Methods of Generating Dense Relaxed Amorphous Polymer Samples for Use in Dynamic Simulations

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ABSTRACT: A comparison is made between different methods of generating relaxed dense amorphous systems of model linear polymer chains. One of these, referred to as phantom chain growth (PCG), has many advantages when compared with self-avoiding random walk procedures. In PCG chains are grown under non-excluded volume conditions such that successive torsion angles in a chain occur with a probability which is related to immediately adjacent torsion angles only. Van der Waals potentials are then introduced, and the structures are dynamically relaxed using loose-coupling, constant-pressure molecular dynamics. We report a series of experiments on a polyethylene-like polymer designed to test the effect of preparational history and heat treatment on the relaxation of the amorphous samples. It is shown that at 500 K a preparational history dependence can be detected but this can be removed using heat treatment. At lower temperatures, below the glass transition temperature, major difficulties are encountered in observing universal behavior.

1. Introduction

There is a growing interest in the atomistic dynamical modeling of dense amorphous polymers using energy minimization[1] or molecular dynamics (MD) simulation.[2,3] The main aim of these studies is to provide understanding of the bulk mechanical properties of these materials in terms of chain motions and interchain forces. There is a clear long-term objective of contributing to the accurate prediction of properties without resort to expensive synthesis and testing procedures.

One basic problem in the dynamic modeling of polymers is that configurational fluctuations in these materials can span many decades of time. Conformational fluctuations, for instance, may occur in the nanosecond regime for fairly flexible chains whereas the longest relaxation time in a polymer melt for a chain with molecular mass of ~10 000 can be of the order of seconds.[4] Diffusional motions of fairly short chains are accessible to dynamical simulations only by using coarse-grain models.[11] Atomistic molecular dynamics simulations are limited by current computing resources to times of order nanoseconds; thus it is quite clear that equilibrium MD simulations of relatively high molecular weight polymer melts, where the chains explore a significant amount of the available configurational space, are not feasible.

The situation in glassy amorphous polymers is different since here both diffusional motion and, to a large extent, conformational fluctuations are frozen out. What one then observes as a polymer melt is cooled, for instance, depends on the time scale of the experiment. If it is performed sufficiently slowly, then changes in properties will be observed at the glass transition which arise as first diffusional motions and then conformational motions are frozen out (for some materials these effects are sufficiently distinguished that they give rise to separate liquid–rubber and rubber–glass transitions). If the cooling is performed rapidly, as in molecular dynamics simulation, then the material is already configurationally arrested on the time scale of the experiment and only the conformational motions will be frozen out. The latter transformation has already been observed in previous simulations;[2] the cooling rates were much higher (of order 10^{12} K s^{-1}) than could be achieved in even the fastest laboratory splat-quenching experiments but nevertheless the procedure was well-defined. It has been shown[2] that the mechanical properties of glassy samples produced in this way bear a striking resemblance to those of real laboratory polymers.

In order to proceed therefore with atomistic-level dynamic simulations the essential starting point is an independent set of samples which are representative of configurations in the macroscopic material. The conformational properties should be consistent with statistical mechanical predictions and, where possible, with experimental data. Self-avoiding random walk procedures have been used previously[1,5,6] in attempts to grow entangled chains at the required density and temperature with realistic conformational and configurational statistics. These samples can then be relaxed at the same temperature using molecular dynamics[2] or molecular mechanics.[1] If the material is the melt the target equilibrium conditions (such as the conformational distribution) required for this sampling procedure are well specified.

In this article we introduce a new method for growing amorphous samples of polymer melts which can then be efficiently and economically relaxed at a specified temperature and pressure using molecular dynamics. During chain generation we have assumed, following Flory,[7] that successive torsion angles in a chain occur with a probability which is related to immediately adjacent torsion angles only. All long-range van der Waals interactions are ignored except those between sites separated by three others, i.e. the so-called "pentane" effect. This provides the necessary weighting which mediates against the occurrence of unlikely torsion angle pairs. We refer to this method as phantom chain growth (PCG); once a configuration has been produced the long-range van der Waals interactions are introduced and the structure is allowed to relax to mechanical equilibrium. We show that the new method offers a significant improvement upon self-avoiding random walk routines which lead to nonuniform distributions of conformational states. We also show that it is possible to build structures directly within the glassy state at lower temperatures, although in this case it is difficult to predict the conformational distribution a priori since it is inherently nonequilibrium and depends in reality on the exact thermal history of the sample. In the future it is possible that new efficient Monte Carlo methods could be used for sampling equilibrium melt configurations;[8] it is not clear however how such methods could be used to sample nonequilibrium states such as polymer glasses.

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For these simulations we have used a polymer model which has been previously described.[2,6] It consists of a linear polymer chain which forms dense and entangled amorphous systems through the replicative properties of periodic boundaries. The continuous chain is not confined to the primary sample cell but can span several neighbors; the model is that of a monodisperse polymer entangled with replicas of itself. For small numbers, N, of monomers there is no doubt that the model will give a poor representation of bulk behavior, but as N increases it is expected to give an increasingly better approximation to a macroscopic system. For a polymer resembling polyethylene it was found[2] that satisfactory results can be obtained with $N = 1000$.

In section 2 information concerning the choice of potential parameters and the simulation details are given. In section 3 we discuss the methods of sample preparation, and in section 4 the results of relaxation experiments are presented and discussed.

2. Details of the Model and Simulations

In the polyethylene-like polymer each of the 1000 monomer units is treated as a single site and is given a mass corresponding to that of a CH_2 group. Neighboring sites on the chain are connected together by rigid bonds of length $b_0 = 0.153$ nm. Flexibility of the chains is limited by incorporating a harmonic valence angle potential, $\Phi(\theta)$, and a torsional potential, $\Phi(\alpha)$, into the model, $\Phi(\theta)$ is of the form

$$\Phi(\theta) = {}^1/_2 k_\theta(\cos\theta - \cos\theta_0)^2 \tag{1}$$

where $k_\theta = 520$ kJ mol^{-1} and $\theta_0 = 112.813°$.

The torsional potential restricting internal rotations about a bond in the chain is parametrized in terms of the dihedral angle, α, formed by a central bond and the two adjacent bonds. The exact form used is that due to Steele[9] and is given by

$$\Phi(\alpha)/(\text{J mol}^{-1}) = C_0 + C_1\cos\alpha + C_2\cos^2\alpha + C_3\cos^3\alpha \tag{2}$$

where $C_0 = 8832$, $C_1 = 18087$, $C_2 = 4880$, and $C_3 = -31800$. We use a convention whereby the lowest energy conformation (trans) is characterized by a dihedral angle of $\alpha = 0$. The two equivalent gauche states, termed G^+ and G^-, occur in the region of $\alpha = \pm 120°$.

Finally, nonbonded monomer interactions, i.e. those between sites separated by at least three others, are represented by a Lennard-Jones (LJ) 12–6 potential

$$\Phi_{LJ}(r) = 4\epsilon\{(\sigma/r)^{12} - (\sigma/r)^6\} \tag{3}$$

with $\epsilon/k_B = 57$ K and $\sigma = 0.428$ nm. These parameters are the same as those given before[2] and give a reasonable fit to the density of real polyethylene at 500 K as obtained by extrapolating the data of Richardson et al.[10]

To perform the molecular dynamics we use a loose-coupling, constant-pressure MD technique, originally proposed by Berendsen et al.,[11] which we have adapted and extended for use on polymer samples. The implementation of this technique has been described in detail elsewhere.[12] The temperature was also controlled using the constant-temperature, loose-coupling method previously discussed[7,8] with a coupling constant τ_T of 0.1 ps.

The LJ 12–6 potential was truncated at $r_c = 2.5\sigma$, and the appropriate long-range corrections were made to the potential energy and the virial at each step according to the density and assuming $g(r) = 1$ for $r > r_c$. A check was also made at each step to ensure that the perpendicular distance between any of the opposite faces of the primary cell did not drop below $2r_c$. This is important as the cell can distort significantly away from its cubic origins, especially when subjected to anisotropic pressure fields. To calculate the LJ interactions more efficiently a standard Verlet neighbor list technique[13] was used. Further details of how this was implemented and optimized have already been given.[8]

The bond constraints were maintained to a relative tolerance of 10^{-6} using an iterative scheme. The reconciliation of using a constrained bond length in a simulation where coordinates are constantly being rescaled to facilitate changes in the shape and size of the primary cell has been addressed previously[7] and is discussed in great detail in ref 8. Further tests of the basic algorithm are given in ref 2.

All the simulations were performed either on the Amdahl VP1200 at the Manchester Computing Centre, using programs optimized to take advantage of its vector architecture, or on a Silicon Graphics 260 GTX Power Series machine. Each time step consumed approximately 0.054 s of CPU time on the VP. The corresponding CPU time for code scalar optimized to run on one processor of the SG 260 GTX is ~2.2 s.

3. Methods of Sample Preparation

There are two stages to the preparation of amorphous samples. First we have to generate an initial set of coordinates for the positions of the N sites of the chain. Second these initial configurations are dynamically relaxed to give samples at mechanical equilibrium.

Two methods have been compared for generating initial chain configurations and both utilize modified random walks carried out within the confines of periodic boundary conditions. The first method (EV) is the same as that used previously[4] and employs sequential site-by-site generation of the linear chain incorporating realistic excluded volume and intramolecular potentials. In the second method growth takes place in the same way as for EV except all excluded volume effects are ignored apart from those between sites separated by three others, i.e. the so-called "pentane" effect. Both methods employ a simple Monte Carlo acceptance criterion applied successively at the addition of each monomer in the chain.

3.1. Growth Including Excluded Volume (EV). In the EV method, a new proposed site is generated by choosing an intended dihedral angle (α) using a random number generator. The coordinates of the next site, $\mathbf{r}_{i+1}$, are calculated using the equilibrium bond length b_0, the equilibrium valence angle θ_0, and the coordinates of the three previous sites. The total energy change, $\Delta\Phi$, resulting from the introduction of this site is then determined by summing all new interactions (using the minimum image convention) and adding to this the new contribution to the dihedral angle energy $\Phi(\alpha)$. The probability of this energy change is calculated from the Boltzmann factor, $\exp(-\Delta\Phi/k_BT)$, and a comparison between this value and a random number between 0 and 1 is then made. The new site is accepted only if the random number is less than the Boltzmann factor; otherwise a new proposed site is generated. Should repeated trials (50) fail to find an acceptable position for the new site, the chain is shortened by one site and the process starts afresh by attempting to generate a new $\mathbf{r}_i$ and if successful a new $\mathbf{r}_{i+1}$. If again a suitable $\mathbf{r}_{i+1}$ cannot be found, then the chain is shortened this time by two sites and so on until a route circumventing the obstruction is found. The process stops when all N sites have been placed.

It is important to eliminate all high-energy contacts prior to starting the molecular dynamics; otherwise large forces lead to an immediate breakdown of the algorithm. With this method it is not practical to generate configurations at high densities. For the polymer model used here a reasonable choice for the initial density was found to be 0.5 g cm^{-3}. A more fundamental problem is that even at this low density there is an increasing discrimination against trans states as the growth proceeds. It was to avoid these problems that we devised the PCG method of growing chains with a uniform distribution at an arbitrary density.

3.2. Phantom Chain Growth (PCG) Followed by the Introduction of Excluded Volume. An unavoidable side effect of phantom chain growth at melt densities is that there will be a large number of overlaps between sites. In principle, energy minimization could be used at this stage to remove the high-energy contacts. As this effectively means quenching the system to 0 K it could lead to a shift in the carefully prepared distribution of conformers. We thus prefer to maintain the system at the desired temperature using dynamic techniques. Any attempt, however, to begin the MD simulations using the full LJ potential with such configurations is doomed to failure due to the enormous forces generated.

Four methods were considered to resolve this problem. Each entailed substituting in the initial stages of the MD simulation, a potential much smaller in magnitude at low separations than the full LJ potential. Such an approach should permit the high-energy contacts to be relaxed away gently after which the full LJ potential could then be used. In each case during this initial stage the dynamics were run at constant volume. The first three methods involved moderating the interactions at short range via an adjustable energy parameter ϵ, which was gradually increased with time, in conjunction with the following forms of potential:

(i) the Lennard-Jones potential

(ii) a cosine potential, similar to that used by Kremer and Grest[14]

$$\Phi(r) = \epsilon(\cos\{2\pi r/d\} + 1) \qquad (4)$$

(iii) a purely repulsive quadratic potential

$$\Phi(r) = \epsilon(ar^2 + br + c) \qquad (5)$$

The first method was completely unsuccessful. The fundamental difficulty is to define an initially acceptable value for ϵ which allows the initial integration of the equations of motion with the desired time step but does not lead to further catastrophic overlaps.

Use of the cosine form for the potential also proved unsuccessful. At zero separation the potential is finite but unfortunately the force is also zero and some sites steadfastly refused to move apart. These sites nominally in metastable positions must be in some way stabilized by their near neighbors.

The method employing the quadratic potential was successful at moving sites apart but proved very awkward to use when the transition to the full LJ potential was attempted. The instantaneous change in potentials frequently caused breakdowns in the integration algorithm. The problem could be circumvented by temporarily reducing the time step but this could not easily be automated and consequently this method was considered unsuitable.

The most successful method utilized a modified version of the LJ potential, Φ_{mLJ}. This potential has a form that is a result of constraining the force from the LJ potential to be constant below a critical separation r_{tr}, i.e.

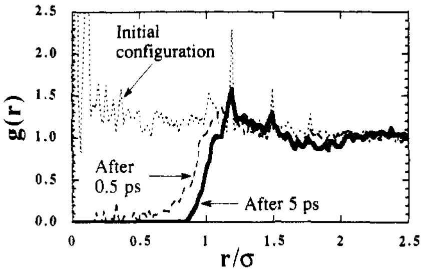

Figure 1. Typical radial distribution functions, $g(r)$, for sites separated by more than three other sites for chains generated using the PCG method. The functions were obtained at various times, t, after the introduction of the modified Lennard-Jones potential (see text for details): (a, dotted line) $t = 0$, (b, dashed line) $t = 0.5$ ps, and (c, solid line) $t = 5$ ps. The initial structure shows essentially uniform density due to the non-excluded volume growth method.

$$\frac{d\Phi_{\mathrm{mLJ}}(r)}{dr} = F_{\mathrm{tr}}\left(=\frac{d\Phi_{\mathrm{LJ}}(r_{\mathrm{tr}})}{dr}\right) \quad \text{for } r \le r_{\mathrm{tr}} \qquad (6)$$

The full definition of the resulting modified potential is then

$$\Phi_{\mathrm{mLJ}}(r) = \Phi_{\mathrm{LJ}}(r) \quad \text{for } r > r_{\mathrm{tr}} \qquad (7)$$

$$\Phi_{\mathrm{mLJ}}(r) = \Phi_{\mathrm{LJ}}(r_{\mathrm{tr}}) + (r_{\mathrm{tr}} - r)F_{\mathrm{tr}} \quad \text{for } r \le r_{\mathrm{tr}} \qquad (8)$$

The choice of r_{tr} is important; it must be sufficiently small so that only a few pairs will be within this distance in the equilibrium distribution (which at this stage is unknown), but not so small that the large magnitude of F_{tr} causes breakdown of the algorithm. For the work here a value of 0.85σ was found to be acceptable.

To automate the transition between the modified potential and the full LJ potential the changeover criterion was set to be the time at which the number of pairs separated by less than r_{tr} becomes less than 10. In fact this occurs very rapidly, usually within 2.5 ps (1000 time steps), and so far this approach has not failed at least for our model. For convenience we also used the same criterion to make the switch from constant-volume to constant-pressure dynamics. The sequence of pair distribution functions shown in Figure 1 clearly demonstrates the effectiveness of the last method for introducing excluded volume.

4. Dynamic Relaxation of Samples

We have recently discussed[2] the mechanical behavior of samples of the polymer model used here as prepared by the EV growth method. The results showed that, on the time scale of the simulations, the transformation from fluid-like to glassy behavior takes place between 400 and 300 K. We have therefore further examined the preparation and relaxation of polymer samples in both the fluid regime at 500 K and the glassy regime at 200 K.

To assess the relative merits of the methods we have measured as a function of time various properties of the systems. We have found that the most useful indicators of the degree of relaxation are the density and the proportion of trans conformers (since we use a continuous torsional potential a dihedral angle is deemed to be in the trans state if $-60° < \alpha < +60°$) and the discussion is limited to these properties. There is a strong correlation between the density and the nonbonded energy and between the trans fraction and the torsional energy.

The choice of the initial density for the introduction of excluded volume in configurations produced by the PCG

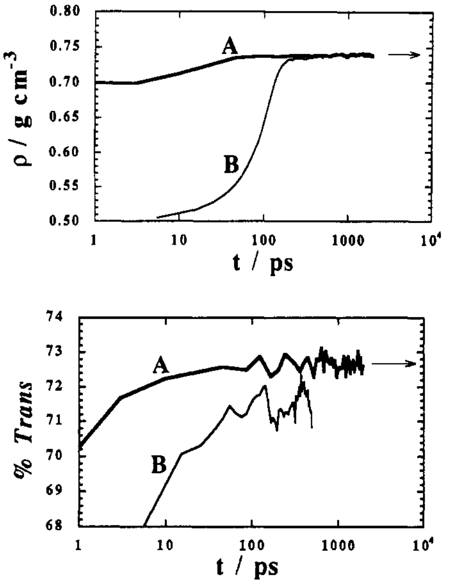

Figure 2. Average variation of (a, top) the density and (b, bottom) the percentage of dihedral angles in the trans state for the comparison of methods: (A) PCG and (B) EV at 500 K.

method is not so critical. It can be the final relaxed density of the model, if known. We show later that, within reason, the choice of initial density does not significantly affect the limiting value obtained by dynamical relaxation but a good initial guess can reduce the amount of time required to reach it. We have already mentioned above the practical restriction[2,4] placed on the starting density for the EV growth scheme.

4.1. Comparison of Relaxation for EV- and PCG-Generated Samples at 500 K. In Figure 2 the variation with time of the density, ρ, and the proportion of trans conformers are shown. In each case the functions are averaged over five independent samples. There are significant differences between results obtained using the two initial growth methods. In particular we point out the different rates at which both the density and trans fraction approach their long-time values. Within the statistical error the PCG-generated configurations are relaxed in less than 250 ps.

As pointed out above one problem with the EV method is the increasing discrimination against trans states due to excluded volume effects as chain growth continues. This is seen in the low value of the % trans in initial configurations: 59.6% averaged over five configurations compared with ~72.6% in the relaxed melt. Examination of the distribution of conformers along the chain shows that there is a monotonic decrease in the % trans from 68% at the start of the growth to 52% at the end. For our linear polymer model this nonuniformity is apparently removed by dynamic relaxation as there is no trace of it in the 500-ps configurations. The overall depression in the number of trans conformers is a possible cause for the slower relaxation properties of EV-generated samples mentioned above. The effect may be a more serious problem for chains where monomer motions are subject to a higher degree of steric hindrance.

Although the distribution of trans states is uniform along the chain in PCG, the overall fraction of trans states (67.3%) is still below that in the relaxed melt configurations. The reason for this is that the growth procedure used here samples a biased distribution of chains.[15] In practice this turns out to be not a problem at 500 K since the discrepancy is relaxed out quickly during the initial stages of the molecular dynamics (see Figure 2). To avoid the problem completely it would be necessary to sample chains from an unbiased distribution. This can be done by growing the entire chains randomly without applying the selection procedure at the addition of each site. For short chains this latter procedure is quite successful but for long chains we have found it completely impractical since the vast majority of randomly grown chains are of low probability due to the inevitable occurrence of 1–5 overlaps.

Since it is expected[7] that the configurational properties of chains in a pure melt should be the same as those in Θ solvent due to screening of all van der Waals interactions beyond 1–5, unbiased phantom chain growth (or RIS calculations using the correct statistical weights) should return the same conformational statistics as observed in the melt where there are interactions between all nonbonded monomer pairs. We have verified this hypothesis by comparing the conformational distributions in melts composed of chains of up to 100 segments using molecular dynamics with those obtained using unbiased phantom chain growth; the fractions of trans conformers agree well in the two cases. The data also extrapolate smoothly to the results shown in Figure 2 for the $N = 1000$ chains.[16]

For the five relaxed melt configurations radii of gyration can be calculated with reasonable accuracy from the dependence of the mean squared separation of sites i and j, $\langle R_{ij}^2\rangle$ against the number separation $|i-j|$. To obtain a set of statistically uncorrelated $\mathbf{r}_{ij}$ vectors it is necessary that the origin of each set is the end of the previous one, and since this depletes the data set rather severely for large $|i-j|$ attention was concentrated on values of $|i-j| \leq 100$. We have compared these data with the N dependence for chains obtained by the biased and unbiased phantom chain growth procedures;[16] all the data fit to the same line and this result not only confirms the expected statistical behavior of melt samples but also suggests that configurational properties are less sensitive to the details of the growth procedure than the conformational distribution.

4.2. Thermal and Preparational History Dependence at 500 K for PCG-Generated Samples. To test the extent of relaxation for the PCG-generated configurations we performed a parallel experiment in which a duplicated set of samples was subjected to a short period of heat treatment after which the temperature was returned to 500 K. It would be expected that the properties of the two sets should converge after some characteristic relaxation time.

The duplicate samples were taken at 1050 ps and heated from 500 K to 1000 K by changing instantaneously the temperature of the external bath in the loose-coupling algorithm. This high temperature was maintained for about 100 ps before returning it back to 500 K. Following this temperature cycle relaxation was continued for a further 850 ps at 500 K; the results are shown in Figure 3. These heat treatment experiments were carried out both at constant volume and at constant pressure, but since there were no significant differences between the final results obtained by the two methods only the constant-pressure data are discussed here.

When the temperature is raised it is seen that the trans fraction (and the density) drop very quickly toward much lower values. Although 100 ps may not be sufficient time for the samples to attain conformational equilibrium at 1000 K, when the temperature is returned to 500 K the system rapidly recovers and after about a further 400 ps the property values are comparable to those of the original unperturbed samples. We can thus be reasonably sure that growth procedure at 500 K does not "trap" the local

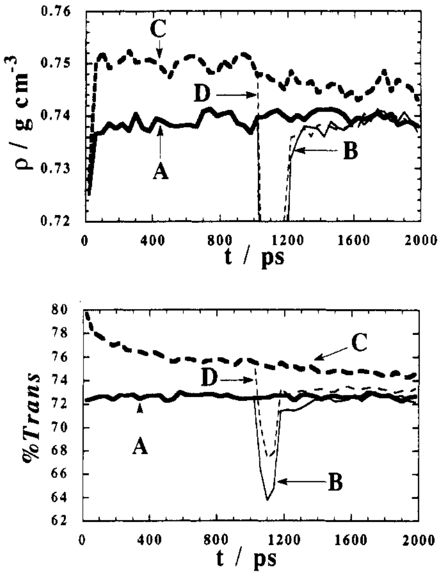

Figure 3. Effect of preparational history and constant-pressure heat treatment on the relaxation of (a, top) the density and (b, bottom) the % trans. The curves in both cases represent chains subject to the following history: (A) generation and relaxation at 500 K; (B) as (A) except heated to 1000 K for 100 ps at constant pressure; (C) generation at 200 K but relaxation at 500 K; (D) as (C) except heated to 1000 K for 100 ps at constant pressure.

chain configurations in some highly nonequilibrium state.

A more stringent test of the relaxation was to prepare samples initially in nonequilibrium configurations, e.g. containing a trans fraction well in excess of the equilibrium value. This was achieved by growing samples using the PCG method at 200 K but carrying out the relaxation at 500 K; the initial configurations contained about 14% greater amounts of trans conformers than at 500 K. The results for the variation in time of both the density and the percentage of trans conformers are shown in Figure 3.

In this case it is evident that relaxation toward the expected state is quite slow. After 1 ns, for instance, the proportion of trans conformers is still 4% in excess of the expected long-time value. We conclude that, as well as producing a different gauche/trans ratio, growth at 200 K also affects the structure on a more coarse grained scale. Even at 500 K the slow relaxation of the coarse grained structure seems to have a residual influence on the conformational equilibrium.

In exactly the same way as described previously a duplicate set of 200 K generated samples was heat treated, and the results are also shown by curves D in Figure 3. What is important for the present discussion is that upon reducing the temperature to 500 K both the proportion of trans conformers and the value of the density return to values characteristic of the fully relaxed configurations at 500 K on a time scale comparable to that seen for the previous heat treatment experiment. These results suggest that although preparational history can affect the properties of the polymer melt samples, to a large extent short periods of heat treatment allow the establishment of at least conformational equilibrium.

4.3. Attempts To Prepare Samples Directly in the Glassy State at 200 K.

In this section we explore the possibility of directly preparing glassy samples of a polymer at 200 K without resorting to computationally time-consuming cooling schedules from the melt. Direct preparation of glassy samples with relaxation by energy minimization has been attempted before in studies of polypropylene.[1]

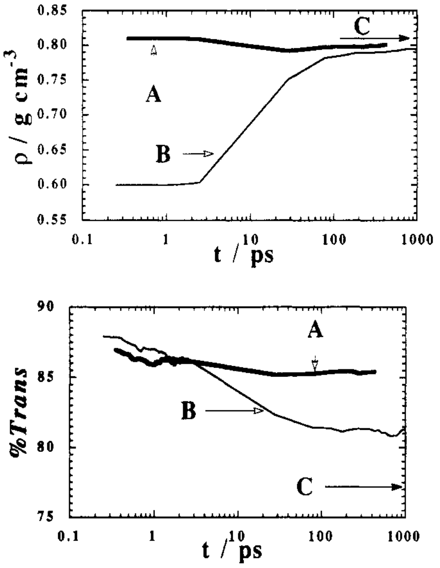

Figure 4. Effect of starting density at 200 K on the relaxation of (a, top) the density and (b, bottom) the % trans. The curves in both cases represent chains initially relaxed at densities of (A) 0.810 and (B) 0.6 g cm^{-3}. Note the logarithmic time scale. The arrows (C) in each case signify the values attained previously[2] via cooling from 500 K.

Two starting densities were employed: 0.81 and 0.60 g cm^{-3}. The first value is that which can be achieved by cooling of 500 K samples through the glass transformation region (~350 K). The second lower value was chosen for comparison with the aim of providing initial spare volume for conformational relaxation. The initially generated structures at the higher density do not however seem to be energetically favorable since there is actually a small but significant initial decrease in density which is not fully recovered. The low initial density samples behave somewhat differently; the proportion of trans conformers does show a sharp decrease and the probable explanation is that the rapid spontaneous densification provides some driving force for net conversion of trans to gauche states as the chains are crumpled into a more close packed state.

The results in Figure 4 show that relaxation of both the trans fractions and the densities to fairly constant values is reasonably fast. For both experiments the densities relax to values which are slightly less than that obtained by cooling.[2] In contrast the relaxed values of the trans fraction are quite different in the two experiments and both are significantly different from the value obtained by cooling. We believe that the explanation for this lies in the very long relaxation times for the coarse grained structure at this low temperature which, as in the case of the 500 K results, have a residual influence on the extent of conformational relaxation. The properties of these samples do not seem to correspond to anything that could be obtained from the melt by any simple cooling schedule.

In one further experiment we have subjected samples generated and relaxed at 200 K to heat treatment in an exactly analogous manner to that described before for the 500 K simulations. The results for the time dependence of the density and % trans are shown in Figure 5. It is notable that the density returns to the pre-heat treatment value when cooled back to 200 K. This is in contrast to the 500 K result where significant densification was observed and suggests that relaxation of the coarse grained structure is far too slow to be significantly affected by what is a fairly brief period of heat treatment. The trans fraction, however, is modified by heat treatment and indeed the relaxed value is very close to that obtained by

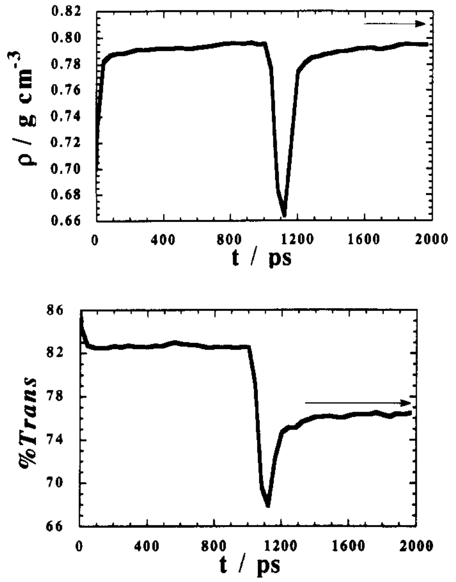

Figure 5. Effect of constant-pressure heat treatment on (a, top) the density and (b, bottom) the % trans for chains generated and relaxed at 200 K. The curves in both cases represent chains subject to heating at constant pressure for 100 ps to 1000 K starting at 1050 ps into the simulation. The arrows in each case signify the values attained previously[2] via cooling from 500 K.

cooling the material from the melt.[2]

5. Conclusions

At temperatures where the conformational relaxation times are short by comparison with the simulation time the phantom chain growth method followed by dynamic relaxation is effective and efficient for producing acceptable initial configurations with appropriate equilibrium conformational distributions.

The same method can be used to grow samples below the glass transition temperature but in this case the properties show a strong preparational history dependence and it is difficult to relate the sample properties to those obtained by cooling from the melt. The problem is that the nonequilibrium conformational distribution required for the growth procedure is difficult to predict a priori. One can use the equilibrium distribution at the temperature in question and relax the conformations using heat treatment. However, configurational relaxation times are so slow at these low temperatures that corresponding relaxation of the built-in coarse grained structure is difficult to achieve.

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