Effects of Chain Configurational Properties on the Stress–Strain Behavior of Glassy Linear Polymers

Jonathan I. McKechnie, Robert N. Haward, David Brown, and Julian H. R. Clarke*

Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.

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ABSTRACT: We have performed a systematic study of the relationship between polymer structure and the phenomenon of strain hardening by employing controlled stress molecular dynamics computer simulation in conjunction with a simple polyethylene-like model. We find that varying the sample preparational history produces materials which, while being chemically identical, differ profoundly in their response to an applied stress.

1. Introduction

The experimental interpretation of the large-strain behavior of glassy amorphous polymeric systems subjected to uniaxial tension remains problematic due to the tendency toward necking, shear banding, etc., which make true stresses and strains difficult to determine. Some progress toward obtaining true stress–strain curves has, however, been made, and links between chain structure and strain hardening have been examined. For example, Bosnyak et al.[1] copolymerized Bisphenol A to produce polycarbonates and polyphthalates of varying chain structure, as exemplified by the substitution of isophthalate for terephthalate monomers, in order to demonstrate a link between chain topology and large-strain behavior. Similar results have been obtained with polyisocyanates which have extremely large Kuhn lengths and pronounced strain hardening so that they extend uniformly without necking.[2]

On a phenomenological level the large-strain behavior of polymers has been rationalized in terms of mechanical models which comprise elements representing the Hookean, viscous, and rubber elasticity components of the stress,[3,4] and in this way a connection between the maximum in the extension ratio λ_{max} and the number of Kuhn lengths has been suggested. This concept has been further developed by Kramer and Donald,[5] who showed that the value of λ_{max} was a crucial factor in controlling the crazing process in glassy polymers.[6]

There is therefore considerable evidence for a link between the mechanical properties of a polymer and the underlying chain topology. However, in the laboratory it is difficult to alter the topology without changing the chemistry of the polymer and consequently there remains the problem of ambiguity in the interpretation of the mechanical experiments. In this paper we describe molecular dynamics simulations which are designed systematically to explore the way in which the stress–strain behavior of an amorphous, linear polymer glass depends on its configurational properties. One of the advantages of computer simulation is the ease with which the system parameters can be controlled, and we have utilized this approach to prepare samples of the *same* polymer with different configurational properties. In this way we are able to make a less ambiguous test of the predicted relations between the mechanical behavior and the configurational properties of a polymer glass. It must be emphasized that this control of the configurational properties is only possible for nonequilibrium states below the glass transformation where relaxation times are extremely slow. The realization of such experiments in the laboratory remains a difficult challenge for the experimentalist.

The model polymer on which we base these simulations has been described previously,[7] it resembles amorphous linear polyethylene, although the aim of the work was not primarily to reproduce the properties of any real material.

In principle, the configuration of a polymer is completely specified by the sequence of torsion angles, valence angles, and bond lengths. Such information is however quite intractable and not easy to interpret. Instead we have chosen to discuss two aspects of the structure, namely, the fraction of trans conformers and the persistence length which is a measure of the overall coil size. Both of these quantities are in principle accessible to experiment.

If we consider the ways in which an amorphous polymer can deform, then elongation can be achieved either by uncoiling of the overall structure or by lengthening the chains on a more local scale. This alternative "local" mechanism corresponds in our model to segments of chains being converted from the gauche ("short") form to the long ("trans") form; the latter is the lowest energy state and has a planar zigzag structure. It follows that chains which are either less coiled or contain fewer gauche states to begin with will be harder to deform.

In this paper then we describe the preparation of four sets of samples of the same model polymer with differing correlation lengths and fractions of conformers *at the same temperature and pressure*. We obtain stress–strain curves for these *chemically equivalent* samples by applying uniaxial tension. The results provide further evidence of the link between chain structure and mechanical properties.

To perform these simulations, we make use of a novel controlled-pressure molecular dynamics (MD) technique[8] which is an adaptation of the loose-coupling algorithm proposed by Berendsen et al.[9] It allows the shape and size of the primary MD cell to adjust to imbalances between an externally applied tensorial pressure field and that measured internally. As in our previous work[7] we use a model in which a single linear polymer chain of $N = 1000$ sites forms a dense amorphous polymeric system through the replicative properties of periodic boundaries. The continuous (primary) chain is not confined to the primary MD cell but can span neighboring cells. The model is therefore one of a monodisperse polymer entangled with replicas of itself. With $N = 1000$ the size of the chain

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* Author to whom correspondence should be addressed.

should be several times the entanglement length of this polymer.

The characterization of glass transformation for this model polymer has already been discussed in terms of its mechanical properties.[7] Only ultrafast quench rates currently are accessible to MD simulations, and at a cooling rate of order 10^{12} K s^{-1} the glass transformation occurs between 400 and 300 K. The relatively high temperature and the breadth of the transition can be related entirely to the very short time scale on which the glass is formed. At 200 K the mechanical properties are those expected of a glassy solid and the nonequilibrium proportion of trans conformers is completely frozen-in on the time scale of the simulations.

In the following section we give brief details of the potential parameters which define our model polymer. We proceed then to describe the method for preparing samples of the same polymer with different persistence lengths and fractions of conformers; this is done first in outline and then by giving the exact prescriptions. In sections 4 and 5 the results are presented and discussed.

2. Polymer Model

In our 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

$$\Phi(\theta) = \frac{1}{2}k_\theta(\cos\theta - \cos\theta_0)^2 \qquad (1)$$

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 this bond and the two adjacent bonds. The exact form used is that due to Steele[10] and is given as

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

where $C_0 = 8832$, $C_1 = 18\,087$, $C_2 = 4880$, and $C_3 = -31\,800$. Finally, nonbonded van der Waals interactions, i.e., those between sites separated by at least three others, are represented by Lennard-Jones (LJ) 6–12 potential between pairs of monomers with $\epsilon/k_B = 57$ K and $\sigma = 0.428$ nm.

Details of the simulation, potentials and parameters, have been given previously.[7]

3. Sample Preparation in Outline

The preparation of samples was based on a recently described method of directly generating dense entangled polymers.[11] There are four stages to the preparation: (1) generation of an initial set of coordinates for the N monomer sites (this is performed using phantom chain growth (PCG), so-called because all the van der Waals interactions are ignored except those between sites separated by three others, i.e., the so-called "pentane" effect); (2) introduction of van der Waals interactions; (3) dynamic relaxation of the samples at the desired temperature below the glass transformation; and (4) a (optional) short period of heat treatment at melt temperatures.

Step 1 largely determines the overall topology of the entangled polymer. Structure imparted at this stage is very difficult to modify on anything but a local scale using molecular dynamics. In PCG the monomers are added sequentially with a probability proportional to $\exp(-\zeta\Delta\phi/k_BT)$ where $\Delta\phi$ is the associated change in energy. There are only two components to $\Delta\phi$ arising respectively from the 1–5 direct interaction and the torsional potential. The value chosen for the parameter ζ determines the relative probabilities of different conformers, and this provides some degree of control over the configurational properties. A decrease in ζ can be thought of either as scaling down the potential energy at constant temperature or conversely raising the temperature at constant potential.

Step 2 removes overlaps between monomers, and it is at this stage that the density of the system becomes defined by the introduction of periodic boundaries.

Step 3 allows relaxation of the fractions of conformers and the establishment of local mechanical equilibrium. At temperatures below the glass transformation the long-range configurational properties are "frozen-in" and there is very little change in the overall topology during this phase of the preparation.

Step 4 can be used to change the fractions of the different conformers (which relax rapidly) but without allowing sufficient time for changes in the persistence length (which occur very slowly).

By exploiting control over these various stages, we can produce chains either differing solely in their overall topology, as characterized by the persistence length, or differing in the fraction of trans conformers. This independent control of the fractions of conformers and the persistence length would be extremely difficult to achieve in the laboratory.

4. Detailed Prescriptions for the Sample Preparation

In all, four different sets of samples have been prepared within the confines of the scheme described in the previous section. Each individual sample so prepared is just one of many possible configurational microstates of the polymer that can exist under the prescribed conditions. To obtain results that are representative of the bulk polymer, we have averaged properties over five independent samples in each set.

Each set of samples was allowed to relax at 200 K and 1 bar of pressure for ~1 ns. The final densities were all the same to within 1%. As discussed in the introduction we expect 200 K to be well below the glass transition temperature of all four of the different sets. The exact preparation procedure used in each case follows:

Set A was produced by stepwise quenching to 200 K from a melt prepared and relaxed at 500 K. This is the same procedure as used previously.[7]

Set B was obtained by generating samples at 200 K with $\zeta = 1$ and relaxing them at the same temperature. These samples have a much higher trans fraction and larger persistence length.

Set C was prepared by taking the relaxed set B, heating them to 1000 K for 100 ps, and then rapidly cooling back to 200 K. This produced a set of samples with a much lower fraction of trans conformers than B but a very similar persistence length.

Set D was obtained from configurations generated by PCG at 200 K but with $\zeta = 0.02$ which produced highly coiled, high gauche fraction samples. The van der Waals interactions were then introduced, ζ was reset to 1, and dynamic relaxation allowed us to proceed at 200 K.

As discussed in the introduction, we have chosen the proportion of trans conformers and the persistence length to characterize the different chain structures that we have produced in the manner described above. Flory[12] gives

Table I
% Trans and Correlation Length, a_{100}, Calculated for Each of the Four Sample Sets

sample	% trans	a_{100}/Å	sample	% trans	a_{100}/Å
A	78	5	C	77	12
B	82	16	D	70	6

the definition of persistence length a as

$$a = b_0 \sum_{k=0}^{\infty} \langle \mathbf{e}_i \cdot \mathbf{e}_{i+k} \rangle \tag{3}$$

where $\mathbf{e}_i$ is the unit vector in the direction of the bond connecting the $(i-1)$th to the ith backbone carbon atom. He further shows that

$$a = \frac{1}{2} b_0 (1 + C_\infty) \tag{4}$$

where

$$C_\infty = \lim_{k\to\infty} \frac{\langle r_k^{\,2} \rangle}{k b_0^{\,2}} = \frac{\langle (\mathbf{r}_i - \mathbf{r}_{i+k})^2 \rangle}{k b_0^{\,2}} \tag{5}$$

We have used eq 5 to evaluate the averages over five independent configurations for $k = 100$. We cannot expect to achieve the asymptotic limit for this rather modest number of monomers. Nevertheless we shall deduce correlation lengths from this data and will assume that to a good approximation the ratios of these values reflect the ratios of the true persistence lengths. The average correlation lengths, a_k, and trans fractions for these sets are shown in Table I. The standard error on the correlation lengths is at most 13%.

Comparison of the properties obtained for samples B and C illustrates how we can exploit the difference in time scales of configurational and local relaxation to control the trans fraction independent of the persistence length. As shown in Figure 1, 100 ps of heat treatment at 1000 K for samples initially prepared at 200 K causes a rapid equilibration of the fraction of trans states. Upon returning the temperature to 200 K the trans fraction returns to values appropriate to a fast quench of the melt. The density, however, behaves in a different manner, returning to the preheat treatment value when cooled back to 200 K. It seems evident that the overall configurational relaxation is far too slow to be significantly affected by what is a fairly brief period of heat treatment.

To emphasize this point, a comparison of typical configurations in the B and C sets is shown in Figure 2. The higher fraction of trans conformers results in the straighter sections visible in the chain represented by the thicker line. These change to a more kinked structure after heating with a noticeable retraction of the ends of the chain down the "tube". Note in particular how the overall envelope or gross structure is relatively unchanged.

5. Tension Experiments

The stress–strain behavior of all four sets of samples was obtained by subjecting them to an externally applied uniaxial tension which was increased at a rate of 5 bar ps^{-1}, exactly in the same way as described in detail previously.[7] As a result of the small system size, data were obtained only up to extensions of ~100%. Beyond this, contraction of the cell in the transverse direction can lead to a violation of the interaction potential truncation criterion.[7] Simulations were thus terminated when this happened.

In Figure 3a the tension developed within the sample is plotted as a function of the strain; similar plots are shown for the load in Figure 3b. The "load" is determined from the product of the tension and the cross-sectional area, and since the samples are very small, the loads are also extremely small (of order 10^{-9} N). The boundary conditions employed in our simulations result in a cross-sectional area that is uniform in the direction of the applied tension; consequently, the stresses reported are true stresses.

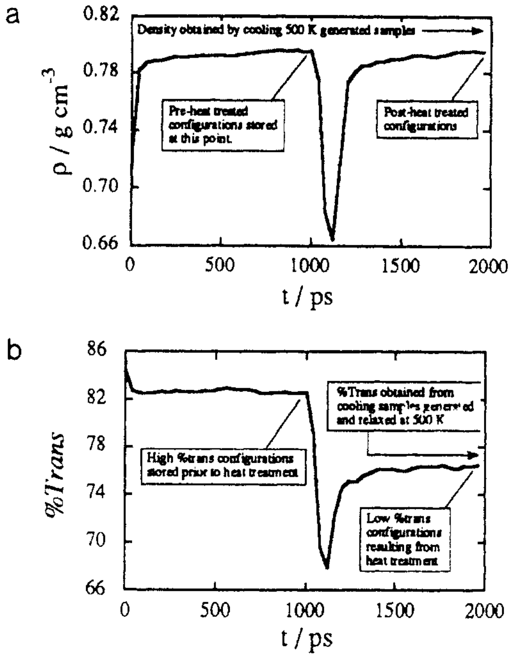

Figure 1. Time variation of (a) the density and (b) the percentage of trans conformers for samples of the model linear polymer initially generated and relaxed at 200 K and then subjected to heating to 1000 K for 100 ps before being cooled back to 200 K. The data shown have been averaged over five independent samples. The points at which samples B and C are extracted are shown. The arrows show the values of the average density and the % trans obtained previously[7] by cooling samples generated and relaxed at 500 K (set A).

Figure 2. Comparison of the chain structure for one sample before (thin line) and after (thick line) heat treatment. Only the coordinates of the continuous primary chain have been shown in both cases. The periodic MD cell which is filled by images of the primary chain is also shown.

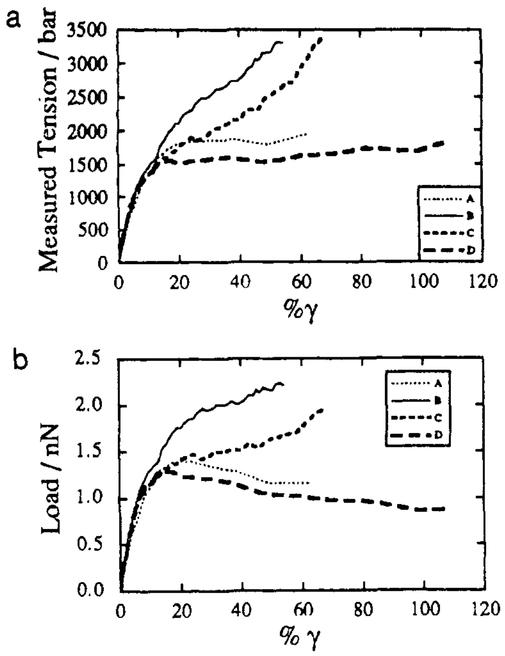

Figure 3. Measured tension (a) and load (b) plotted as a function of the extension for the four sets of samples of the model linear polymer subjected to an applied uniaxial tension increasing at a rate of 5 bar ps^{-1}. The curves represent the results obtained for the four sets of samples A–D of differing configurational and conformational properties as characterized by the persistence lengths, a, and percentage of trans conformers, % trans, shown in the figure and also given in Table I.

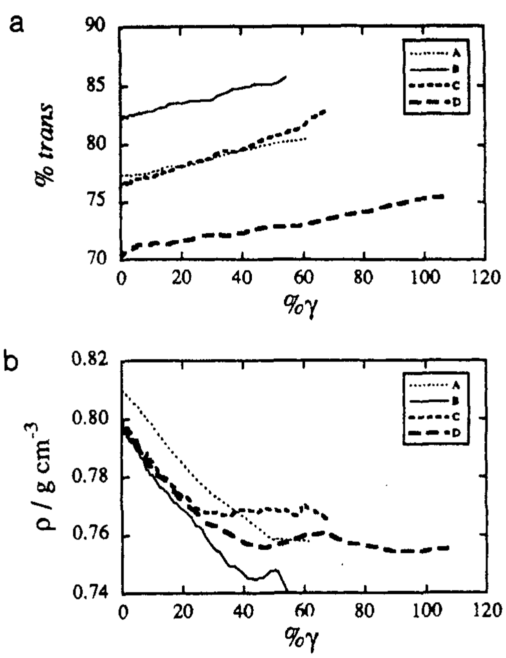

Figure 4. Percentage of trans conformers (a) and density (b) plotted as a function of the extension for samples of the model linear polymer subjected to an applied uniaxial tension increasing at a rate of 5 bar ps^{-1}. The curves represent the four sets of samples A–D as in Figure 3.

The pattern of the stress–strain plots is similar to that previously reported for set A; there is an initial elastic response followed by yield and plastic flow. In detail, however, the four sets of samples show quite different behavior. The differences begin to be noticeable after about 10% extension. Samples B and C both show enhanced resistance to extension beyond the point at which the A samples yield (~20% extension). The high % trans–high correlation length samples (set B) show the largest extent of strain hardening and in particular produce significantly more stress than the set C which, within the error, has a similar correlation length but lower trans fraction. Conversely sample set C has practically the same % trans as set A so the differences here must be due to their contrasting configurational structure. Set D shows the lowest resistance of all to the applied tension as was expected from its highly coiled structure with a smaller fraction of trans conformations. It seems clear from these results that both an increase in the fraction of trans states and an increase in the persistence length can *independently* contribute to strain hardening. There are two effects contributing to the differences between the samples.

We can gain further insight into the nature of the changes that occur during deformation of these materials from the strain dependence of the fraction of trans conformers. These data are shown in Figure 4a. This figure reveals a common feature of all our uniaxial tension experiments to date; namely, that there is a consistently linear dependence of the % trans upon the extension. The lack of any discontinuities or breaks in the plots at the yield points confirms the conclusion that this mechanical property has nothing directly to do with the onset of transitions between different conformational states. The gradients of these plots are however different, and this warrants further examination. In particular we point out the smaller gradients for sets A and D. The small correlation lengths in these samples means that configurations are highly coiled before straining so that a greater proportion of an extension can be absorbed by *uncoiling* the chains so there is less increase in the fraction of trans states. The large difference between the trans fractions of sets B and C that exists before deformation is gradually eroded with increasing extension.

The changes in density upon straining the samples are shown in Figure 4b. The marked linear decrease up to the region of the yield point has been previously discussed.[7] The initial rate of decrease of density is related to Poisson's ratio, and the values obtained here, ~0.4 for all four sets, are toward the higher end of the range obtained experimentally for typical amorphous polymers, 0.3–0.4.[13-16] Although this implies smaller changes in density for the simulated materials when extended, it is more than compensated for by the higher yield strains such that the overall decreases in density are much larger than typically observed in laboratory experiments. This behavior can be explained by the very high rate of strain which enhances that part of the extension attributable to elastic (Hookean) deformation at the expense of that due to slower relaxation processes, such as viscous flow and creep. The lack of any distinct yield point for sample set B may explain the larger decrease in density.

6. Conclusions

We have described a series of molecular dynamics simulation "experiments" which provide compelling evidence for a strong correlation between the conformational and configurational properties of a polymeric glass and its mechanical behavior. In particular chains which are either more extended (higher persistence length) or contain a higher fraction of trans conformers to begin with will be harder to deform. Close control of the preparation of the glasses in the simulation permits the separation of these two contributions to the stress–strain behavior.

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