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# Direct Atomistic Modelling of Deformed Polymer Glasses

Alexey V. Lyulin and M.A.J. Michels

*Group Polymer Physics, Eindhoven Polymer Laboratories, Technische Universiteit Eindhoven,*
*P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
*and Dutch Polymer Institute, P.O. Box 902, 5600 AX Eindhoven, The Netherlands*

**Abstract.** We use molecular-dynamics computer simulations to explore the influence of thermal and mechanical history of typical glassy polymers, atactic polystyrene (PS) and (bis)phenol A polycarbonate (PC), on their deformation. Polymer stress-strain and energy-strain developments have been followed for different deformation velocities, also in closed extension-recompression loops. The latter simulate for the first time the experimentally observed mechanical rejuvenation and overaging of polymers. Energy partitioning reveals essential differences between mechanical and thermal rejuvenation. All results are qualitatively interpreted by considering the ratio's of relevant timescales: for cooling down, for deformation, and for intrinsic segmental relaxation.

## INTRODUCTION

Severe post-yield strain softening for PS is usually connected to the process of structural relaxation (or "physical aging") [1]. After the yield point the stress drops to a value which is independent of aging time, and it was concluded that mechanical extension erases the polymer thermal history [2]. A molecular understanding of aging via structural relaxation and strain softening is still lacking, and even more so for polymers. The sum of the aging and deformation times compared to the internal relaxation time is what finally determines the yield stress of low-molecular-weight glasses, as has been shown recently by molecular-dynamic (MD) simulations [3].

In the present paper we perform direct atomistic MD modelling of the processes of deformation, mechanical rejuvenation and overaging (acceleration of aging) for the two typical polymer glass formers, PS and PC, which differ in the time scales of their segmental relaxation, each case we prepared different thermal histories (annealing and quenching). We show that the differences observed under deformation can be understood in terms of the ratios of three different characteristic time scales: $\tau_c$, the characteristic time of cooling down from high-temperature melt, $\tau_\beta$, the relaxation time of segmental motions within the cage formed by the neighboring polymer segments and, finally, $\tau_y$, the time to reach the yield peak. We also show that mechanical and thermal rejuvenation involve different segmental processes, and are indeed different, in agreement with recent experimental observations [4].

United-atom models for non-entangled polymer melts are used; they have been described in detail by Lyulin et al. [5]. Briefly, constant temperature-pressure *NPT* MD simulations are carried out for a system of 4-8 atactic PS chains of $N = 80\text{-}160$ monomers each, and 64 PC chains of $N = 10$ monomers. The size of the PS and PC samples is comparable to or even larger than the samples of the previous computational studies [6] for much simpler models. A Berendsen barostat and a collisional thermostat have been used. Five independent samples are created for each polymer and the final results are averaged. The samples are equilibrated at $T = 540K$ (highly mobile melt) for 10 ns. The quality of the equilibration is checked by standard methods.

After equilibration continuous cooling is implemented, with cooling rates spanning more than three decades in time: from more than 30 K/ps (simulated quenching) to 0.01 K/ps (simulated annealing). These cooling rates are extremely fast from an experimental point of view. However, the glass-transition temperature increases only logarithmically with cooling rate [5], and realistic values of $T_g$ can be obtained by extrapolating the simulated data

towards experimental cooling rates. The PS and PC samples are cooled down to the corresponding glass transition temperatures ($T_g$ = 375 K for PS and $T_g$ = 435 K for PC) [5], and to the room temperature $T$ = 300 K.

## RESULTS AND DISCUSSION

For both non-deformed polymers the distribution functions of the segmental orientational relaxation times reveals the existence of two different processes: relaxations within the cage, $\beta$ motions, and $\alpha$ relaxation of the cage itself. The simulated $\beta$ relaxation for PS monomers is rather fast (time scale $\tau_\beta$ is about 50 ps), and is well separated from the $\alpha$ relaxation (time scale $\tau_\alpha$ for both polymers is above 100 ns). The simulated $\beta$ relaxation for PC monomers is slower, $\tau_\beta$ is about 500 ps. Uniaxial deformation is applied with different deformation velocity (from 0.05 Å/ps to 0.0005 Å/ps) at $T$ = 300 K to polymer samples prepared by the cooling procedure explained above. The deformation was simulated in the *NPT* ensemble, with the same barostat and thermostat as earlier, and was applied along one of the Cartesian axes (X, Y or Z) to each of the five samples for each polymer. Extension-recompression loops have been applied to annealed (and quenched, not shown) samples of PS and PC with different velocities, Fig. 1 and 2. The energy at maximum strain strongly increases with strain rate, i.e. with $\tau_y^{-1}$; this is logical since in all simulations $\tau_y$ (time for forced out-of-cage-motion) is much smaller than the time $\tau_\alpha$ (time for cage relaxation), and $\alpha$ processes are unable to relax the corresponding barrier for this out-of-cage motion. The energy after recompression is a combination of energy increase by forced out-of-cage motion, and possible energy recovery under $\beta$ relaxation. For annealed PS it is significantly higher than the original energy, so the polymer appears "rejuvenated". Upon recompressing PS relaxes its energy on the timescale of the $\beta$ motion, 50 ps, after which the energy increases again since new barriers will have formed; the "rejuvenating" PS will thus explore a different part of phase space (see below, Fig. 3). For annealed and stretched PC under the same deformation
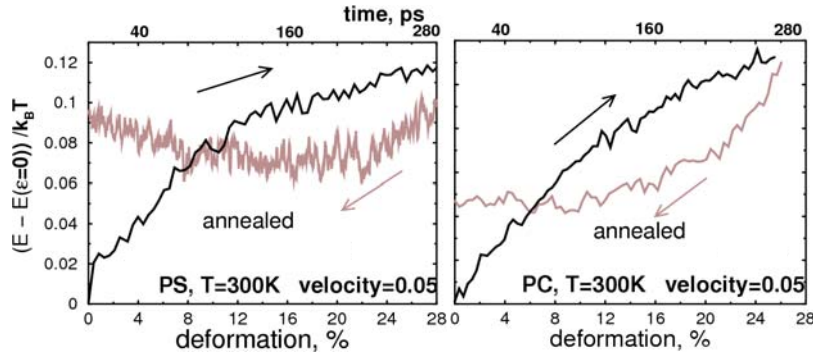


**FIGURE 1.** Energy evolution during closed deformation-recompression loops for annealed polymers. Temperatures and deformation velocities (in Å/ps) are indicated. Results demonstrate mechanical rejuvenation.



**FIGURE 2.** Energy evolution during closed deformation-recompression loops for annealed polymers. Temperatures and deformation velocities (in Å/ps) are indicated. Results demonstrate mechanical rejuvenation for PS and some overaging for PC.
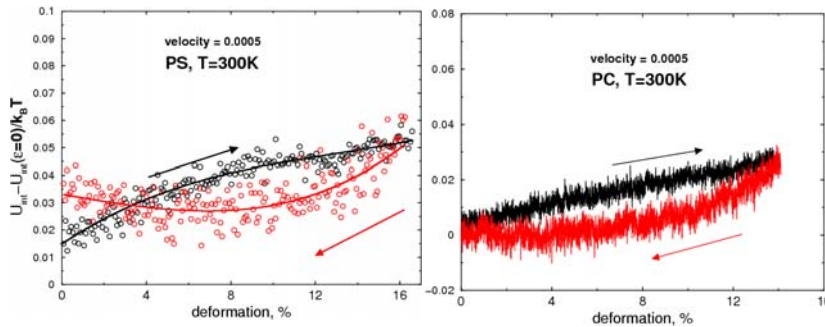
velocity the recompression time is shorter than the time of $\beta$ motion, 500 ps, and no significant new barriers seem to appear. At the lowest deformation velocity the annealed and stretched PC even decreases in energy after recompression, Fig. 2, i.e. it overages, also due to the low energy at maximum strain. Such an overaging is observed in recent experiments on PC under long-term loading [7] and in simulations of a binary Lennard-Jones liquid [6].

Partitioning of the energy between different force-field contributions clearly shows that the energy differences upon cooling (quenched minus annealed), or overaging (quenched minus end-of-loop), or mechanical rejuvenation (end-of-loop minus annealed) may be very different, see Fig. 3. For PC the thermal rejuvenation is for more than 80% due to weaker Van der Waals interactions, while the difference after a mechanical rejuvenation is for about 40% due to increased torsion of the chains. The partitioning of the energy for mechanically overaged initially quenched PC is very similar to the partitioning of the energy for thermally rejuvenated polymer, so $\beta$ relaxations may indeed play the same role in both. For PS the in-monomer (stretching, bending, torsion) and inter-monomer (van der Waals) contributions are roughly equally partitioned. In their recently reported MD simulations of a model polymer glass Capaldi et al. [8] also observed pronounced changes in the torsional energy under the deformation. The much more diverse partitioning for PS in the various simulations indeed points at exploration of different parts of phase space.

The main message of our study is that differences in stress-strain and energy-strain curves between the polymers could be interpreted in terms of ratios between the relevant time scales: the times for cooling down from the high-temperature melts, the times for deformation up to the yield point (forced out-of-cage motion), and the $\beta$-
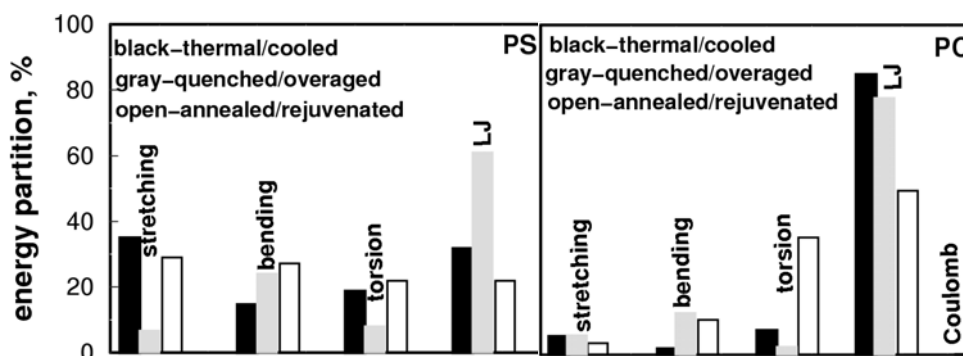


**FIGURE 3.** Partitioning of the final-energy difference for three cases ($T$=300 K): quenching vs. annealing, black; quenching vs. additional mechanical overaging (deformation velocity 0.05 Å/ps), gray; annealing and mechanically rejuvenation (deformation velocity 0.005 Å/ps) vs. annealing, open.

relaxation times. The results give insight into the energy landscapes and relaxation mechanisms of the deforming polymer glasses, in terms of differences between quenched and annealed samples, between deformations at different rates, and between thermal and mechanical rejuvenation. Qualitatively these conclusions can be translated towards upscaled experimental conditions.

## ACKNOWLEDGMENTS

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