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# MOLECULAR-DYNAMICS SIMULATION OF AMORPHOUS POLYMERS IN THE ISOTROPIC STATE AND UNDER UNIAXIAL DEFORMATION

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Molecular-dynamics computer simulations have been carried out of a chemically realistic non-entangled model of glassy atactic polystyrene both in the isotropic state and under the influence of uniaxial mechanical deformation. Simulations show a logarithmic increase in  $T_g$  with cooling rate in agreement with existing experimental data. Cross-over from monomer motion in the cage to Rouse-like dynamics has been studied. The characteristic cross-over time follows a power law behavior at  $T > T_g$ , as predicted by mode-coupling theory, and a simple activated law at  $T < T_g$ . In the deformed state the simulated strain-hardening modulus is in quantitative agreement with existing experiments. The deformationally-induced anisotropy in the global and local segmental orientation is accompanied by an anisotropy of the local translational mobility: the mean-square translational displacement of the individual segments in the direction of the deformation is drastically increased just beyond the yield point as compared to the isotropic state.

## 1. INTRODUCTION

Investigation of the local dynamical properties of amorphous polymers has been a subject of many studies, both experimental<sup>1</sup> and by means of computer simulation<sup>2,3</sup>. Nevertheless, questions concerning mechanisms of segmental mobility in the vicinity of the glass transition still remain open. Dynamical characteristics of amorphous polymers in the glassy state influence such important properties as ductility, toughness and impact resistance. Amorphous atactic polystyrene (PS) is, by no doubts, one of the most important examples of widely used industrial plastics and a classical example of mechanically brittle polymers (in contrast to polycarbonate, for example). It suits perfectly to study the connection between local chemical and physical microstructure and global mechanical behaviour.

In the present paper molecular-dynamics (MD) computer simulations are reported for a chemically-detailed model melt of atactic PS close to the glass transition both in isotropic state and under the influence of the uniaxial deformation. The motion of the bulky side groups (phenyl rings) is taken into account explicitly. Both the linear-elastic regime and the non-linear regime of large deformation, up to 100%, have been simulated. The main attention has been paid to the investigation of local dynamical properties

(translational mobility of the main-chain and the side-group segments) of the polymer glass in the isotropic and the anisotropic deformed state. The details of the simulation are presented in section 2. In section 3 the simulated glass transition, the results for local translational mobility of the chain segments, the bulk mechanical properties, the onset of the yield behaviour and local dynamical properties under deformation are discussed. Some conclusions are summarized in section 4.

## 2. MODEL AND SIMULATION ALGORITHM

The united-atom model of PS which is used here is described in detail by Lyulin et al.<sup>2,3</sup> The NPT MD simulation has been performed for a few systems. In the isotropic case (at atmospheric pressure) the model consists of a single polymer chain of  $N_p = 80$  monomers (molecular weight  $\sim 8300$ ) and its periodic images generated by periodic boundary conditions. The leap-frog variant of the velocity Verlet algorithm<sup>4</sup> has been used to integrate the Newtonian equations of motion with the integration time step fixed to  $\Delta t = 4$  fs. Deformation experiments have been performed for two many-chain systems: 8 chains of  $N_p = 80$  monomers each and 4 chains of  $N_p = 160$  monomers (about one entanglement length) each. The stereochemic configurations of the aromatic groups were generated at random so that the ratio of the number of *meso* to *racemic* dyads was near unity. For the detailed forms of the potential contributions and the values of the potential constants we refer to our previous publications<sup>2,3</sup>.

The polymer systems have been cooled down with different (over several orders of magnitude, from  $5 \times 10^{-3}$  K/ps to 1 K/ps) cooling rates from the initial high-temperature liquid state at  $T = 650$  K. Step-wise cooling with the steps down in temperature (about 10 K) followed by an equilibration of  $\sim 20$  ns has been implemented as well. Uniaxial deformation along three Cartesian axes was applied to five independent sets of relaxed isotropic PS samples at different temperatures with the constant deformation rate of  $\dot{\gamma} = 0.005$  Å/ps. This is significantly slower than the simulation efforts reported so far in the literature<sup>5,6</sup>. Nevertheless, with the initial size  $L_0 \sim 50$  Å of the box, the relative deformation rate is very large,  $10^8$  s<sup>-1</sup>. Final results have been averaged over all five sets and three directions of deformation. Then nominal strain parallel to the direction of deformation has been measured as  $\gamma_L = \frac{L - L_0}{L_0} \times 100\%$ , where  $L = L_0 + \dot{\gamma}t$  is the instant length of the simulation box parallel to the direction of the applied tension and  $L_0$  denotes the equilibrium value of this length prior to the application of tension.

### 3. RESULTS AND DISCUSSION

#### 3.1. Cooling-rate dependence of simulated $T_g$

The temperature dependence of the specific volume at atmospheric pressure is shown in Figure 1 for different values of the cooling rate. The specific volume decreases almost linearly at both high and low temperature with decreasing temperature. The clear

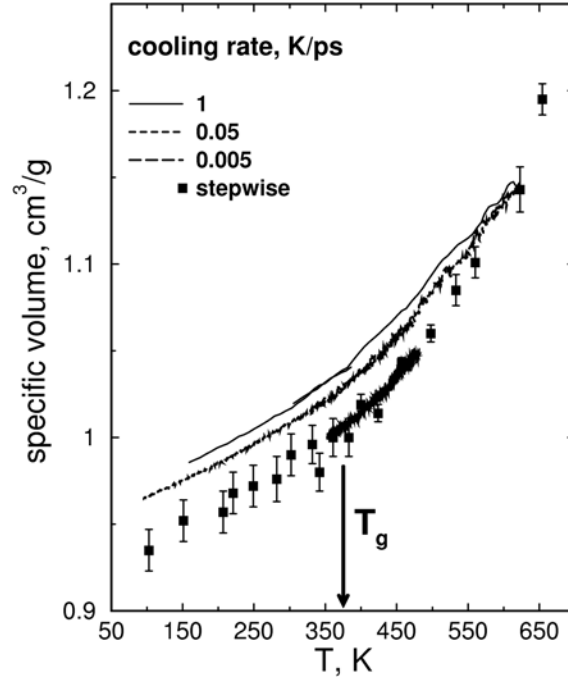


FIGURE 1

Temperature dependence of the specific volume for a single-chain PS at atmospheric pressure, produced with stepwise cooling and with different continuous-cooling rates. The arrow indicates the simulated value of  $T_g$  (375 K) obtained from the stepwise cooling

change in the thermal-expansion coefficient serves as an indication of the glass transition. The values of  $T_g$  produced by different continuous-cooling procedures are displaced towards higher temperatures as compared to the experimental value of  $T_g \sim 370$  K.<sup>2,3</sup> Higher-temperature parts of the specific-volume vs temperature curves produced with different cooling rates are indistinguishable within statistical error.

Assuming that the relaxation time of the system follows a Vogel-Fulcher dependence on temperature, we found that the glass-transition temperature logarithmically increases with cooling rate  $\chi$ <sup>7</sup>

$$T_g(\chi) = T_0 - \frac{B}{\log(A\chi)} \quad (1)$$

The fit (1) represents the simulated data very well. The value of the fitting parameter  $T_0 = 371$  K could be interpreted as a glass transition temperature in the limit of extremely (i.e., realistically) slow cooling.

### 3.2. Local translational mobility in the isotropic state

The local translational mobility has been studied by measuring the mean-square

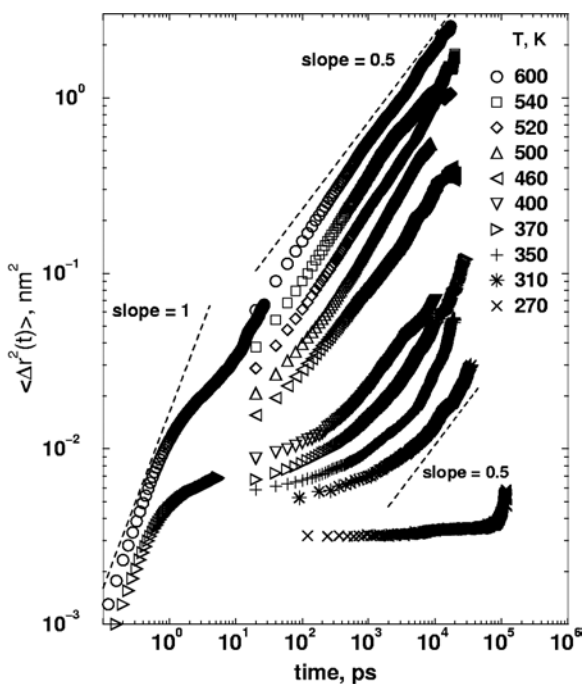


FIGURE 2a

Mean-square translational displacement of the bead in the backbone at different temperatures. Mean-square displacements for the phenyl groups show qualitatively the same behaviour

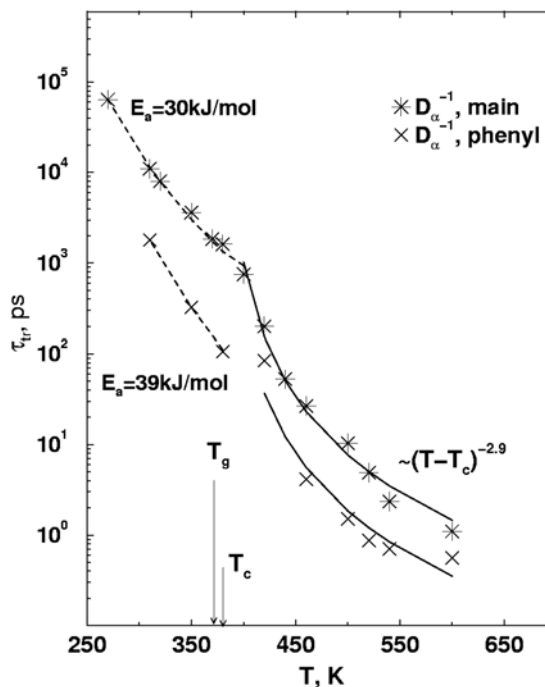


FIGURE 2b

Temperature dependence of the translational relaxation times  $\tau_{tr} = D_{\alpha}^{-1}$  both for the beads in the main chain and in the side group. Solid line is the MCT-based fit. Dashed line is the fit with the simple activation law

translational displacements (MSTD) of individual beads in the main chain and in the side phenyl groups, Figure 2a. At very small times ( $t < 1-3$  ps) the regime of free monomer diffusion, with a slope of about 1, is seen. In a high-temperature melt, when  $T \gg T_g$ , this regime changes into a second diffusive regime, with the slope  $\alpha \sim 0.54$ , which confirms a well-known prediction for the Rouse chain. With decreasing the temperature the motion of the chain bead is becoming more and more restricted: the onset of the Rouse diffusion is

preceded by some plateau. This plateau is connected with the cage effect, whereby very restricted local motions occur in the cage formed by surrounding monomers.

The idealized mode-coupling theory (MCT) for the translational  $\alpha$ -relaxation may apply, which predicts that for temperatures above  $T_g$  the final parts of the curves in Figure 2a can be fitted with the power law  $\langle \Delta r^2(t) \rangle \sim (D_\alpha t)^\alpha$ , where  $D_\alpha$  is a diffusion constant in the regime of the Rouse diffusion. According to the MCT the characteristic time of the  $\alpha$ -relaxation,  $\tau_{ir} = D_\alpha^{-1}$ , should diverge algebraically at some critical temperature  $T_c$  just above  $T_g$ :  $\tau_{ir} = \frac{\tau_0}{(T - T_c)^\gamma}$ . Our data fits this behaviour very well, with a value of  $T_c \sim 380$  K that is indeed somewhat higher than the observed glass transition temperature  $T_g \sim 370$  K. The value of  $\gamma \sim 2.9$  is in a very good agreement with the value of  $\gamma = 2.85$  obtained by van Zon and de Leeuw<sup>8</sup> for a model polyethylene melt. The temperature dependence of  $\tau_{ir} = D_\alpha^{-1}$  is for the full temperature range shown in Figure 2b; as already mentioned this dependence at  $T > T_g$  is well described by MCT (solid lines in Figure 2b). At  $T < T_g$  clearly different behaviour is observed for the onset of the second diffusion regime; a simple activation law is used to fit the data for both the main-chain and side-group translational-diffusion times (dashed lines in Figure 2b),  $\tau_{ir} \sim \exp(E_a / k_B T)$ . This gives for the activation energy the values  $E_a \sim 30$  kJ/mol (main chain) and  $E_a \sim 39$  kJ/mol (phenyl group).

### 3.3 Stress-strain relations and local dynamical properties under deformation

In Figure 3a the calculated tension is plotted against the percentage deformation,  $\gamma_L$ , for few temperatures in the vicinity of  $T_g$ . The initial elastic regime is clearly seen for the extensions up to 3%, and is followed by the yield point at  $\gamma_L \sim 3-4\%$ , the strain-softening regime for  $\gamma_L$  up to 15% and some strain hardening for higher deformations. The simulated value of the Young modulus at low temperatures is about 3 GPa, which is very close to the experimental value of  $\sim 3.2 - 3.4$  GPa.

At  $\gamma_L > 3\%$  the simulated polymer glass starts to yield. After the yield point some strain softening followed by the strain hardening is clearly seen at each simulated temperature, Figure 3a. The strain-hardening modulus  $G_R$  is usually defined<sup>9</sup> as the slope of the curve at large strains (deformation above 15% in the present simulations) of the true stress  $\sigma$  versus  $\lambda^2 - \lambda^{-1}$ , (neo-Hookean behaviour),  $\sigma = G_R (\lambda^2 - \lambda^{-1})$ , where  $\lambda = \frac{L}{L_0}$ . The present

simulation data at  $T = 260$  K give the value of  $G_R = 15$  MPa. The average value  $G_R = 13 \pm 3$  MPa over the range of temperatures from  $T = 260$  K to  $T = 480$  K is in excellent agreement with the experimental result of van Melick et al.<sup>9</sup>,  $G_R = 13$  MPa, produced by the uniaxial-compression measurement at  $T = 300$  K.

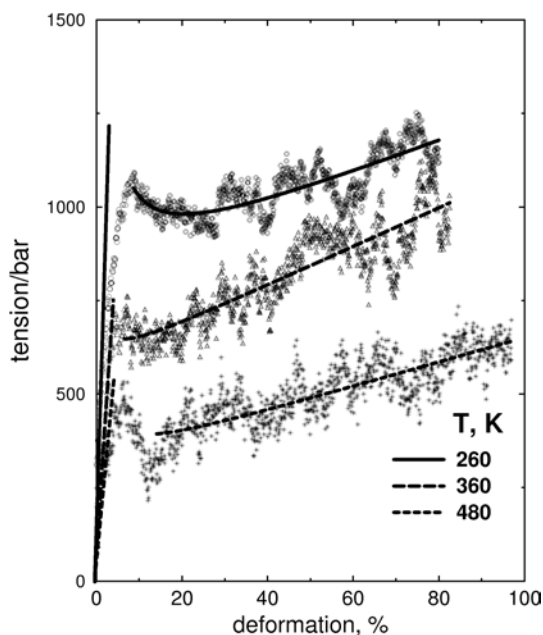


FIGURE 3a

Measured tension as a function of the percentage deformation. The data at each temperature represent the average behaviour over five independent samples and three independent directions of the deformation. Straight lines are drawn as a guide to the eye

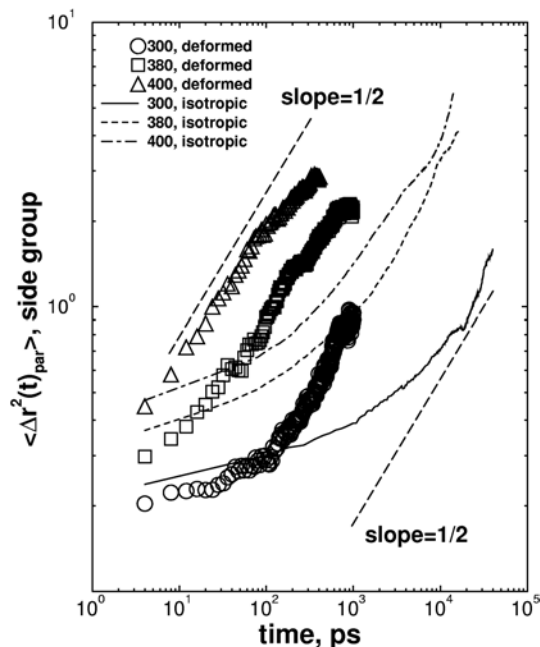


FIGURE 3b

The fluctuating Brownian contribution to the parallel mean-square translational displacement is shown together with the corresponding dependencies in the absence of the deformation. The onset of the Rouse regime in the direction of the deformation starts earlier as compared to the isotropic case. The perpendicular diffusion is weakly changed by the deformation

The uniaxial deformation of the PS sample leads to global orientation of the individual chains in the direction of the deformation. The onset of this orientation starts just after the yield point. The global orientation of the chains takes place together with a local ordering: the monomers in the backbone and the side-group vectors are oriented in the direction of the deformation, and perpendicular to it, respectively. At the same time, the planes of the individual phenyl rings are oriented perpendicular to the direction of the deformation.

To subtract the trivial effect of the convective translational motion due to the uniaxial extension and to reveal the effect of the deformation on the fluctuating Brownian

contribution to the translational mobility, the following procedure is implemented. First, for each bead of each chain in the polymer sample the average-in-time (for a time interval of 40 ps) position is calculated. The length of the time interval is chosen in order to have, on the one hand, almost constant average convective MSD over this time and, on the other hand, almost zero contribution of the stochastic term. The MSD of such averaged positions is then calculated, and is treated as a regular convective MSD. Subtracting this part from the total MSD gives a mean-square displacement due to the stochastic motion under the influence of the external deformation. Such “corrected” displacements are shown in Figure 3b, together with the MSD for the side groups in the isotropic sample at the same temperatures. It is clearly seen that the deformation does not influence significantly the translational mobility below the yield point (up to the deformation less than 3%). Dramatic changes occur in the post-yield behaviour: for the MSD in the direction of the deformation the onset of the “cage escape” starts significantly earlier as compared to the isotropic case, Figure 3b. At the same time the MSD in the perpendicular direction remains almost unaffected by the deformation. We conclude here that the uniaxial mechanical deformation leads to an anisotropy of the local translational mobility, with an acceleration of the parallel diffusion by more than an order of magnitude.

#### 4. CONCLUSIONS

We have performed molecular-dynamics simulations of the united-atom model of bulk atactic polystyrene, both in the isotropic state at atmospheric pressure and under the influence of the uniaxial deformation. It was shown that the determination of  $T_g$  from molecular-dynamics computer experiments is a useful procedure, in spite of the enormous difference of the time scale between the simulation and a real experiment.

Translational mobility has been investigated by using the mean-square displacements of different beads. The slowing down near  $T_g$  of the translational mobility of the monomers in the chain is mainly explained by the existence and diffusion of cages formed by their almost frozen neighborhood. Onset of the second diffusion regime is associated with the escape of the particle from its cage. From the long-time asymptotics of the mean-square displacements the corresponding translational relaxation times  $\tau_{tr} = D_{\alpha}^{-1}$  were defined. The temperature dependence of these times is described by a power law with the exponent  $\gamma = 2.90$  and critical temperature  $T_c = 380$  K at  $T > T_g$  ( $\alpha$ -relaxation regime), in good agreement with the predictions of the MCT. At  $T < T_g$  the temperature dependence of



the characteristic “cage release” time is fitted by a simple activation law with the activation energy of about 30 kJ/mol for the main chain bonds and 39 kJ/mol for the phenyl groups.

Both the linear-elastic and the post-yield regime of deformation (up to 100%), have been simulated. The values of the Young modulus calculated from the initial parts of the stress-strain curves, are in a good agreement with the experimental data. The strain-hardening modulus is calculated from the slope of the stress-strain curves at large strains and is equal to  $G_R = 15$  MPa at  $T = 260$  K, even in quantitative agreement with existing experiments<sup>9</sup>. The fluctuating part of the mean-square translational displacements of the individual monomers, parallel to the direction of the deformation, increases strongly with deformation. At the same time the transversal displacements are weakly influenced by the uniaxial stretching.

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