Glass Transition Temperatures of Polymers from Molecular Dynamics Simulations

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ABSTRACT: Progress has been made recently in using molecular dynamics (MD) simulations to generate *PVT* properties of amorphous polymers. In the present work previous MD simulations of $V-T$ curves for several polymers are extended to lower temperatures, including through the glass transition. It is demonstrated that these $V-T$ curves can be used to locate volumetric glass transition temperatures (T_g) reliably. Four polymers, namely, *cis*-poly(1,3-butadiene), polyisobutylene, atactic polypropylene, and polystyrene were studied, and previously determined MD data for polyethylene (PE) are available. The T_g values span a range of 200 K, from 170 to 370 K. The values from the MD $V-T$ curves tend to be displaced, as expected, to somewhat higher temperature than the longer time experimental values. However, the displacements are minor compared to the range of T_g values considered. Determination of T_g from MD simulations appears to be a practical procedure. The relation of the MD-determined T_g of wholly amorphous PE to experimental values in the semicrystalline environment is discussed.

I. Introduction

Amorphous polymers constitute a large class of polymeric materials. The most important single descriptor of such polymers is the glass transition temperature, T_g. The value of this parameter determines the type of use. Values of T_g well below room temperature define the domain of elastomers; values well above room temperature indicate utilization as rigid structural materials. Obviously the ability to predit T_g values from the chemical structure of the polymer repeat unit would be of great value in the selection and design of new materials.

There has been a recent surge of interest in using molecular simulation techniques to determine the structure and properties of amorphous polymers.[1,2] In our own work we have been using the molecular dynamics (MD) method to model the equation-of-state (*PVT*) properties of these polymers.[3–6] One of the motivations for our work has been to provide reliable modeling of amorphous polymer matrices in order that diffusion of penetrants through them could be studied. In carrying out this work, it has become evident that good representations of the volume vs temperature curves of a number of polymer melts could be effected from simulation. The interesting question then arises as to whether the $V-T$ curves can be extended to lower temperatures in order to locate volumetric glass transitions and if transitions thus located can be favorably compared with experiment. For amorphous polyethylene (PE) it is known that MD simulations do show a volumetric glass transition.[4,5,7,8] However, the issue of the comparing the MD values with experiment is greatly complicated by the fact that PE is actually a semicrystalline polymer. Thus the reliability of MD predictions in this case is not known. In the present work we consider other polymers we have studied and extend the $V-T$ simulations to lower temperature to search for the glass transitions. The polymers included are *cis*-poly(1,3-butadiene) (*cis*-PBD), polyisobutylene (PIB), atactic polypropylene (aPP), and (atactic) polystyrene (PS). Experimentally, the T_g values range over a 200 K interval, from 170 to 370 K. PBD is a well-known elastomer, aPP is at room temperature a tacky adhesive, and PS is a rigid structural material. PIB represents the curious "vinylidene" effect where the T_g of the disubstituted polymer is markedly lower than the monosubstituted counterpart (in this case aPP). Thus the ability to determine the T_g values of these polymers would demonstrate the usefulness of simulation for discriminating between polymers covering a wide range of material properties.

It is well at this point to consider what is implied by experimental T_g values and what would be the likely outcome of successful MD simulations. Vitrification and the glass transition are characterized by the relaxation times for many physical properties becoming extremely long in a non-Arrhenius fashion as temperature decreases. Experiments directed toward T_g determination typically monitor property changes over a time scale that corresponds to the order of seconds or minutes. Because the relaxation times are very sensitive to temperature in this region, the precise time scales of various experiments result in only relatively minor differences in T_g values. Without specifying cooling rates T_g values from different methods often agree to within a few degrees. In volumetric measurements, extending the time scale from the minutes–seconds regime to hundreds of hours can lower the apparent T_g by 5–10 K.[9] MD simulations correspond to much shorter time scales than the typical experiments. Systems are cooled from a higher temperature to a lower one and allowed to equilibrate for a period of time that corresponds to a few nanoseconds. Thus if MD simulations correctly represent the equilibrium melt and the onset of vitrification at this time scale, the volumetric T_g values still can be expected to be displaced upward in temperature from typical experiments (Figure 1). It is not known how large this displacement would typically be. This is one of the points under investigation here.

II. Simulation Details

The details of the MD simulations of the melts of the polymers considered here have all been or will be shortly described elsewhere (*cis*-PBD,[10] PIB,[3] PE[4,5] aPP,[6] PS[11]). Briefly, these simulations use the Nosé constant particle number,

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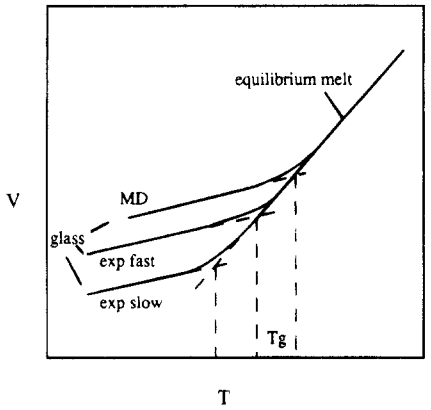

Figure 1. Schematic rendering of the effect of cooling rate or isothermal equilibration time on T_g as determined from $V-T$ cooling curves. The results of MD simulations should be expected to give higher values than either "fast" or "slow" dilatometric experiments.

pressure, and temperature (*NPT*) ensemble method[12] to generate $V-T$ curves at zero pressure (indistinguishable from 1 atm). A united atom ("UA") representation is used for $-CH_2-$, $-CH_3$, =CH, and C(aromatic)−H groups. The further variation of introducing an offset in the center of the potential from the carbon atom (anisotropic united atom, "AUA" potential) is also employed.[13] The nonbonded potential parameters have been adjusted to represent *PVT* data for the melts. The development of these potentials and the parameter values are reported separately.[3-6,10,11] In computing the energy, forces, and pressure, the complete untruncated nonbonded potentials are used. This is accomplished by using a large cut-off radius (9 Å) for the nonbonded lists and making continuum corrections beyond the cutoff.

Each of the systems consisted of a single chain. For PE, PIB, and PBD there were 768 carbon centers and thus the molecular weights were slightly over 10 000. For aPP 768 centers were used also but the CH group was represented as explicit atoms and so there were 576 carbons and a molecular weight of ~8000. For PS the aromatic ring CH is a UA group, but, as in aPP, the main-chain CH groups are explicit atoms. The chain is comprised of 80 monomer units and thus has a molecular weight of ~8000.

The volumes at a given temperature were generated by cooling the systems from the next higher temperature. After setting a new temperature in the *NPT* algorithm, the rate of cooling is determined by the thermal mass parameter. If the parameter is set too high, the adjustment is sluggish. If it is too low, fast response ensues but excessive fluctuations in the measured temperature result. Values of the parameter were selected to give reasonably fast response and acceptable fluctuations. Similar considerations apply to the inertial mass parameter that maintains constant pressure. The parameter is selected to give a fairly fast response to the volume when temperature is changed but reasonably small fluctuations in the volume.

The calculations were performed on a IBM 3090 computer and also on IBM RS6000/560 or RS6000/370 workstations. The CPU time per time step was 0.08 s on the workstations. The time step was 1 fs.

III. Results and Discussion

Volume versus Time. In the work here on glasses the MD runs on the melts were extended to lower temperatures and in general run longer. Results showing the dependence of volume on time for PIB are given in Figure 2. The volume equilibrates rapidly at temperatures 300 K and above. However, as the temperature is lowered, an initial rapid drop in volume is followed by a long-time downward drift. The initial drop is algorithm dependent in that the *NPT* method utilizes thermal and inertial mass parameters to establish

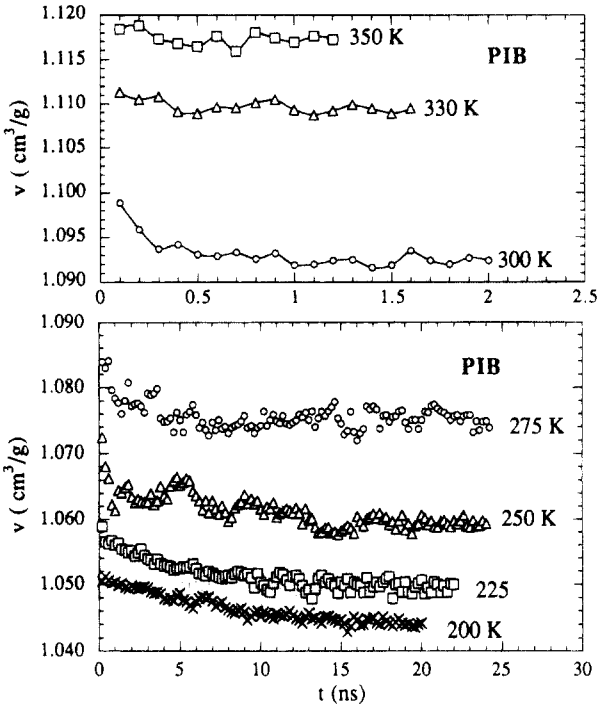

Figure 2. Specific volume vs time for PIB at various temperatures. The points are 100-ps interval averages from MD runs.

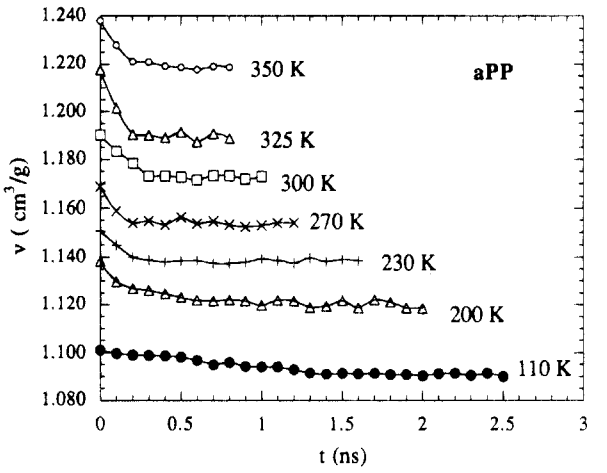

Figure 3. Specific volume vs time for aPP at various temperatures. The points are 100-ps interval averages from MD runs.

constant P,T conditions. The longer term drift appears to be a physical effect occasioned by the densification of the system much like that observed in experimental studies. These results are similar to the volume−time effects seen by us previously in PE.[5] The other polymers here were not run as long. This was the result of the desire to save computation time and the observation that the T_g values were not highly dependent on the long-term drifts. The data for aPP is shown in Figure 3 and that for PS in Figure 4. In Figures 2−4 the volumes displayed are 100-ps time interval averages. Thus the volume fluctuations in the *NPT* method are largely smoothed out. For most of the curves the entire trajectory is shown. That is, the curves display, within the limitations of the smoothing, the response starting from the higher temperature. For *cis*-PBD, the volumes were recorded only after an initial constant T,P equilibration period of at least 0.5 ns. Volumes over comparatively short time intervals after this equilibration period are shown in Figure 5. The volumes are 10-ps

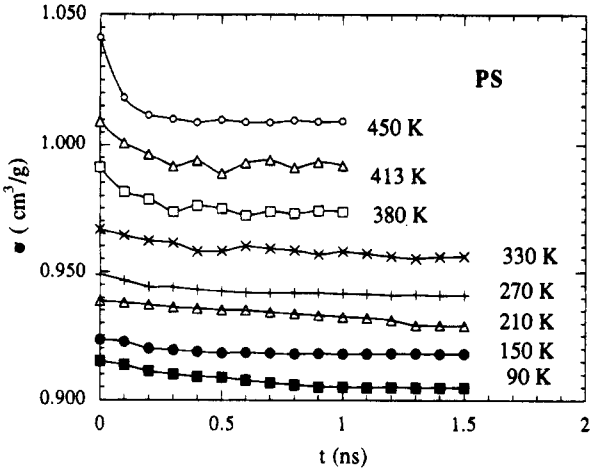

Figure 4. Specific volume vs time for PS at various temperatures. The points are 100-ps interval averages from MD runs.

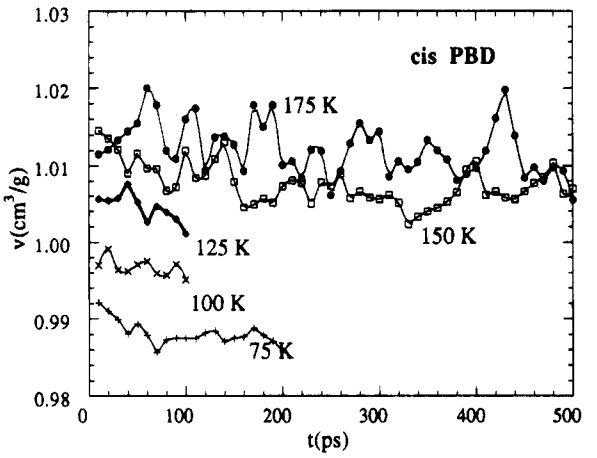

Figure 5. Specific volume vs time for *cis*-PBD at various temperatures. The points are 10-ps interval averages from MD runs. Each of these runs was preceded by an isothermal equilibration period of at least 500 ps.

interval averages, and the fluctuations are more apparent on this scale.

T_g from Volume versus Temperature. The volumes at the longest times in runs such as those in Figures 2–5 and from previous work for PE[5] are plotted against temperature for *cis*-PBD and aPP in Figure 6 and for PE, PIB, and PS in Figure 7. The higher temperature MD points for each polymer were smoothed visually by a straight line (displayed as thin solid lines). Similar smoothings of the lower temperature MD points are shown as dashed lines. The intersections of the smoothing lines are marked as "T_g". Also shown in Figures 6 and 7 are available experimental data for *cis*-PBD,[14] PIB,[15] PE,[16] aPP,[17] and PS[18] (heavy lines).

As indicated in the Introduction, this work was motivated in part by the fact that potentials could be calibrated that give good results in MD simulations for the $V-T$ curves of melts. The level of this agreement may be seen in Figures 6 and 7 by comparing the MD points with the heavy lines. In the case of PS it appears that the volume below T_g is also well represented by the simulation. For aPP the experimental data show T_g but the temperature range is not enough to establish a reliable slope for the glass.

Comparison of T_g with Experiment. The MD-determined T_g values are compared with experimental values in Figure 8. The latter were taken from the *Polymer Handbook*.[18] In some cases a range of experimental values is given. These are indicated by con-

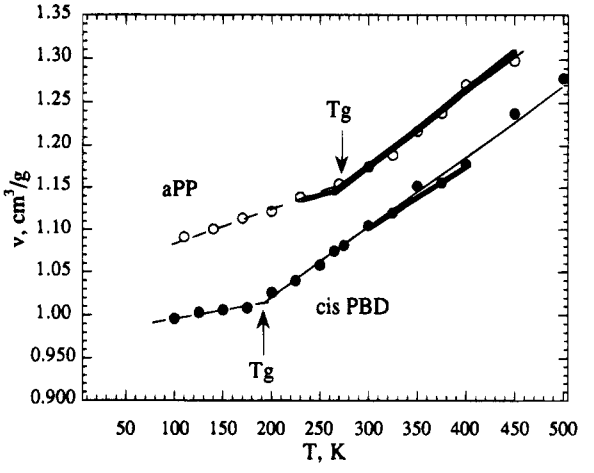

Figure 6. Specific volume vs temperature for aPP and *cis*-PBD. The points for aPP are from the longest times in volume vs time MD runs; for *cis*-PBD they are averages over the last 100 ps (see Figures 3 and 5 for typical data). The thin solid lines smooth the MD data at higher temperatures, and the dashed lines smooth the data at lower ones. The intersections of these lines define the MD T_g. The heavy lines are experimental data.[14,17]

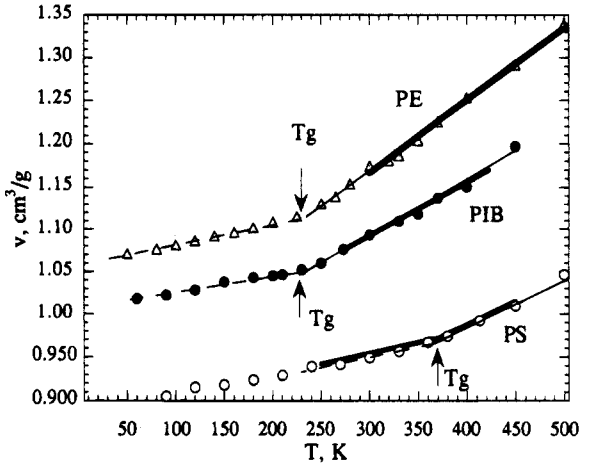

Figure 7. Specific volume vs temperature for PE, PIB, and PS. For PIB and PS the points are from the longest times in volume vs time MD runs (see Figures 2 and 4 for typical data). For PE the points are from ref 5. The thin solid lines smooth the MD data at higher temperatures, and the dashed lines smooth the data at lower ones. The intersections of these lines define the MD T_g. The heavy lines are experimental data.[15,16,18]

nected points. It may be seen that there is a tendency for the MD T_g values to be higher than the experimental ones, especially at lower temperature. The deviation is about 15 K for PBD and 22 K for PIB. The tendency for higher deviations at lower temperature is probably the result of the correlation between T_g and the activation energy for relaxation times. Generally activation energies increase with T_g over a group of polymers. The greater temperature dependence for high T_g polymers results in a smaller temperature change required to effect the same relaxation time shift in a low T_g polymer. However, the results for PS show essentially no difference between the MD and experimental values. This may be due in part to a compensating effect of the molecular weight in the system modeled by MD. The molecular weight is ~8000. This is sufficient in PS to lower the T_g by ~12 K.[19]

T_g of Polyethylene. Due to the semicrystalline nature of PE, the issue of its T_g is complicated. This is definitely a side issue in the present work. However, since the MD results are available, the connection with

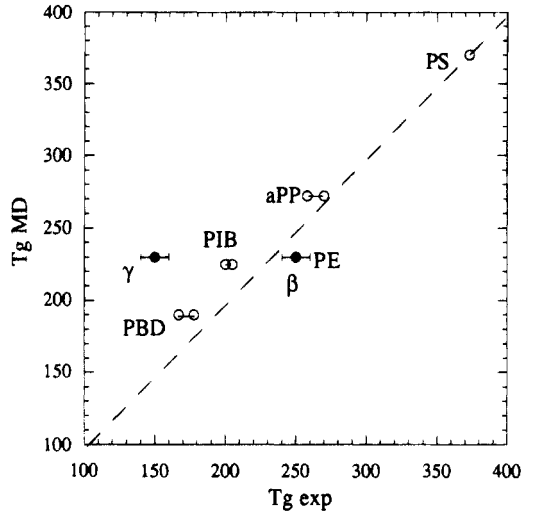

Figure 8. Glass temperatures from MD (Figures 6 and 7) plotted vs experimentally determined values (open circles). The dashed line is the 45° diagonal (T_g MD = T_g exp). For PE the experimental values are from the semicrystalline polymer. Points (filled circles) and intervals are shown for both the γ and β loss peaks (at 1 Hz) in BPE. The points represent typical mechanical and dielectric loss data.

experiment deserves comment. As with most crystalline polymers polyethylene is actually semicrystalline and has an amorphous fraction. The amorphous fraction in such polymers shows a glass transition. However, its nature is strongly influenced by its occurrence in the semicrystalline environment.[20] The most dramatic effect is that the relaxation region is greatly broadened over the corresponding region in the wholly amorphous counterpart. The relaxation time distribution is immensely broadened by the restraints placed by the amorphous phase chain segments being attached to the crystal surfaces. Generally there is also a shift in the apparent T_g to higher temperature. Thus, in principle, the glass transition region can be identified by dynamic mechanical or dielectric relaxation spectroscopy and a T_g value appropriate for the *semicrystalline environment* can be established. The MD results, of course, apply to a free *unconstrained* amorphous phase.

In PE the situation is further complicated by the fact that there are a total of three relaxation peaks (α, β, γ).[20,21] The α process is associated with the crystal phase. The β and γ processes arise in the amorphous fraction. Because of its breadth the β process is poorly resolved from the α and γ processes. In linear PE (LPE) the β process is difficult to observe,[20,22] but it is much more prominent in branched PE (BPE). The most straightforward interpretation of the β and γ processes is that the β peak represents the glass transition region and the γ peak is a subglass local motion process. Because of the poor resolution of the β process in LPE, some workers have preferred to consider the better resolved γ process to be the glass transition region. The approximate locations of both the β and γ peaks at low frequency (1 Hz) in BPE[20-22] are shown in Figure 8. It may be seen that the MD location of T_g falls between the two peak locations. But, especially if allowance is made for the experimental value for the amorphous phase in the semicrystalline environment being higher than for the unconstrained amorphous phase, it would seem that the MD T_g value is more consistent with the β peak interpretation.

Conclusion. It appears that MD-produced $V-T$ curves are useful in locating glass transition temperatures. Further it seems that the upward temperature displacement due to the MD time scale is small enough that it should be possible to make useful materials predictions using simulation techniques. A structure–property oddity such as the vinylidene effect in PIB vs aPP is reproduced. Since the calculations made here can be made on current generation workstations, it seems reasonable to anticipate that, although the calculations are numerically intensive, they are quite practical and will be more so in the future. A more serious impediment will be the development of reliable potential function parameters for a variety of polymers.

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