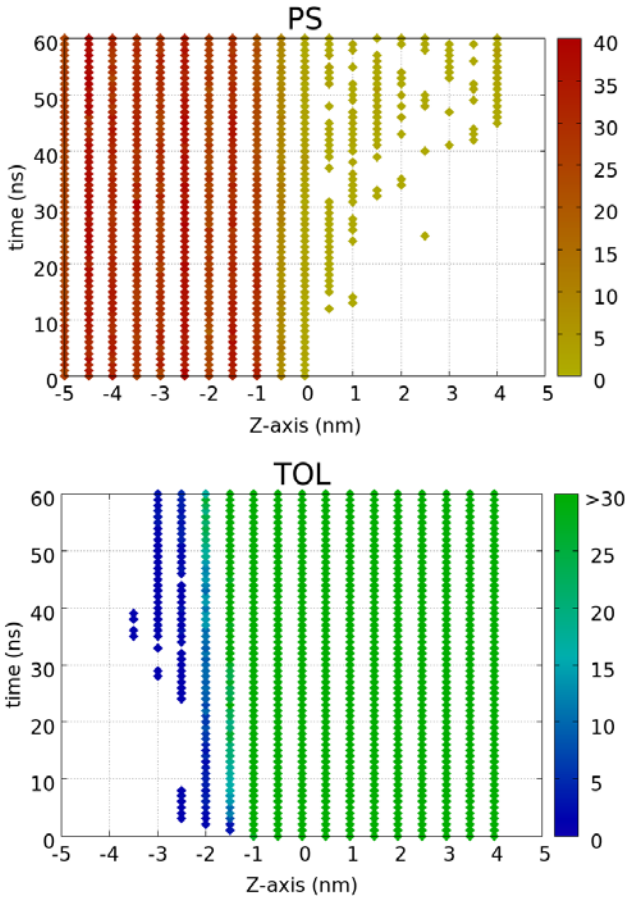
is not feasible to get equilibrated at the atomistic level. The length of the chains is 10 monomers, so we are well below the entanglement length. The simulations were performed at 298 K. The experimental value for the T_g of polystyrene is 380 K. The atomic mean square displacements shown in Figure 5, which show essentially frozen atom dynamics on nanosecond time scales, indicate that the surfaces are glassy. Reference simulations with the free polystyrene surface (i.e. the surface against vacuum) were performed at 298 K and 305 K. All the simulations have been performed with the GROMACS package[35].



"Figure 2. Number of polystyrene (top) and toluene molecules (bottom) present in 0.5 nm thick slabs cut perpendicular to Z-axis of the simulation box. The origin of the Z-axis is located at the

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position of the PS/toluene interface at the beginning of the simulation. The color code refer to the number of molecules present in each slab."

The left panel of Figure 1 shows the simulation box after 60 ns of simulations. It is clearly seen that both processes involved in polymer dissolution happen at this short timescale, namely toluene molecules have started to penetrate into the polymer matrix and polystyrene molecules have been solvated and are freely diffusing in the liquid phase. On the right side of Figure 1 the sequence of the phenomena taking place is schematically represented. The quantitative analysis of the time evolution is presented in Figures 2 and 3.

In the first 3-4 ns of the simulation, toluene penetrates the interfacial region up to a depth of 2.5 nm. This thickness is larger than the intrinsic roughness of the polymer surface due to the atomistic corrugation, which we calculated as described in Reference [33] to be 0.502 nm. After this initial fast swelling of the polymer matrix, the first polystyrene chain escapes into the liquid phase. After 30 ns, two phenomena happen simultaneously, more polymer chains are getting solvated and the toluene front moves deeper in the polymer matrix. The time evolution of these processes is quantified in Figure 3. Toluene molecules penetrate the polymer matrix up to a depth of 2.5 nm within the first 3 ns. This maximum depth reaches up to 3.4 nm during the remaining simulation time up to 60 ns. In order to calculate the position of the toluene front we used the sigmoidal function in Eq.1:

$$\rho(z) = \frac{1}{2}\rho^{l} - \frac{1}{2}\rho^{l} tanh\left(\frac{2(z-z_e)}{d}\right) \quad (1)$$

where $\rho(z)$ is the toluene density profile across the interface, ρ^{l} is the liquid toluene density, z_e is the position of the equimolar dividing surface and d is a measure of the interfacial thickness.

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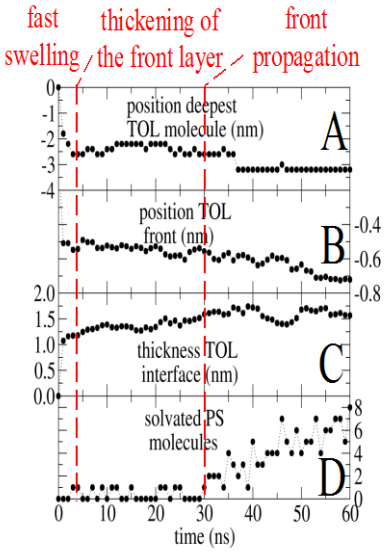

"**Figure 3** Panel A: maximal depth (nm) of toluene molecules inside the polymer matrix. Panel B: position (nm) of the toluene front (z_e in Eq.1). Panel C: thickness (nm) of the toluene front layer (d in Eq.1). Panel D: number of solvated PS molecules."

The position of the toluene front moves 0.5 nm inside the polymer matrix as soon as the liquid is brought in contact with the polymer. Its position remains fairly constant for about 20-25 ns, time in which the thickness of the interface reaches the value of around 1.5 nm. The toluene front starts then to propagate and it further enters into the polymer matrix, with the interface thickness remaining almost constant. The polystyrene molecules also follow a two steps behavior as can be seen in Figure 3-D, where the number of solvated molecules is shown. A solvated chain is defined as a chain, which, within a radius of 1 nm around each atom, has no contact with another polystyrene chain. In the first 30 ns just one PS chain gets solvated and is then reabsorbed on the surface. In the following 30 ns of the simulations up to 8 PS chains are present in the liquid phase. Despite the noise on the data in Figure 3-D (owing to "recapturing" of escaped chains) an overall dissolution rate can be derived from the data. The diffusion coefficient of a single PS

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chain in a toluene box at 298 K was calculated in an independent simulation to be $5.2*10^{-5}$ cm^2/s. In the case of the chains that detach from the surface and stay in the liquid phase, we have calculated a diffusion coefficient for the x and y directions (parallel to the surface) of $5.8*10^{-5}$ cm^2/s, while the diffusion coefficient in the z direction (perpendicular to the surface) is $3.5*10^{-5}$ cm^2/s. From the data of the position of the toluene front (Fig. 3-B) the velocity with which the front propagates can be extracted with a linear fitting of the last 30 ns of the simulation time and the same can be done to obtain the dissolution rate with the data in Figure 3-D. We assume a constant velocity of the front and a constant dissolution rate. The velocity of the toluene front ($0.56*10^{-2}$ nm/ns) was calculated to be twice as big as the velocity of dissolution of the surface ($0.27*10^{-2}$ nm/ns). The velocity of dissolution was calculated by using the PS bulk density to convert solvated chains per unit time to the location of the front as a function of time. This result is depicted by the arrows in the scheme on the right side of Figure 1. After the initial immediate swelling, there is a transient time period in which the interfacial thickness d of the toluene front increases (Fig. 3-C) and PS molecules occasionally get solvated. Then, the toluene front starts moving into the film and two mechanisms concurrently happen: the "outside-in" mechanism and the increasing dilution of the chains due to osmotic swelling ("inside-out" mechanism).

To better understand the propagation of the toluene front we have analyzed the concentration profiles of both polystyrene and toluene, which are shown in Figure 4. In the case of polystyrene the position of the surface remains constant in space, but the concentration of polystyrene in the liquid phase constantly increases with time. On the contrary in case of toluene a slow displacement of the front with time is visible, as already indicated by the previous analysis. The interesting feature is that parallel to the displacement of the main front, after 30 ns the formation a smaller advanced front, whose concentration increases with time, can be observed. This bump

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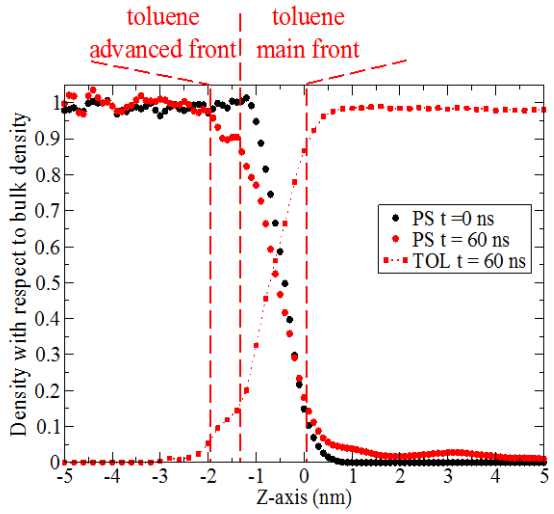
can be due to the osmotic swelling of the matrix. The role of this advanced toluene front may be better understood when observing both the polystyrene and the toluene profiles. At the position in the z-direction corresponding to the advanced toluene front it can be observed that the density of the polystyrene matrix is reduced to 90%. It can be inferred that the advanced toluene front acts as a lubricating agent for the polymer matrix, allowing then the main front to easily move in the polymer matrix, since the diffusion constant of toluene increases rapidly with increasing toluene concentration.



"**Figure 4** Concentration profiles of toluene and PS at the end of the simulation."

Because experiments[11, 12, 15] suggest the presence of a surface layer with higher mobility, we have calculated the mean squared displacement of the polystyrene atoms as a function of their proximity to the interface. Even if the atoms of the polymer matrix exhibit small mobility, the atomic mean squared displacements give a hint on the effect of the surface and of the solvent on the glassy dynamics of the atoms. The results presented in Figure 5 show the atomic mean squared displacement for three different simulations: one with the PS surface in contact with

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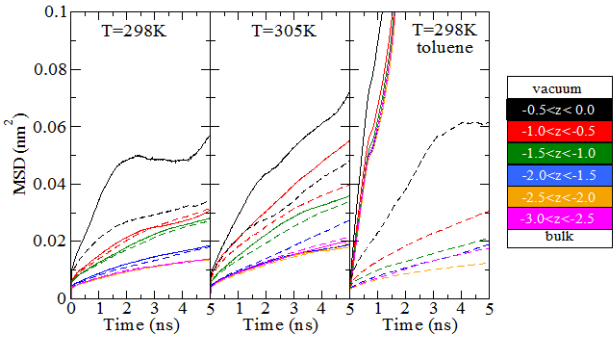
vacuum at 298K, in the middle the same surface at 305K, and the last panel refers to the PS surface at 298K in contact with toluene. The extremely small atomic displacements for the first two cases indicate that on the nanoseconds timescale the dry surfaces are glassy. In the first case the dynamics of the matrix atoms is affected by the presence of the interface if they are located between 2 nm and 0.5 from the interface, atoms located more than 2 nm away from the surface do not feel the effect of the interface. The slab in contact with vacuum shows in addition to the highest mobility, a difference in the behavior in the direction parallel to the surface then perpendicular to it. The atoms of the interfacial layer preferentially move along the surface than perpendicular to it. By slightly increasing the temperature (middle panel of Figure 5), this anisotropy moves deeper in the polymer matrix, involving atoms up to 1.5 nm away from the interface. The major effect induced by the presence of toluene at the interface (right panel of Figure 5) is to drastically increase the atomic mean square displacement in the direction parallel to the surface for matrix atoms up to 3 nm away from the interface. The displacement in the direction perpendicular to the surface is comparable to the one of the surface in vacuum at 305K.



"**Figure 5** Atomic mean square displacement of the polystyrene matrix. The continuous lines refer to the displacement in the x direction (y is equivalent) and the dashed lines refer to the

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displacement in the z direction. Left panel: PS surface in vacuum at 298 K. Middle panel: PS surface in vacuum at 305K. Right panel: PS surface with toluene at 298K."

Our previous coarse-grained simulations[33] showed that the polymer chains of the surface layer tend to lie more parallel to the surface, in comparison to the chains in the bulk. This is also the case in these atomistic simulations. We have computed the components of the radius of gyration (R_g) of the chains with respect to their distance from the interface. The x and y components of R_g are larger than the z component for the chains located at the proximity of the surface. The difference disappears when considering the chains in the bulk. This different alignment at the interface may be the reason for the anisotropical behaviour of the atoms at the surface.

In summary, we were able to track with atomistic simulations the real time evolution of the processes involved when a glassy low-molecular-weight polymer substrate is brought in contact with a solvent. One would expect that to observe chain detachment from an initially dry glassy surface some extent of osmotic swelling is required to increase the local mobility of the chains. Due to the very slow solvent diffusion rates in glassy polymers, one would, in fact, not expect immediate chain detachment as observed in our simulations, where the chains detach after only a few nanoseconds during which the solvent invades a 1.5 nm thick surface layer. This, extremely rapid, surface swelling or plasticization is probably favoured by the roughness of the amorphous surface and allows for chain detachment before the actual osmotic swelling of the underlying material takes place. After this initial swelling, the inside-out mechanism, with an increasing osmotic dilution of the polymer chains, and the outside-in one, which is favoured by the rapid surface plasticization, are concurrent. An accurate quantification of the kinetics of dissolution, which is relevant for applications involving low-molecular-weight polymers like maltodextrins[9], is at the atomistic scale however not possible. The computational costs to increase the statistics

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by running several independent simulations and to extend the simulation time till the end of the dissolution process are not affordable. In order to obtain a better statistics on the presented results and also to investigate the dissolution on longer polymer chains, coarse-grained simulations are necessary. A coarse-grained model study of these processes requires, however, that the relative rates of solvent diffusion, chain relaxation, and chain diffusion are all correctly described. We are currently developing dissipative particle dynamics models that include friction terms, derived by a bottom-up calculation procedure, which restore the original relative dynamics of the atomistic system. These models will then be used to quantify the kinetics of dissolution at the coarse-grained level. We furthermore confirm with our simulations that the surface layer has an enhanced mobility, which is increased in the presence of the solvent, but the mobility is not isotropic. The interfacial atoms of the polymer matrix move more parallel to the interface than perpendicular to it, due to flatter conformation of the chains at the surface.

EXPERIMENTAL SECTION

The box size is 10 nm x 10 nm x 30 nm. The system consists of 672 10mer atactic polystyrene chains and 8801 toluene molecules. The PS and the toluene slab are 13 nm and 17 nm thick, respectively. The simulation box is periodic in three dimensions. For the free PS surface, the box size of 30 nm in the z-direction is big enough to avoid interactions of the parent chains with their periodic images in this direction. The forcefield for polystyrene is described in Ref. [36] and the forcefield for toluene is OPLS-AA[37]. All the simulations were run in the NVT ensemble using the version 4.5.5 of the GROMACS package[35]. The temperature was kept constant, either at 298 K or 305 K, with the velocity rescaling[38] thermostat with a coupling time of 0.2 ps. The cutoff distance for the Lennard-Jones non-bonded interactions was 1.0 nm. The electrostatic interactions were calculated with PME (Particle Mesh Ewald)[39] with a grid spacing of 0.12 nm and a real space cutoff of 1.0 nm. Isotropic long range dispersion corrections for energy and pressure have been used. The timestep was 1 fs and the simulations were run for 60 ns. The bond lengths were kept fixed during the simulation.

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Notes

The authors declare no competing financial interest.

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