Notes

Molecular-Weight and Cooling-Rate Dependence of Simulated T_g for Amorphous Polystyrene

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Received April 1, 2003

Revised Manuscript Received August 27, 2003

Simulated Model

The glassy state of matter and the glass transition itself are still great, unsolved problems in condensed matter physics. The glass transition is probably the most important property of amorphous polymers both practically and theoretically because it involves a dramatic slowing down in the motion of chain segments, whereas one can hardly see any accompanying change in the static structure. No general, unified analytical theory of this phenomenon is available yet. Dynamical computer simulations face up to the challenge of understanding the glass transition and the amorphous state of matter.

In the present Note we report on *NPT* molecular dynamics (MD) simulations of a united-atom model of amorphous atactic polystyrene (PS). Simulations have been performed at atmospheric pressure in the vicinity of the glass transition for two models: (i) a one-chain model (in a box with periodic images) of $N_p = 40$ ($M_w =$ 4300), $N_p = 80$ ($M_w = 8600$), and $N_p = 160$ ($M_w =$ 17 200) monomers, to study the molecular-weight dependence of the value of glass-transition temperature; and (ii) eight chains of $N_p = 80$ monomers each in the simulation box. Model, force field, and other parameters of the simulation have been described already in previous publications.[1,2] The systems have been cooled with different cooling procedures and rates from the initial high-temperature liquid state at $T = 650$ K.

For the one-chain model, the cooling has been performed quasi-statically; starting from the well-equilibrated initial melt the steps down in temperature (10−20 K) have been performed subsequently, allowing for sufficient relaxation (up to 20 ns, while monitoring the fluctuations of the density) before the next temperature step is taken.

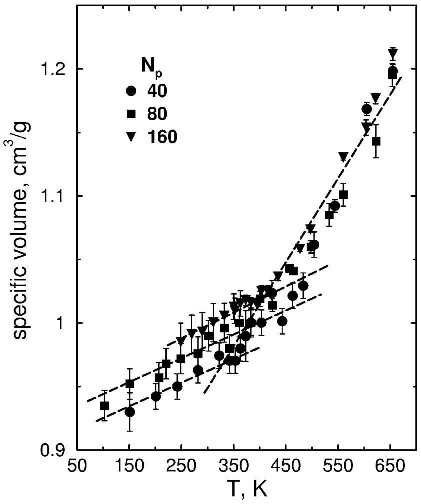

Figure 1. Temperature dependence of the PS specific volume for one-chain systems with $N_p = 40$, 80, and 160 monomers, produced with stepwise cooling. Dashed lines represent the least-squares fits of data at high temperature and low temperature.

Results and Discussion

Molecular-Weight Dependence of Simulated T_g. Figure 1 shows the results for the temperature dependence of the specific volume for three different molecular weights. The specific volume decreases almost linearly at both high and low *T* with decreasing temperature. At high temperature, the values of the specific volume for different samples are close to each other. The clear change in the thermal expansion coefficient occurs at $T \sim 400$ K and serves as an indication of the glass transition.

The simulated data were fitted by straight lines using a least-squares fit. Data above $T = 400$ K and below $T = 350$ K were used to produce high-temperature and low-temperature fits. The high-temperature fits were further averaged for all molecular weights used in the present study. The intersections of the high-temperature and the three low-temperature fits have been used to determine the glass-transition temperatures: $T_g =$ 360 K ($N_p = 40$), $T_g = 375$ K ($N_p = 80$), and $T_g = 420$ K ($N_p = 160$). Standard pressure−volume−temperature measurements[3] for atactic PS of $M_w \sim 9000$ (close to $N_p = 80$) give $T_g = 370$ K. Clearly, the simulated value of T_g increases with molecular weight, but the quite big error bars (about 15 K) and only three different molecular weights do not allow making any quantitative comparison with the Fox−Flory[4] dependence.

Cooling-Rate Dependence of Simulated T_g. The dependence of T_g on the cooling rate has been determined experimentally[5] for some metallic glasses and polymers (poly(methyl methacrylate), polycarbonate resin). Assuming that the relaxation time of the system follows a Vogel−Fulcher dependence on temperature,

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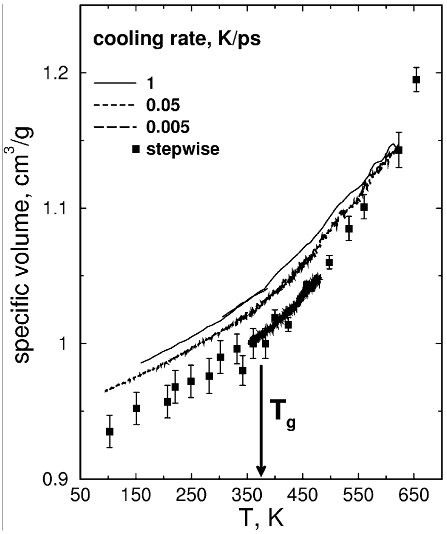

Figure 2. Temperature dependence of the specific volume for a system of eight PS chains with $N_p = 80$ monomers each, produced with stepwise cooling and with different continuous-cooling rates. The arrow indicates the simulated value of T_g (375 K) obtained from the stepwise cooling.

it was found that the glass-transition temperature logarithmically increases with cooling rate γ[5,6]

$$T_g(\gamma) = T_0 - \frac{B}{\log (A\gamma)} \tag{1}$$

This fact was confirmed later by Monte Carlo and MD simulation of model low-molecular-weight and model polymer glasses.[6-8] Stepwise cooling (from a higher temperature to a lower one and equilibration for a few nanoseconds) has been performed by MD in ref 9 for four polymers, *cis*-poly(1,3-butadiene), polyisobutylene, atactic polypropylene, and polystyrene (PS), based on a one-chain model. It was generally concluded that the values of T_g determined from MD simulations are displaced, as expected, to somewhat higher temperatures than the longer-time experimental values, but the displacements are minor.

For the one-chain and many-chain models of atactic PS with $N_p = 80$ monomers, we have performed both the stepwise cooling, from an initial temperature $T \sim 650$ K to a lower one with equilibration from 10 to 20 ns, and linear-in-time cooling with different (over several orders of magnitude, from 5×10^{-3} to 1 K/ps) cooling rates (Figure 2). The stepwise cooling with the steps down in temperature (about 10 K) followed by the equilibration of ~20 ns gives an effective cooling rate of 5×10^{-4} K/ps. The values of T_g produced by different continuous-cooling procedures are displaced toward higher temperatures as compared to the experimental value of $T_g = 370$ K. At the same time the stepwise procedure gives $T_g = 375$ K, quite close to the value from experimental *PVT* data for amorphous PS of the same molecular weight. Higher-temperature parts of the specific volume vs temperature curves produced with different cooling rates are indistinguishable within statistical error. A fit to the data with the functional form given by the eq 1 is shown in Figure 3. We see that the fit represents the 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, but as correctly mentioned by Baschnagel et al.,[7] such an extrapolation should be viewed with some caution because the scale of the available time window used for this extrapolation lies in the range of nanoseconds, with a time-dependent viscosity that is many orders of magnitude smaller than that of experimental time scales.

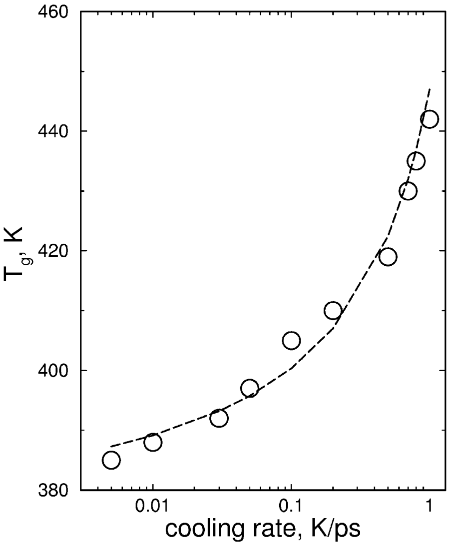

Figure 3. Cooling-rate dependence of the simulated T_g obtained with different cooling rates. The dashed line represents the best fit to eq 1, with $A = 0.23$ ps/K and $B = 110$ K. The fitted value $T_0 = 371$ K could be interpreted as a value for the glass-transition temperature in the limit of extremely (i.e., realistically) slow cooling.

In conclusion, we can say that the determination of T_g from molecular dynamics computer experiments is a useful procedure, despite the enormous difference of the time scale between the simulation and a real experiment. Stepwise cooling (performed with effectively lower cooling rate) produces values of T_g closer to the experiment than continuous cooling.

Acknowledgment. The authors acknowledge discussions with prof.dr.ir. L. C. E. Struik which inspired them to the present study. This work is the part of the research program of the Dutch Polymer Institute.

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MA034406I