Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for

Molecular Dynamics Simulations of the Uniaxial Deformation of Thermoplastic Polyimides

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The influence of the degree of equilibration on mechanical properties

We studied the influence of the degree of equilibration of a polymer sample on mechanical properties of a polymer. During simulations instant configurations of a polymer sample with degree of polymerization N_p=8 were saved every 100 ns, in total 31 samples were produced. Each sample was further cooled down from 600 K to 290 K with a cooling velocity $\gamma_c = 1.5\times10^{12}$ K/min. Then, the samples in the glassy state were deformed with a rate $\gamma_d = 10^{-3}$ nm/ps.

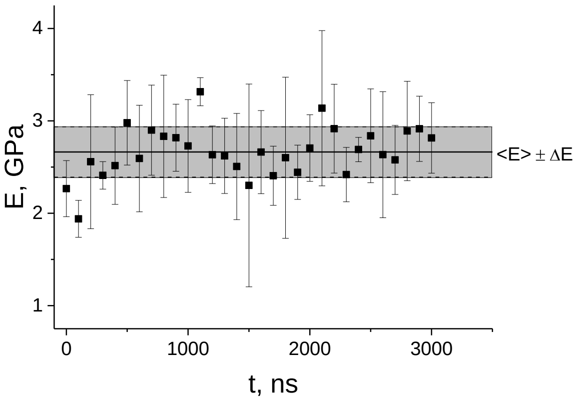

Fig. S1. Dependence of the PI R-BAPO elasticity modulus on simulation time, including the equilibration (first 2000 ns) and the production run (last 1000 ns). Error bars for each value of the modulus were determined as mean-square deviations from the average value obtained by averaging over all three deformation directions. Solid squares show the mean elasticity modulus calculated by averaging over all samples deformed in three directions. The mean-square deviation is highlighted in grey.

The results obtained show that the modulus of elasticity depends only very slightly on the equilibration degree, see Fig. S1.

The influence of molecular weight and simulation box size on mechanical properties

The influence of molecular weight. To explore whether the degree of polymerization N_p affects mechanical properties, some polymers were additionally generated with N_p=4, 6, 10 and 12. Using the quantitative structure-properties relationship analysis (QSPR-analysis) of the Synthia module in the Materials Studio package, the number-average entanglement molecular weight M_e was evaluated as ~ 2300 g/mol. With the molecular weight of the PI R-BAPO repeat unit of 750 g/mol, the number of repeat units between the entanglements is N_e ~ 3. Therefore, all the selected values N_p in simulations exceeded the value N_e. For the considered polymerization degrees (from 4 to 12), each polymer chain has from 1 to 4 entanglements.

The average gyration radii of individual polymer chains of different length reached their limiting values after 2 μs of simulations, see Fig. S2, Table S1.

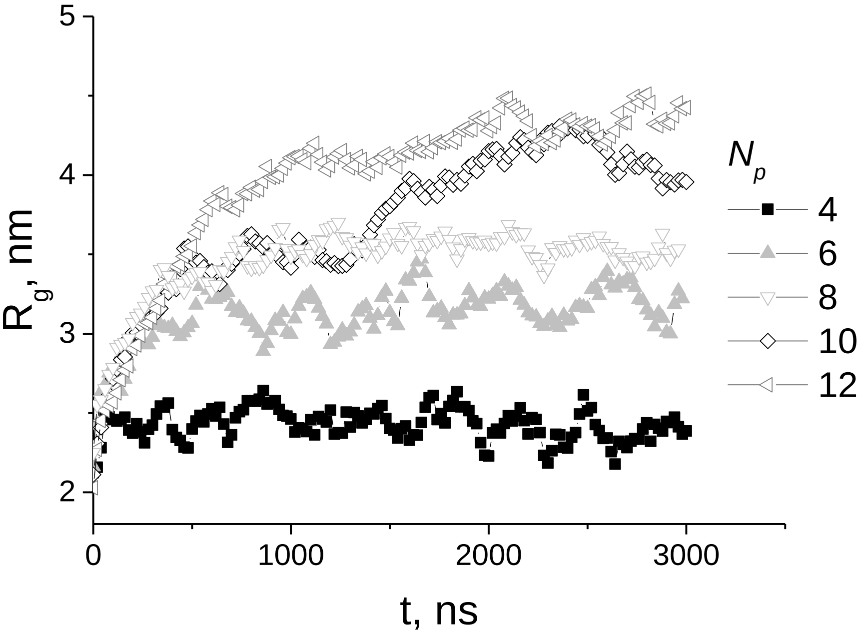

Fig. S2. Dependence of the PI R-BAPO average radius of gyration on simulation time (3 000 ns) for different polymerization degrees, N_p=4, 6, 8, 10 and 12 at T=600 K.

In our previous study[2] we calculated the persistent length and average end-to-end distance ($H_{e\text{-}e}$) of a separate chain of thermoplastic PI R-BAPO with N_p=8, using the virtual bonds formalism[3] for models with fixed valence angles and both free and interdependent rotation around the adjacent bonds. Similar to the results reported previously,[2] $H_{e\text{-}e}$ values were calculated for N_p = 4, 6, 10 and 12, see Table S1.

Table S1. Average end-to-end distances $H_{e\text{-}e}$ of an individual chain, both simulated and obtained using virtual bonds formalism based on free and interdependent rotation around the adjacent bonds.[3] The simulated values $H_{e\text{-}e}$ are obtained by averaging the results over 1 μs of simulations at T= 600 K.

N_p	$H_{e\text{-}e}$, nm		
	simulation, T=600 K	Free rotation model	Interdependent rotation model
4	6.2 ± 0.4	6.7	6.9
6	8.3 ± 0.3	8.2	8.4
8	8.9 ± 0.5	9.5	9.7
10	10.6 ± 0.6	10.6	10.9
12	10.7 ± 0.4	11.5	11.9

Table S1 contains the comparative results for $H_{e\text{-}e}$ of an individual chain calculated in simulations (T = 600 K) and using virtual bonds formalism. The simulation results display quite good correlation with the theoretical data. It suggests that all considered systems have reached their equilibration after 2 μs. Similar to our previous studies,[1,2,4] we used 11 different instant configurations of the PI R-BAPO sample to improve the calculation statistics.

The obtained equilibrated samples were further cooled down from 600 K to 290 K with velocity $\gamma_c = 1.5\times10^{11}$ K/min[4] and deformed with velocity $\gamma_d = 10^{-3}$ nm/ps.

Fig. S3 shows stress-strain dependences *σ(ε)* used to produce the elastic modulus $E(N_p)$, see Fig. S4.

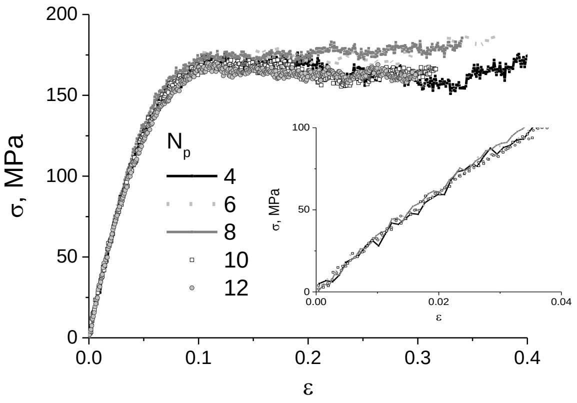

Fig. S3. Stress-strain dependence of PI R-BAPO for N_p=4, 6, 8, 10 and 12. The insert shows the linear viscoelastic regime.

We observed no dependence of *E* on N_p, see Fig. S4.

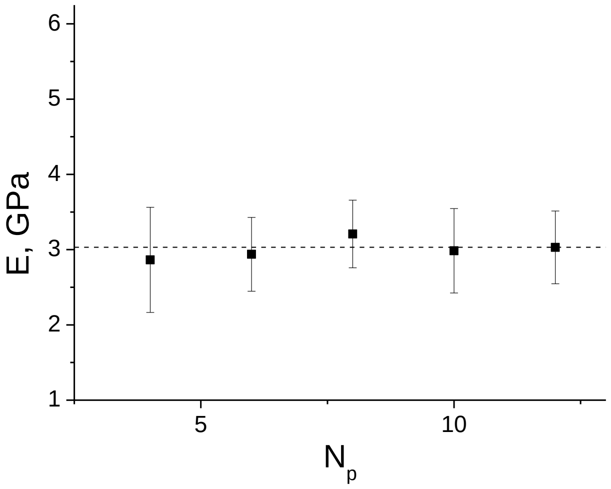

Fig. S4. Dependence of the PI R-BAPO elastic modulus of *E* on polymerization degree N_p. The error bars are calculated as mean square deviations of the average value determined for 11 samples and three deformation directions (33 systems in total). The dotted line indicates the average value of the modulus calculated for all considered N_p values.

The results obtained are qualitatively well supported by the known experimental data suggesting a weak dependence of *E* on N_p, both for advanced PIs[5] and for commodity polymers.[6] Particularly, the simulations of polyethylene melts using coarse-grained models showed that the *σ(ε)* dependence in the linear viscoelasticity area is hardly influenced by changing the polymer chains length.[7] The weak impact of N_p was also established in studies of mechanical properties of some semi-crystalline polymers.[8]

The influence of a simulation box size. In order to verify the box size influence on the mechanical properties of PI R-BAPO, the samples were generated consisting of 64 and 125 polymer chains, with a fixed polymerization degree of N_p=8. For the calculation of the mechanical characteristics the samples were cooled down with cooling velocity of γ_c=1.5×10^{11} K/min. The obtained densities of polymer samples with a different number of polymer chains in a glassy state (T=290 K) are almost identical, see Table. S2.

Table S2. Simulated samples with different number of polymer chains.

Number of polymer chains	Number of atoms, N	Simulation box size at T= 290 K, nm	Density at T=290 K, kg/m^3
27	17,982	5.9	1,351 ± 3
64	42,624	7.8	1,353 ± 4
125	83,250	9.8	1,354 ± 4

PI R-BAPO samples in a glassy state (T = 290 K) were deformed with a constant velocity of γ_d=10^{-3} nm/ps.

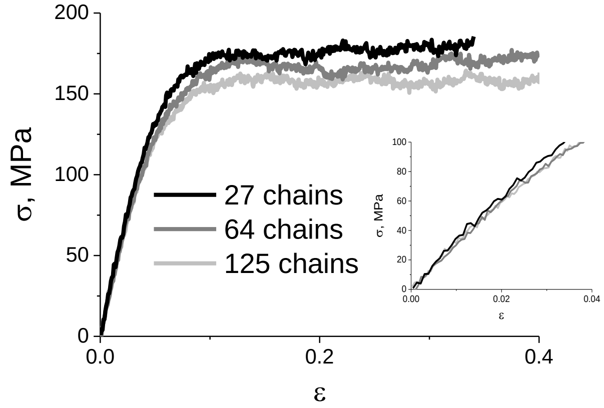

Fig. S5. Stress-strain dependence of PI R-BAPO with a polymerization degree N_p=8 and with different number of polymer chains. The insert shows the stress-strain dependence in the linear viscoelastic regime.

The results obtained, see Fig. S5, showed that the E values are practically independent on the number of polymer chains and the corresponding simulation box size, and in all cases are equal to 3.2 ± 0.4 GPa. We conclude that for the samples considered in this study, the molecular weight and simulation box size have practically no influence on the polymer mechanical properties. For this reason the influence of the temperature and the external pressure on the mechanical characteristics has been investigated for rather small samples consisting of 27 polymer chains only, with a polymerization degree of N_p=8.

References:

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