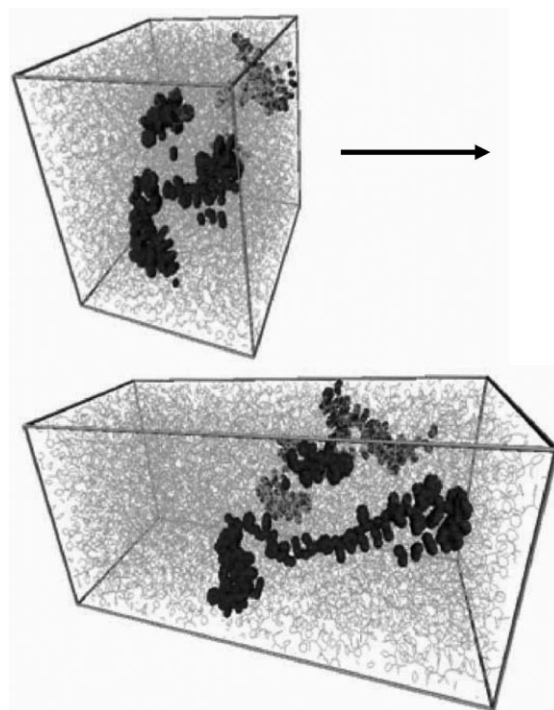


Equilibration and Deformation of Amorphous Polystyrene: Scale-jumping Simulational Approach

Tim Mulder, Vagelis A. Harmandaris, Alexey V. Lyulin,* Nico F. A. van der Vegt, Bart Vorselaars, Matthias A. J. Michels

A polymer sample-preparation method (extended-chain condensation, ECC) based solely on molecular-dynamics simulations has been compared to a connectivity-altering Monte Carlo method (coarse-grained end-bridging, CGEB). Since the characteristic ratio for the CGEB samples is closer to the experimental value, ECC results in polymer structures that are too compact. The stress–strain relations are different in the strain-hardening regime. For CGEB samples, a stronger strain hardening is observed and the strain-hardening modulus is more realistic; for the CGEB polystyrene (PS) sample $G_R = 9 \pm 1$ MPa is found versus $G_R = 4 \pm 2$ MPa for the ECC samples. These differences have to be attributed to a steeper increase in the contributions to the total stress from bond- and dihedral angles for CGEB than for ECC samples.



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Introduction

The mechanical properties of polymers are known to depend on the processing history.^[1] For example, the yield stress is dependent on the age of a polymer material; aging leads to an increase in the yield stress with time. By heating a polymer above its melting point and subsequently quenching into the glassy state, the age can be reduced (the so-called rejuvenation) and therewith the yield stress. Mechanical predeformation can result in even stronger rejuvenation; the yield stress can be reduced such

that the material exhibits no strain softening anymore.^[2] Ultimately, processing can turn a brittle polymer into a ductile one.

Also in atomistic simulations these observations have been made. Lyulin et al.^[3] were able to reproduce typical stress–strain curves for the amorphous polymers polystyrene (PS) and bisphenol-A polycarbonate (PC). They succeeded in approximately reproducing quantities like Young moduli, yield point, and strain-hardening moduli; deviations of the values obtained in the simulations from experimental values were of the order of 20%. Note however that, due to limitations of the molecular-dynamics method used, deformation rates had to be applied that are orders of magnitude larger than typical experimental deformation rates. Later Lyulin and Michels^[4] also reported on their extensive studies of the energy development during aging and rejuvenation for the same two polymers; the differences in behavior between those two polymers could be interpreted by considering ratios between time scales for cooling, deformation, and segmental relaxations.

In computer simulations involving polymers, especially simulations of polymer melts, initial-sample preparation is a serious challenge. Primitive sample-generation methods such as excluded-volume chain growth (EV) and phantom-chain growth (PCG), see ref.,^[5] followed by attempts to equilibrate by basic simulation techniques [Monte Carlo (MC), molecular dynamics (MD), and Brownian dynamics (BD), to name a few] will not result in samples that are equilibrated on all length and time scales (for very long chains, in this case the time to reach equilibrium is beyond the computational limits of these techniques). Still these approaches are being explored^[3,4,6] to obtain initial samples that are subsequently used for simulations in which statistical and dynamical quantities have to be studied. The effect of poor equilibration on simulated mechanical behavior has not extensively been studied yet. As very convincingly shown by Brown and coworkers^[5] preparation (on purpose!) of model polymer samples with large differences in both persistence length and percentage of dihedral angles in the *trans*-conformation, will lead to large differences in the post-yield stress–strain behavior. Whether differences between existing equilibration methods result in differences in polymer structures that have a strong effect on mechanical behavior is an open question.

To learn more on the role of the sample-preparation method in the mechanical behavior observed in computer simulations, one could subject samples that are prepared by widely different methods to the same mechanical tests. Here, we follow such an approach for PS. One PS sample is prepared by starting from one all-*trans*-chain in vacuum that is allowed to collapse, under melt conditions, to a coil in an orthorhombic box. The orthorhombic box is subsequently multiplied by a factor of two in all three

directions in Euclidian space, generating eight independent chains. Finally, the sample is subjected to equilibration at elevated temperature. The second sample has been prepared by making use of coarse-graining and end-bridging (CGEB) MC techniques to equilibrate at intermediate to large length scales, and united-atom PS MD to equilibrate at length scales of a few monomer segments. The details of this preparation procedure will be published elsewhere.^[7] After preparation, the initial samples are characterized first, using pair correlation functions and internal-distance distributions,^[8,9] to clearly show the structural differences resulting from the different preparation methods. Subsequently, both samples undergo the same computational cooling and deformation procedures. The mechanical stress response to applied strain is carefully analyzed for both samples; in addition the contribution of the various interaction types in the system to the total stress has been investigated. Also the amount of energy stored in the various degrees of freedom of the sample, i.e., energy partitioning, has been studied. Finally, structural evolution during deformation has been looked at.

The remainder of this paper is organized as follows. In the next section, the details of both the sample-preparation methods and the deformation protocol are explained. An extended comparison of the mechanical behavior of samples prepared by two very different preparation methods, based on stress partitioning, energy partitioning, and evolution of various structural properties, is described in the subsequent section. Conclusions are drawn in the last section.

Details of Simulations

As explained, two different sample-preparation methods are compared. One method, from now on referred to as the extended-chain condensation (ECC) method, is quite primitive. The other, more sophisticated, method, based on coarse graining and end bridging (EB), will be referred to as the CGEB method. In 2:1 coarse-grained PS model of the present study, one monomer is represented by two different beads in the CGEB method. One needs bonded potentials controlling bond lengths, bond angles, and dihedrals of the polymer backbone, and non-bonded potentials to control interactions of beads in different chains or in the same chain but separated by more than three bonds (excluded-volume effects have to be taken into account properly). The various bond lengths, bond angles, and dihedral angles in the coarse-grained model are controlled by force-field terms that are potentials of mean force of the coarse-grained degrees of freedom. These potentials of mean force have been obtained in atomistic simulations of isolated PS random walks, by sampling conformational

distribution functions $\rho^{CG}(\{b_i\}, \{\theta_i\}, \{\phi_i\}, T)$, where $\{b_i\}$, $\{\theta_i\}$, $\{\phi_i\}$, and T represent the bond lengths, bond angles, dihedral angles, and temperature, respectively. The bonded potentials are obtained from inverse Boltzmann relations $U^{CG}(x, T) = -k_B T \ln \rho^{CG}(x, T)$, x being a spatial coordinate. The Lennard-Jones-type potentials concern both the interactions between coarse-grained beads in different chains and the interaction between coarse-grained beads within one chain of type 1–4 and beyond, i.e., separated by at least three coarse-grained bonds. Tacticity information is also incorporated, the details of the force field are explained in ref.^[8] The CGEB method used in this study will be described separately in a future publication,^[7] see also ref.^[6] for a general description of the method. First, a polymer sample is prepared and equilibrated in the melt phase ($T = 463$ K) at a 2:1 level of coarse-grained description as given by Harmandaris et al.^[8] The density of the prepared samples was $0.96 \text{ g}\cdot\text{cm}^{-3}$. Two different beads [one for a CH_2 group, another one for a $\text{CH}(\text{C}_6\text{H}_5)$ group] have been used to represent the PS monomer unit. Subsequently, the sample is further equilibrated at the intermediate and long time scales, i.e., beyond the length scale of a few monomer segments, with the EB technique. After the system has completely forgotten its initial state, as could be concluded from the decay to zero of the orientation autocorrelation function of the end-to-end unit vectors, atomistic detail is reintroduced in the system. The atomistically detailed system is subjected to MD simulation to obtain a sample that is also locally, i.e., at the scale of a few monomer segments, equilibrated for 50 ps. In this way, a sample is prepared consisting of 50 chains of on average 100 monomers (due to the EB algorithm the polydispersity is introduced).

The ECC method starts from an extended united-atom PS chain in vacuum, a situation that is mimicked by putting the chain in an orthorhombic box with periodic boundary conditions, with a box size larger than the size of the chain. This system is subjected to melt-pressure and -temperature conditions, resulting in a collapse of the chain and an evolution of the density toward its melt value, $0.914 \text{ g}\cdot\text{cm}^{-3}$ at $T = 540$ K.^[10] After the collapse the sample is doubled in all three directions of Euclidian space; in this way a sample of 8 chains of 80 monomers is generated. This final system is equilibrated for another 10 ns at 540 K, again using periodic boundary conditions. More details of the model and the used force field can be found in ref.^[11,12] Using this method five samples are prepared in order to have comparable statistics as in case of the much larger system created by the CGEB method. The results of the production runs for these five independent samples are indistinguishable within the statistical errors; the final results are produced by their averaging.

After preparation via either of the methods we have samples in the melt; in both cases the same united-atom

description of the PS polymer is employed. Details of the used force field can be found elsewhere.^[12] Since our purpose is to study and compare the ECC and the CGEB sample in the glassy state the samples have to be cooled down. To that end all samples are cooled into the glassy state in NpT MD simulations, employing the velocity Verlet integration scheme with a time step of 4 fs. For the ECC samples, the cooling (with the fixed and the same cooling rate) has been performed from different initial temperatures, not only from $T = 540$ K. The properties of the final glass are not influenced by this initial temperature (as far as it is above the glass transition). The pressure is controlled using the Berendsen barostat^[13] ($\beta_p = 0.2$, where β_p is the ratio of the isothermal compressibility and the time constant of the barostat) and the temperature via the collisional-dynamics thermostat^[14] ($\lambda = 10$ ps, $m_0 = 0.1$ Da). The cooling rate employed is $0.1 \text{ K}\cdot\text{ps}^{-1}$, which is a typical cooling rate used in molecular simulations;^[3,4] the final temperature is 300 K. From the plot of the specific volume versus temperature we deduce, similarly as done in ref.,^[3] that our systems vitrify at approximately 400 K. The glassy samples resulting from cooling are deformed uniaxially at a constant deformation velocity of $0.05 \text{ \AA}\cdot\text{ps}^{-1}$, keeping the pressure equal to atmospheric pressure in two other directions.

Differences Between CGEB and ECC Samples

In order to obtain insight in the importance of careful equilibration on all length and timescales, both the PS samples prepared according to the CGEB method and the PS samples prepared according to the ECC method are subjected to uniaxial deformation. To understand the comparison, we start by presenting some structural properties of both equilibrium samples and make a short reference to established literature on those properties. Subsequently, both samples are deformed and the mechanical behavior is compared. Finally, the evolution of the polymer structures is studied in both cases.

Structural Properties Prior to Deformation

The structural properties can be compared using pair correlations functions. Most pair correlation functions of polymer systems are dominated by the trivial correlations between atoms that are separated by one or two chemical bonds. These correlations are very similar for many polymers.^[15] Londono et al. subtracted these trivial correlations, as well as correlations between atoms within the phenyl ring, from the total structure functions obtained by their X-ray measurements on PS and other polymers. The remaining parts of the structure functions

are Fourier transformed into pair correlation functions $G_{\text{rem}}(r)$. As shown by Londono et al. these functions G_{rem} contain very specific structural information, from conformational and intermolecular degrees of freedom, on the basis of which chemically different polymers can be distinguished.

Following their approach, we calculated G_{rem} for our PS samples, see Figure 1. Both preparation methods resulted in samples that possess the same structural features as measured by Londono et al.^[15] Small discrepancies between G_{rem} as calculated in either of the simulations on the one hand, and as obtained from the experiments on the other hand, can probably be attributed not to the sample-preparation method applied but to details of the force field. In the present simulations, a united-atom model for the PS melt has been used, so hydrogen atoms are lumped into neighboring carbon atoms. In X-ray experiments, the fact that hydrogen atoms are spatially separated from the carbons does influence the observations.

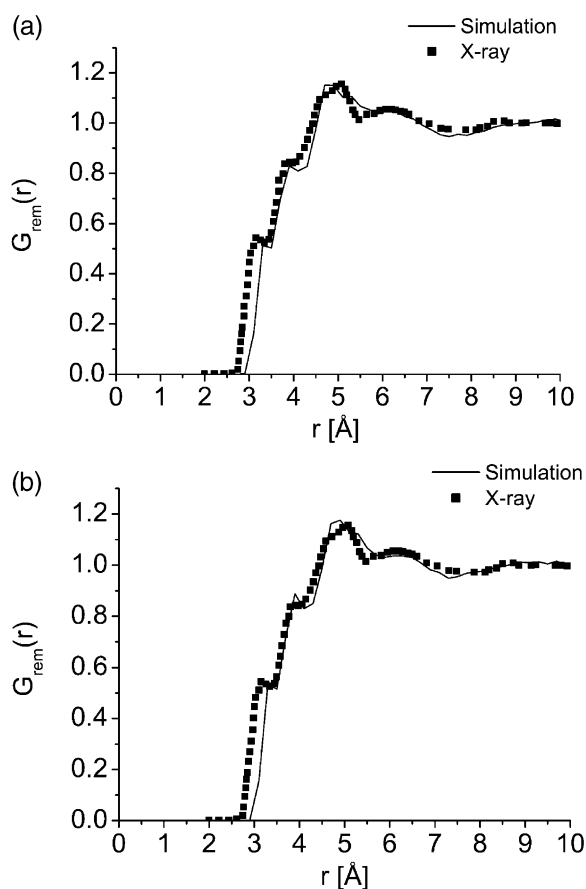


Figure 1. Pair correlation functions G_{rem} for both the polymer sample from CGEB (a) and from ECC (b). Trivial correlations between atoms separated by less than three chemical bonds or atoms in the same phenyl ring are excluded. Clearly, the experimentally reported correlations are accurately reproduced.

The pair correlation functions discussed here are indicative for how well realistic polymer structures are resembled on short length scales. However, especially at larger length scales clear differences should be expected, since the approach to equilibration followed in this paper, EB, aims at improving equilibration at the longest length and time scales; for local equilibration similar approaches are followed for both samples. To investigate the structures at larger length scales one could calculate gyration radii or end-to-end distances. A better alternative chosen here, providing information on all length scales, is the internal-distance distribution.

The distribution of internal distances in a chain is very informative on how well a sample has been equilibrated. The precise quantity calculated here is ratio C_N , defined as:

$$C_N = \left\langle \frac{R^2(N)}{Nl^2} \right\rangle \quad (1)$$

where R is the spatial distance between two atoms in the backbone of the same polymer, N the number of backbone bonds separating those atoms, and l is the length of a chemical backbone bond. The averaging is done over all pairs in all chains and also over time. Figure 2 shows these internal-distance distributions for both polymers. For large N the curve should tend asymptotically to the characteristic ratio C_∞ . Clearly, for the well-equilibrated polymer sample this requirement is met. From a linear fit of the data $R^2(N)$ versus $1/N$ for $N > 100$, it is found that, for large N , C_N approaches 8.5, which is lower than typical values of C_∞ reported in the literature; Mark et al.^[16] report 9.85 for PS at room temperature. The cause for this is that the sample has been equilibrated at a temperature corresponding to the melt phase, producing the correct value for C_∞ at that temperature, and subsequently cooled down many orders of magnitude faster than experimentally achievable. Apparently at this cooling rate the system is

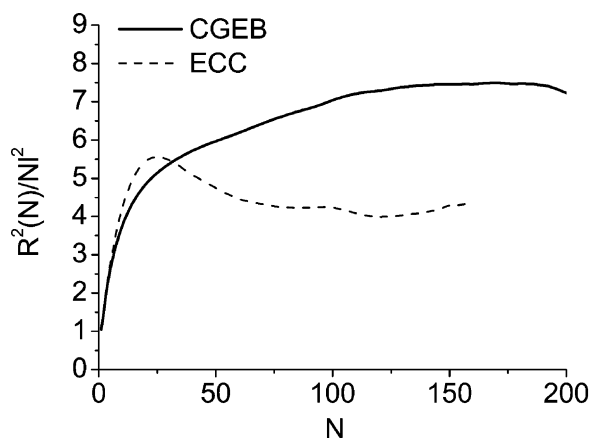


Figure 2. Distribution of internal distances in the polymer prepared by the CGEB method and by the ECC method.

not capable of adjusting its value toward the value at room temperature. For the ECC-equilibrated sample the situation is worse; first, $R^2(N)$ shows an increase, however for larger N $R^2(N)$ decreases again to a plateau at 4.3 ± 0.5 . According to Auhl et al.^[9] this is indicative for locally overstretched polymer chains. The low plateau value from ECC can be understood from the fact that the sample preparation started from extended chains in vacuum and not in the melt. In the melt, the attractive interactions between monomers in the same chain are shielded beyond a distance of a few monomer segments, whereas in vacuum this is not the case. In other words, the effective intra-chain attractive interactions are larger during the ECC sample preparation than in a PS melt. The result is a much more compact structure obtained from the ECC procedure than should be expected for a PS melt. However, another reason could be that short chains behave non-ideally in dense polymer melts. This is caused by non-screened excluded-volume interactions. As shown recently by Wittmer et al.^[17] this could also lead to a non-monotonic dependence of C_N on N , even when the system of polymer chains is in equilibrium. This has a stronger effect on the ECC sample, because its chains are somewhat shorter.

Stress–Strain Behavior

Both samples are deformed uniaxially in tension. The true stress is monitored and plotted versus strain in Figure 3. In both cases, the stress–strain curve has the typical form as observed experimentally;^[18] one can see the characteristic regimes of initial quasi-elastic response, yield at a few percent strain, then further deformation at constant stress,

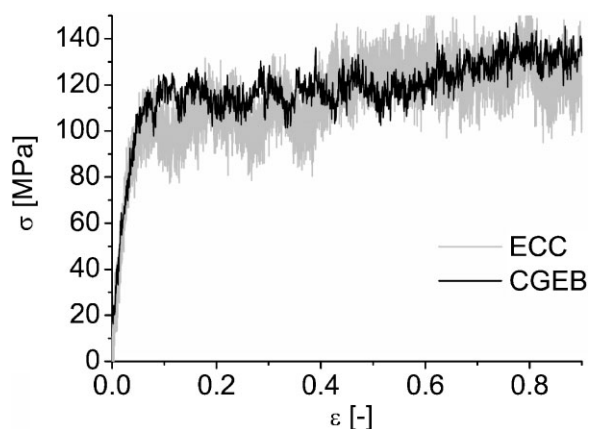


Figure 3. Stress versus strain for both the PS glass prepared by the CGEB method and the PS glass prepared following the ECC method. The typical form of experimentally known stress–strain curves are reproduced in both cases, although the CGEB case exhibits a more pronounced strain hardening. Quantitative data on the comparison of both cases are given in Table 1.

Table 1. Mechanical properties of both the PS glass samples prepared by the CGEB method and those prepared via the ECC method. Young moduli, yield stress, yield strain, and strain-hardening moduli of PS take realistic values.

| Sample | E (GPa) | σ_y (MPa) | ε_y (-) | G_R (MPa) |
|--------|---------------|------------------|---------------------|-------------|
| CGEB | 2.3 ± 0.5 | 115 ± 5 | 0.045 ± 0.005 | 9 ± 1 |
| ECC | 3.3 ± 0.4 | 105 ± 15 | 0.050 ± 0.005 | 4 ± 2 |

and finally an increase in stress for large extensions, called strain hardening. Strain softening, i.e., a drop (up to a few tens of MPa) in the stress after the onset of yielding, can be observed also if during the sample preparation a slower cooling rate ($0.01 \text{ K}\cdot\text{ps}^{-1}$) is used.

To make a quantitative comparison among the two polymer samples, Young's moduli E , yield points (ε_y, σ_y), and strain-hardening moduli G_R have been determined. The E -moduli are determined as the slopes of the stress–strain curves during the first percent deformation, the yield point as the intersection of the stress curve with the straight line $f(\varepsilon) = E(\varepsilon - 0.02)$ ^[19] and the G_R -moduli as the slope of the linear fit to the stress curve for $\varepsilon > 0.6$.^[19] The values of these quantities are collected in Table 1. The value of the E -modulus from the CGEB sample is low compared to typical experimental values ($3.2\text{--}3.4 \text{ GPa}$),^[20] whereas the value from the ECC sample is closer; the reason for this is not clear. The yield stresses from both samples are overestimated by approximately 30%,^[18] and are comparable to those reported by Lyulin et al.^[3] The strain-hardening moduli are underestimated again (Melick^[18] report 13 MPa for PS); G_R from the CGEB sample is closer to the experimental value than the G_R from the ECC sample. This last observation is correlated with the fact that the chains in the ECC sample are less extended than in the EB sample. For ECC samples at deformations above 80%, fracture can also take place.

Stress Partitioning and Energy Partitioning

In order to learn which degrees of freedom are important in which stages of deformation, the separate contributions of the various types of interactions to stress (its normal component in the direction of active deformation) and energy, i.e., the partitioning of stress and energy, have been calculated.

Figure 4(a) and (b) show the contributions from all types of interactions to the stress for the CGEB and ECC samples, respectively. In first approximation, the attractive contribution from the bonds is balanced by repulsive intra-chain Van der Waals interactions, i.e., Van der Waals interactions between monomers within the same polymer chain, before and during deformation. Most remarkable is

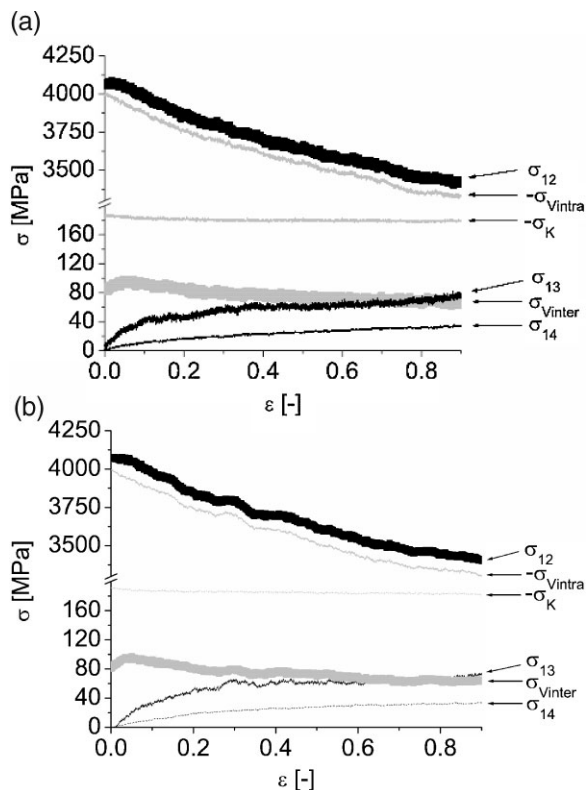


Figure 4. Stress partitioning as a function of strain for both the polymer prepared by the CGEB method (a) and the polymer prepared following the ECC method (b). There are six contributions to the total stress: contributions from bond lengths (σ_{12}), bond angles (σ_{13}), dihedral angles (σ_{14}), intra-chain (σ_{Vintra}) and inter-chain (σ_{Vinter}) Van der Waals interactions and a kinetic contribution (σ_K). The dominant contributions, σ_{12} and σ_{Vintra} , are more than an order of magnitude larger than all other contributions. More detailed information on the separate contributions is given in Figure 5.

that the absolute value of both the stress contribution to the bond lengths and the contribution from the intra-chain Van der Waals interactions is decreasing during deformation. Apparently the deformation induces structural rearrangements reducing the absolute values of the internal stress components in the material. The sum of these two contributions, plotted in Figure 5(a) for the CGEB sample and (b) for the ECC samples, is attractive and goes over a maximum at a strain $\varepsilon \approx 0.05$, suggesting some potential-energy barrier at the onset of yield, and is constant for larger strain. Some conformational changes are promoted in active deformation, they occur around the yield point, and the corresponding torsional contribution to the potential energy increases, see for example the work of Capaldi et al.^[21] and Lyulin et al.^[3] The stresses from the chemical bonds and intra-chain non-bonded interactions start to relax around the yield point.

The kinetic stress contribution is more or less constant, since the settings of the thermostat were such that our

deformations are isothermal and the volume approximately remains constant (apart from a few percent increase at the onset of yield, not shown). In experimental situations there will be, unless special measures have been taken for heat exchange, some heating of the sample. Further study would be very desirable to determine the extent to which this influences stress–strain relations.

The remaining contributions, coming from bond angles, dihedral angles and inter-chain Van der Waals interactions, are given in Figure 5(c) and (d), corresponding respectively to the CGEB and the ECC case. At a first glance the evolutions of all three components are similar for CGEB and ECC. But there are differences in the details. For example, in the stress contributions σ_{13} from bond angles and σ_{14} from dihedrals: prior to deformation for the ECC case the contribution from bond angles is repulsive ($\sigma_{13} = -6$ MPa) and the contribution from dihedrals vanishes ($\sigma_{14} = 0$ MPa), whereas for the CGEB case both contributions are attractive ($\sigma_{13} = 5$ MPa and $\sigma_{14} = 2$ MPa). Furthermore, for larger strain values ($\varepsilon > 0.5$) the contributions σ_{13} and σ_{14} rise faster for CGEB than for ECC. This can be understood by realizing that the chains in the ECC samples are in more compact conformations than the chains in the CGEB sample. Consequently, in the CGEB sample bond angles and dihedrals will be more seriously affected by the deformation. The average slope of the curve of ($\sigma_{13} + \sigma_{14}$) versus ε (not shown), in the interval beyond $\varepsilon = 0.6$, have been determined for both samples; in case of CGEB a value $\partial(\sigma_{13} + \sigma_{14})/\partial\varepsilon = (60 \pm 1)$ MPa is obtained and in case of ECC a value $\partial(\sigma_{13} + \sigma_{14})/\partial\varepsilon = (44 \pm 1)$ MPa. This has to be at least partly responsible for the fact that the strain-hardening modulus for the CGEB is higher than for the ECC sample, see Figure 3. However, if one compares the slopes of the contributions σ_{Vinter} (from inter-chain Van der Waals interactions) for both samples, then a larger negative value is found for the CGEB case [$\partial(\sigma_{\text{Vinter}})/\partial\varepsilon = (-18 \pm 1)$ MPa] than for the ECC case [$\partial(\sigma_{\text{Vinter}})/\partial\varepsilon = (-9 \pm 1)$ MPa]. The cumulative effect of the different slopes $\partial\sigma_{13}/\partial\varepsilon$, $\partial\sigma_{14}/\partial\varepsilon$, and $\partial\sigma_{\text{Vinter}}/\partial\varepsilon$ for the CGEB and the ECC cases, is the difference in strain-hardening modulus. A possible explanation lies, again, in the fact that the CGEB sample starts from more extended-chain conformations, and during deformation this difference remains, since at larger length scales (longer than the Kuhn length) the simulated polymer chains are not able to relax and their conformations are determined by the overall deformation of the sample. The differences at larger length scales are compensated by the fact that more local conformational changes via dihedrals occur in the CGEB case than in the ECC case, see next subsection. In addition to that, bond- and dihedral angles show larger departures from their equilibrium values in the CGEB case than in the ECC case. The result is more severe structural reordering in case of CGEB, which leads to stronger

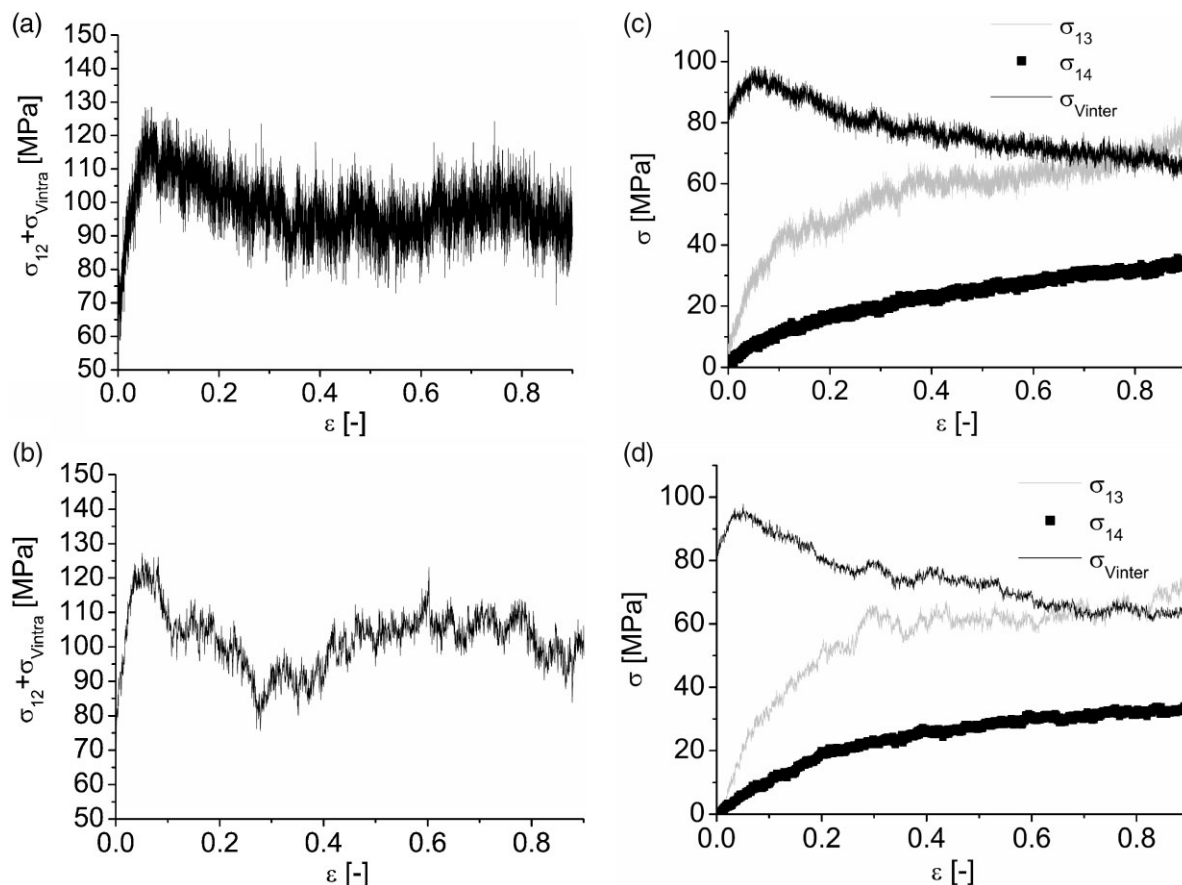


Figure 5. Stress partitioning as a function of strain for both the polymer prepared by the CGEB method [subfigures (a), (c)] and the polymer prepared following the ECC method [subfigures (b), (d)]. The largest stress contributions, coming from bond lengths (σ_{12}) and intra-chain non-bonded interactions (σ_{Vintra}), are given for the CGEB sample in (a) and for the ECC samples in (b). σ_{Vintra} and σ_{12} largely cancel each other. All other contributions, concerning bond angles, bond lengths, and dihedral angles, are given in (c) for the CGEB sample and in (d) for the ECC sample.

reduction in the stresses that are due to inter-chain Van der Waals interactions.

In Figure 6, the partitioning of energy per particle is shown for both samples. How does this partitioning of energy fit into the total picture? In the CGEB case, we observe an instantaneous increase in the energies from bond lengths, bond angles, and dihedrals. This instantaneous increase is not observed in case of ECC, because the chains are already initially less extended for ECC. In case of ECC even a decrease in dihedral energy with strain is observed. This difference in dihedral-energy evolution cannot be ascribed to more transitions from gauche states to the *trans*-states for the ECC sample than for the CGEB sample; further discussion on this point can be found in the next subsection. Another interesting issue is the difference between inter-chain Van der Waals interactions. For the CGEB case, the inter-chain Van der Waals energy rises first, then goes over a maximum at $\epsilon = 0.25$ and subsequently decreases again. Such a barrier is absent for ECC. These observations support the picture that once

bonds (and angles) feel the deformation, which only happens in the CGEB case, where the chain conformations are not too compact, some local orderings are disturbed, giving rise to the barrier, see Figure 6(c), in the inter-chain Van der Waals energy.

Evolution of PS Structure

In order to obtain insight in the influence of deformation on chain conformations, from the level of a few monomer segments to the level of the size of a polymer chain, distributions of dihedral angles in the polymer backbones, pair correlations, and internal distances have been studied as a function of strain. In Figure 7, the distributions of dihedral angles for both cases are given, with the convention that has been used to calculate dihedral angles displayed in Figure 8. Clearly both in the case of the CGEB and in the case of the ECC samples, the amount of dihedrals in the *trans*-conformation increases during deformation,

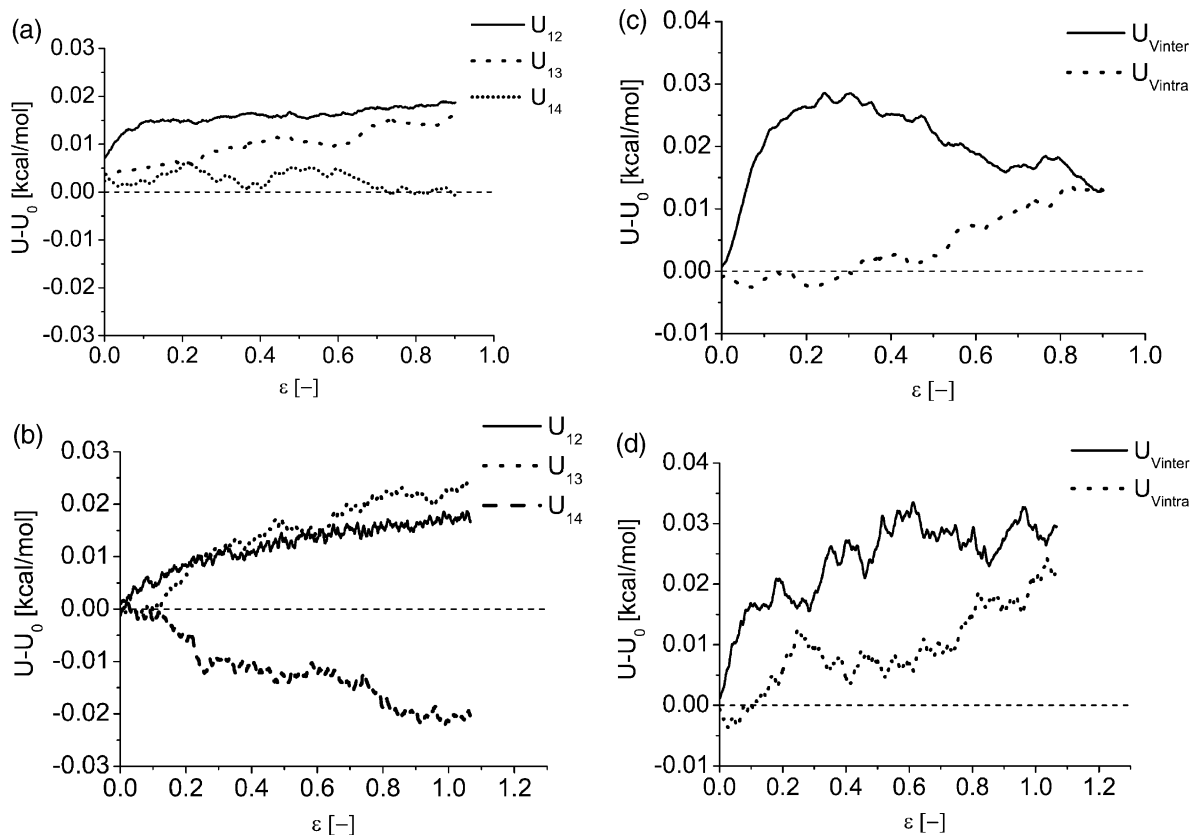


Figure 6. Energy partitioning for both polymer samples. The evolution of the energies related to bond lengths U_{12} , bond angles U_{13} , and dihedral angles U_{14} is given in (a) for the CGEB and in (b) for the ECC samples. The intra-chain and inter-chain Van der Waals energies, respectively U_{vintra} and U_{vinter} , and the total energy U_{pot} are plotted versus strain in (c) and (d), for the CGEB and the ECC samples, respectively. Note that all the differences are of the order of $0.02\text{--}0.03\text{ kcal}\cdot\text{mol}^{-1}$ which is very small compared to k_{BT} (about $0.6\text{ kcal}\cdot\text{mol}^{-1}$).

although more so for CGEB (from 60.4 to 64.7%) than for ECC (from 69.3 to 70.4%). In case of CGEB, this increase is completely at the cost of the number of dihedrals in the \bar{g} state; the number of angles in the g state remains unchanged. For the ECC case also an increase is observed in the g state (from 1.1 to 1.9%).

Given the fact that the *trans*-state is lower in energy than either of the other states, the stronger increase in the *trans*-population for the CGEB sample may seem in contrast with the observation in the previous section that the ECC sample shows the larger decrease in dihedral energy. However, this can probably be explained by a broadening of the peaks in the distribution in the CGEB case; on average dihedrals are forced, by deformation, away from values corresponding to local energy minima. This effect is probably less for the ECC case, since the intra-chain degrees of freedom are less affected at the level of a few bonds, again because the chains were less extended from the beginning.

Also the pair correlation functions G_{rem} have been studied. The changes with strain are negligible; therefore

the curves have been omitted here. Finally, the internal-distance distributions have been studied, see Figure 9(a) for CGEB and (b) for ECC. Both in the case of the CGEB and of the ECC sample, all intra-chain distances for atoms separated by more than 20 backbone bonds are increased by the deformation. Most distances are increased by a comparable factor, which suggests that at length scales corresponding to intra-chain separations beyond 20 backbone bonds the samples deform affinely.

Conclusion

In this paper, the importance of proper equilibration on all length scales for simulating the mechanical properties of PS in the glassy state has been investigated. Two sample-preparation methods have been compared. One method, termed the extended-chain condensation (ECC) method, starts from an extended chain in vacuum, which is allowed to relax at melt temperature and at ambient pressure in an NpT MD simulation. Subsequently, the system is dupli-

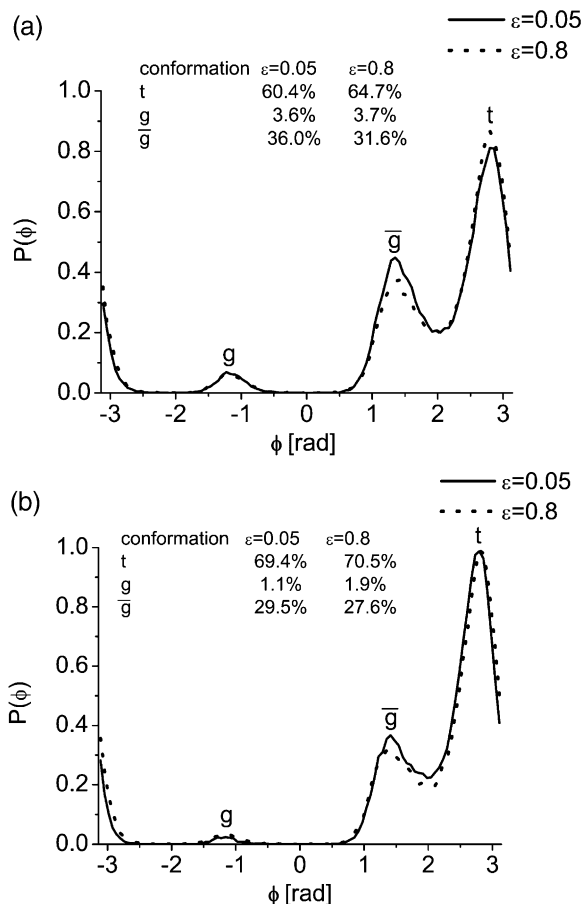


Figure 7. Dihedral distributions for both the CGEB (a) and the ECC (b) sample, before yield and in the strain-hardening regime. The percentages of *t*, *g*, and \bar{g} are produced by integrating the distribution function between corresponding minima.

cated in all three Euclidian directions, after which additional equilibration in MD is performed. The other method is called the CGEB method. It uses end-bridging Monte Carlo in combination with a coarse-grained description of PS, to equilibrate the PS sample at length scales beyond the length scale of a few monomer segments. In a next step, atomic details are reintroduced and the sample is equilibrated, using MD, at the length scales below that of a few monomer segments as well.

The structures obtained from both methods have been compared on all length scales. The intra-chain distances between atoms separated by more than 20 backbone chemical bonds are very different for the two samples. Whereas for the CGEB sample the characteristic ratio C_N as a function of chain length approaches a value of 8.5 (versus $C_\infty = 9.85^{[20]}$) for large values of N , for the ECC sample the deviation is much larger [$C_N \rightarrow (4.3 \pm 0.5)$].

The stress-strain behavior observed when both samples are subjected to uniaxial extension is similar. The most

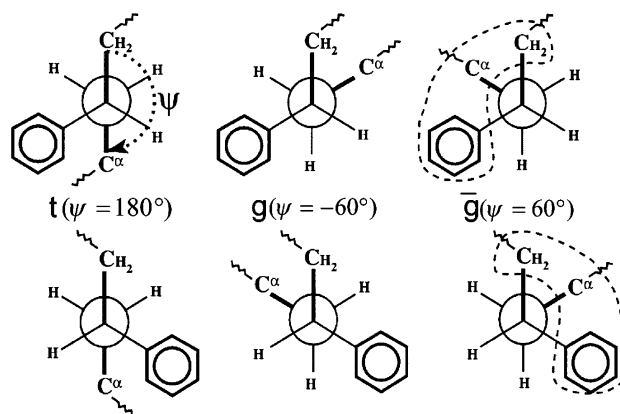


Figure 8. Backbone dihedrals are calculated as explained in ref. [22] All backbone dihedrals (determined by positions of four consecutive atoms in the backbone) are viewed in the same direction, that is always starting from a CH_2 -unit: $\text{CH}_2\text{-CH}(\text{C}_6\text{H}_5)\text{-CH}_2\text{-CH}(\text{C}_6\text{H}_5)$. The direction of positive orientation is such that sterically equivalent conformations are assigned the same dihedral angle. (Conformations that are mirror-images of each other have the same dihedral angle.)

clear difference is that for the CGEB sample a stronger strain hardening is observed than for the ECC sample, in accordance with too compact chains in the ECC sample.

With regard to this strain-hardening difference between the two samples, the following is observed. The contributions from bond- and dihedral angles to the stress show a stronger increase for larger strains ($\varepsilon > 0.5$) for the CGEB sample than for the ECC sample. In contrast, a steeper decrease is observed of the inter-chain Van der Waals contribution to the stress. The net effect is a larger slope of the total stress for large strain values, i.e., a larger strain hardening. These observations can be understood by realizing that at larger length scales chain conformations are not able to relax during deformation and are essentially dictated by the affine increase in the size of the simulation box. Since, already before deformation, chains in the CGEB sample are in more extended conformations than chains in the ECC sample, the chains in the CGEB sample are in more extended conformations at any strain value. These large-scale differences are compensated at length scales of a few monomer segments in two ways. The first is by more local conformational changes via dihedral angles. For the CGEB sample, an increase in the amount of dihedrals in the *trans*-state is 4%, for the ECC sample the amount in the *trans*-state increases by only 1%. The second way is by larger deviations of bond- and dihedral angles from their equilibrium values. The result of these differences in local conformational changes is more severe structural reordering in the case of CGEB, which leads to stronger reduction in stresses due to inter-chain Van der Waals interactions.

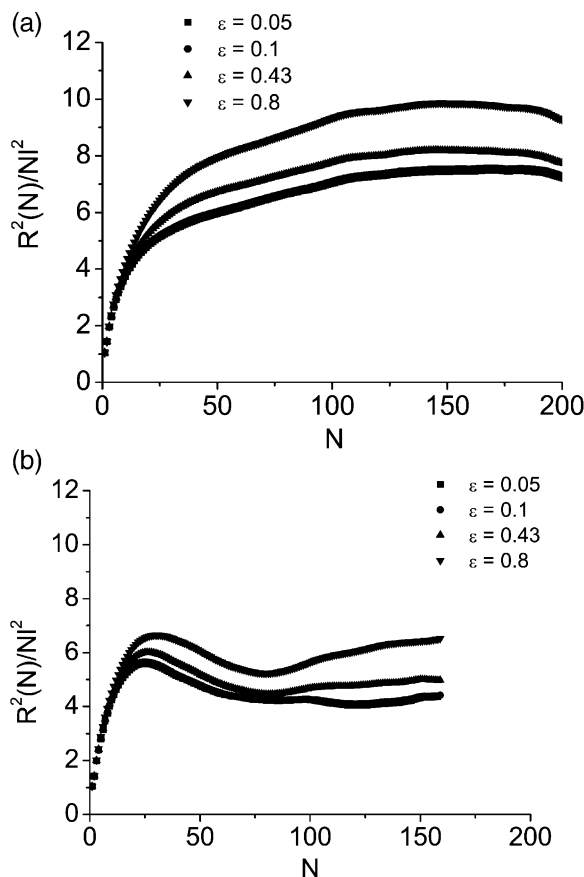


Figure 9. Distributions of intra-chain distances as a function of the strain for both the CGEB (a) and the ECC (b) sample, before yield and in the strain-hardening regime. The pictures of the two cases are comparable for atoms separated by less than 20 backbone bonds; the intra-chain distances are not influenced by deformation, whereas for atoms separated by more than 20 backbone bonds, intra-chain distances are multiplied by the same factor, suggesting affine deformation.

Energy partitioning as a function of the strain confirms the picture that during active deformation the polymer conformations are affected at smaller length scales for the CGEB sample than for the ECC sample. Energies related to intra-chain degrees of freedom exhibit for the CGEB sample an almost instantaneous increase, which is not observed for the ECC sample; for the energy related to dihedral angles, even a decrease is observed in the ECC case. Moreover a barrier in the intra-chain Van der Waals energies for the CGEB sample, which is absent for the ECC sample, may suggest that some local ordering involving monomers of different chains is disturbed.

In summary, we observe that two different sample-preparation methods, our new CGEB^[7] and the existing ECC, result in some structural differences beyond the length scale of a Kuhn segment. These structural differences give rise to differences in the degree of strain hardening, which can be explained as follows. Chains prepared by the

CGEB method are in more extended conformations than chains prepared according to the ECC method; the chains resulting from the latter method are too compact, because screening of excluded-volume interactions was not properly taken into account. Because of this, during deformation, bond- and dihedral angles are more seriously affected for the CGEB sample than for the ECC sample; contributions from bond- and dihedral angles to the stress show a stronger increase for larger strains ($\epsilon > 0.5$) for the CGEB sample. At the same time more structural reordering takes place in the CGEB sample than in the ECC sample, which translates in a steeper decrease, after $\epsilon = 0.5$, of the inter-chain Van der Waals contribution to the stress. The net effect accounts for the difference in strain-hardening moduli observed between the two samples. Still the present simulation data show no considerable difference in the mechanical behavior of two different simulated models.

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