Atomistic simulation of pVT data of amorphous polymers in the rubbery range

(Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Kantstr. 55, 14513 Teltow, Germany)

M. Heuchel

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Helmholtz-Zentrum
Geesthacht
Zentrum für Material- und Küstenforschung

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Matthias Heuchel

10 pages with 6 figures

Abstract

This short report summarizes the modeling calculations carried out 2010 and 2011 at Helmholtz-Zentrum Geesthacht, Campus Teltow during the project "Multiscale prediction of gas solubility in high performance polymers" in VIGONI 2010 Personnel Exchange Program with Italy (CRUI) and Germany (DAAD) – 2010-2011. The modeling part of this project consisted of atomistic computer simulation to calculate simulated sets of pressure-volume-temperature (pVT) data for four polymers which can be used, e.g., for the prediction of physical parameters for these polymers used in macroscopic models.

Atomistische Simulation von pVT-Daten amorpher Polymere im gummielastischen Bereich

Zusammenfassung

Dieser kurze Bericht fasst die Modellrechnungen zusammen, die 2010 und 2011 am Helmholtz-Zentrum Geesthacht, Standort Teltow im Rahmen des Projektes „Multiskalige Vorhersage der Gaslöslichkeit in Hochleistungspolymeren" (DAAD Programm des Projektbezogenen Personenaustauschs mit Italien VIGONI 2010) durchgeführt wurden. Der Modellierungsteil dieses Projekts bestand in der atomistischen Computersimulation von Druck-Volumen-Temperatur (pVT)-Daten von vier Polymeren. Die Daten können z.B. zur Bestimmung physikalischer Stoffparameter für diese Polymere in makroskopischen thermodynamischen Modellen verwendet werden.

Atomistic simulation of pVT data of amorphous polymers
in the rubbery range

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Institute of Polymer Research, Helmholtz-Zentrum Geesthacht,

Kantstr. 55, 14513 Teltow, Germany

Summary

This short report summarizes the modeling calculations carried out 2010 and 2011 at Helmholtz-Zentrum Geesthacht, Campus Teltow during the project "Multiscale prediction of gas solubility in high performance polymers" in VIGONI 2010 Personnel Exchange Program with Italy (CRUI) and Germany (DAAD) - 2010-2011. The modeling part of this project consisted of atomistic computer simulation to calculate simulated sets of pressure-volume-temperature (pVT) data for four polymers which can be used, e.g., for the prediction of physical parameters for these polymers used in macroscopic models.

Polymers

The following four polymers were studied:

1) Polyetherimide (PEI, *Ultem*® 1000) ($T_g \approx 490$ K).
2) Poly(4,4'-oxydiphenylenepyromellitimide) (*Kapton*® H, $T_g \approx 670$ K)
3) Matrimid 5218, (based on a diamine, 5(6)-amino-1-(4' aminophenyl)-1,3,-trimethylindane, fully imidized)
4) Amorphous poly(ε-caprolactone) (PCL) ($T_g \approx 213$ K).

Modelling

For all polymers, three independent atomistic packing models (a single chain of 70-80 repeat units, about 5000 atoms) were created with the Materials Studio software by Accelrys using the universal COMPASS force field. The step wise procedure to create well-equilibrated atomistic packing models (initial packing at low density with the Amorphous Cell routine, force field parameter and density scaling by a cycle of

minimization and MD-steps, simulated annealing, and final relaxation with long NpT-MD simulations) is described in detail e.g. in Ref [2].
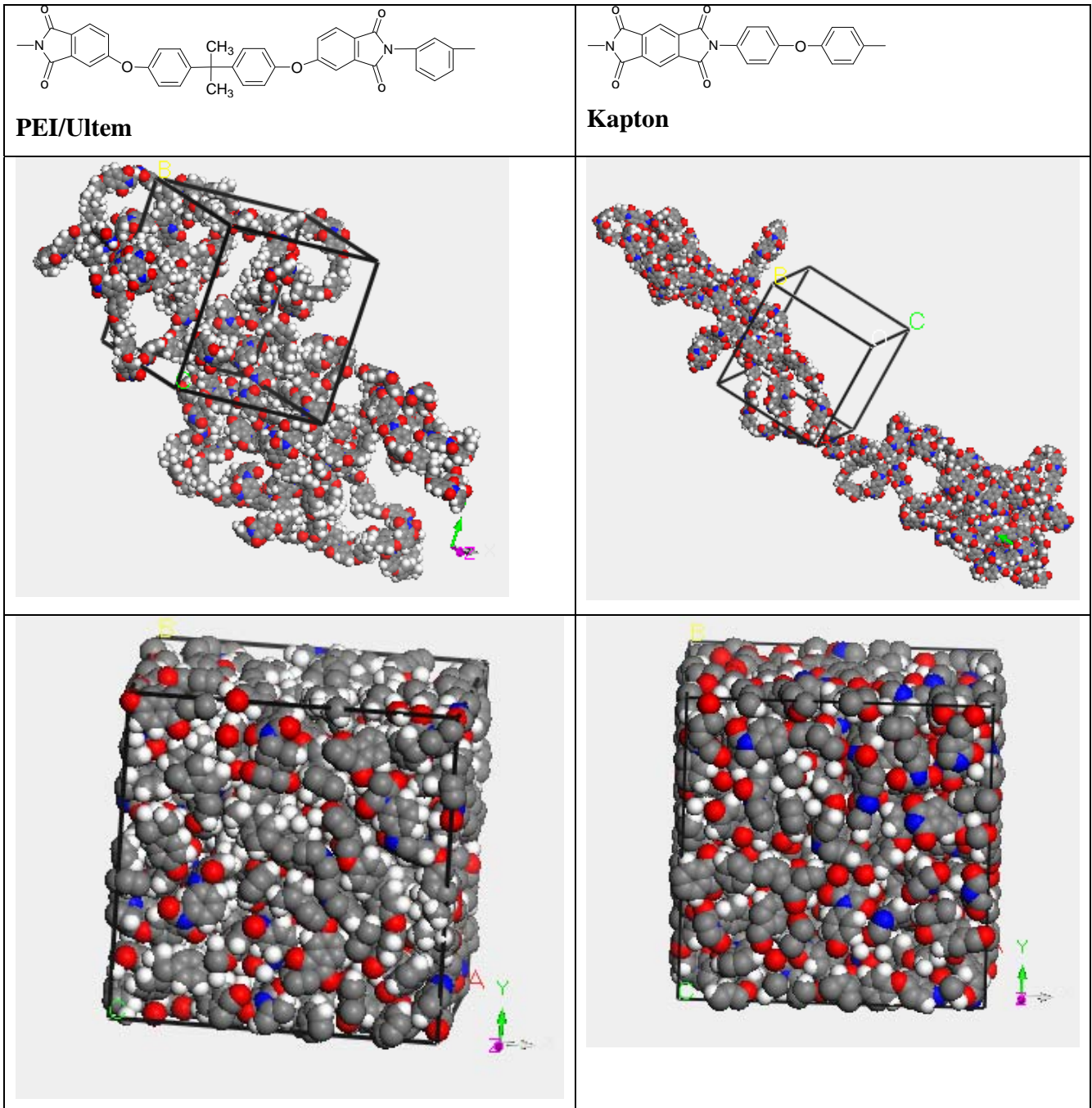

Figure 1. Atomistic packing models for PEI/Ultem (left) and Kapton (right). Above: Single polymer chain and the cubic simulation cell. Below: "packed state" under periodic boundary conditions
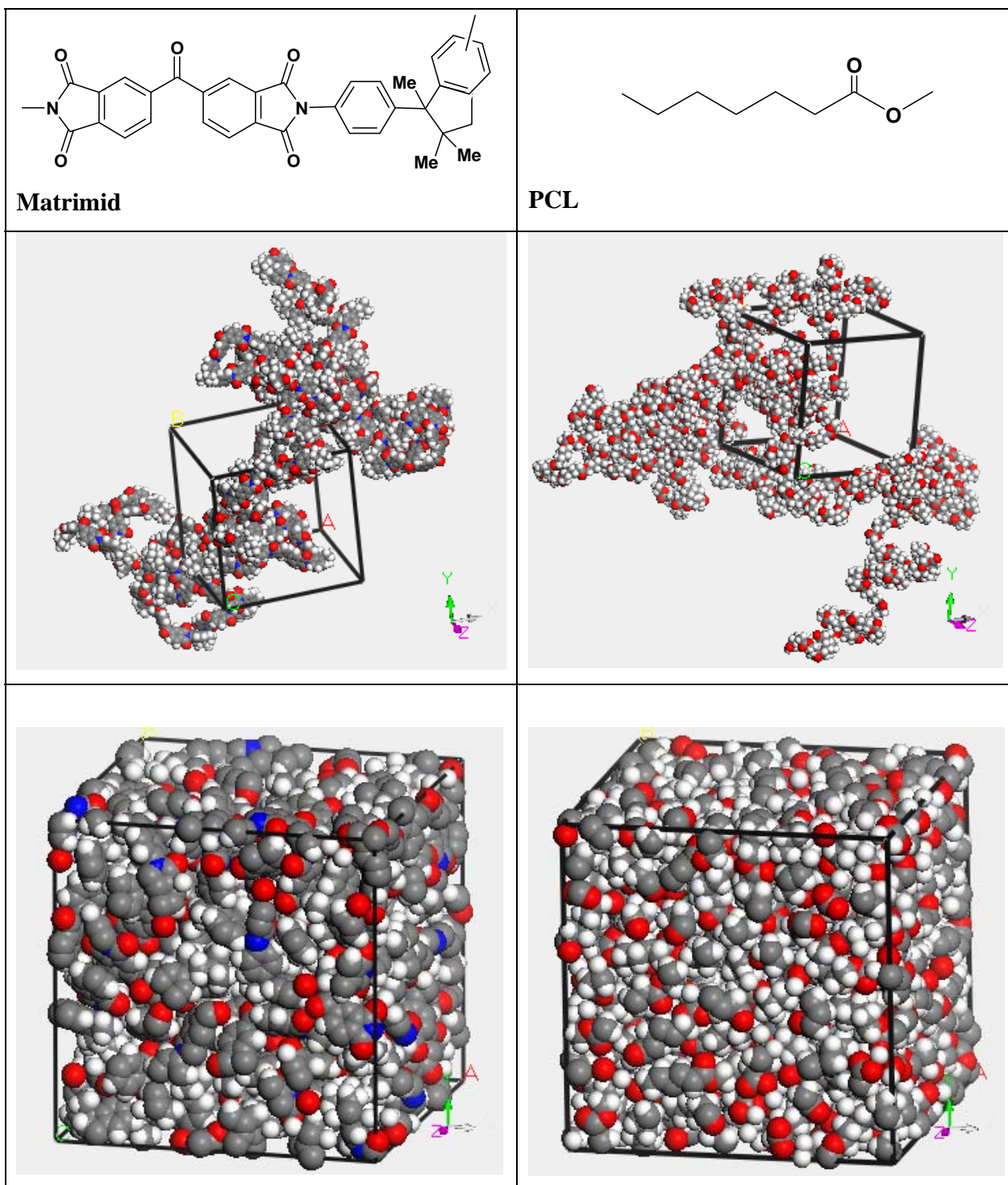
| **Matrimid** | **PCL** |

Figure 2. Atomistic packing models for Matrimid and PCL. Above: Single polymer chain and the cubic simulation cell. Below: "packed state" under periodic boundary conditions

During the project a strategy was developed to create models directly at a hypothetical rubbery state at T=900 or 1000 K (at p= 1 bar). The advantage is that the mobility of the chains is much higher at this temperature, resulting in faster relaxation processes. As target density at this high temperature, a value predicted from a group contribution method (*Synthia*) was employed. Figures 1 and 2 present typical atomistic packing models for all four polymers at T=1000 K and p= 1bar.

Calculation of "cooling curves": Isobaric curves at different pressure have been simulated in a NpT ensemble ranging from 200 K up to 900(1000) K. The "cooling curve" was calculated from the highest temperature T=900 or 1000 K, stepwise ($\Delta T = 20$ K) with NpT-MD simulations using the pressure control method after Andersen. The temperature was controlled with a Berendsen thermostat. A temperature step was composed out of a 20 ps NVT-simulation, followed by a 100 ps NpT simulation at the new temperature, and a final 100 ps NpT-production run at the same temperature. The pVT data points presented in the following are the average over three single packing models.

Results

PEI/Ultem. Figure 3 shows for PEI a very good agreement of the specific volumes with experimental data. At lower temperatures, i.e. in the range of the experimental glass transition and below, the simulated specific volume is slightly higher than the experimental values, but the slope, i.e. the thermal expansion coefficient, is well represented by the simulations. The reason for the deviation is that the cooling rate adopted in the simulations (about 10^{11} K/s) is orders of magnitude higher than the experimental values. Figure 3 shows further the comparison of experiment and simulations at the higher pressure values of 1000 bar and 2000 bar. The agreement both in the rubbery and glassy states is satisfactory. In particular, the deviation between simulated and experimental glass density at room temperature is equal to 1.8%, 0.2%, and 0.1% at the three pressures, while the deviation between the simulated and experimental values of the thermal expansion coefficient, near T_g, is equal to 1%, 6% and

4

8% at the three pressures. The agreement between experimental and calculated density values is more satisfactory for temperatures well above the experimental T_g.
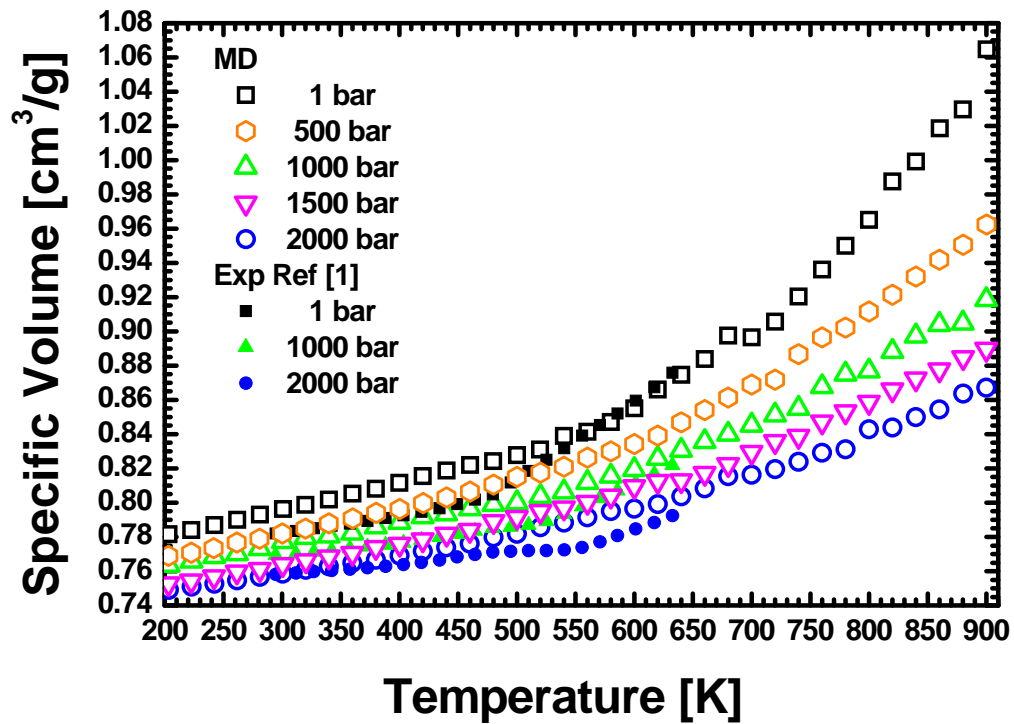

Figure 3. Specific volume vs. temperature for PEI packing models at all pressure values in comparison to experimental data points [1]. Presented values are averaged over three packing models.

At all five studied pressures, the simulated packing models for PEI/Ultem give comparable results within themselves. It should be noticed that at 1 bar, as usual for many polymer melts, there is also a drift at very high temperatures (T> 800 K).

Kapton: A similar simulation approach was applied to Kapton in the temperature range 200-1000 K. Figure 4 shows specific volumes as function of temperature for the average out of three packing models of Kapton at three pressures.
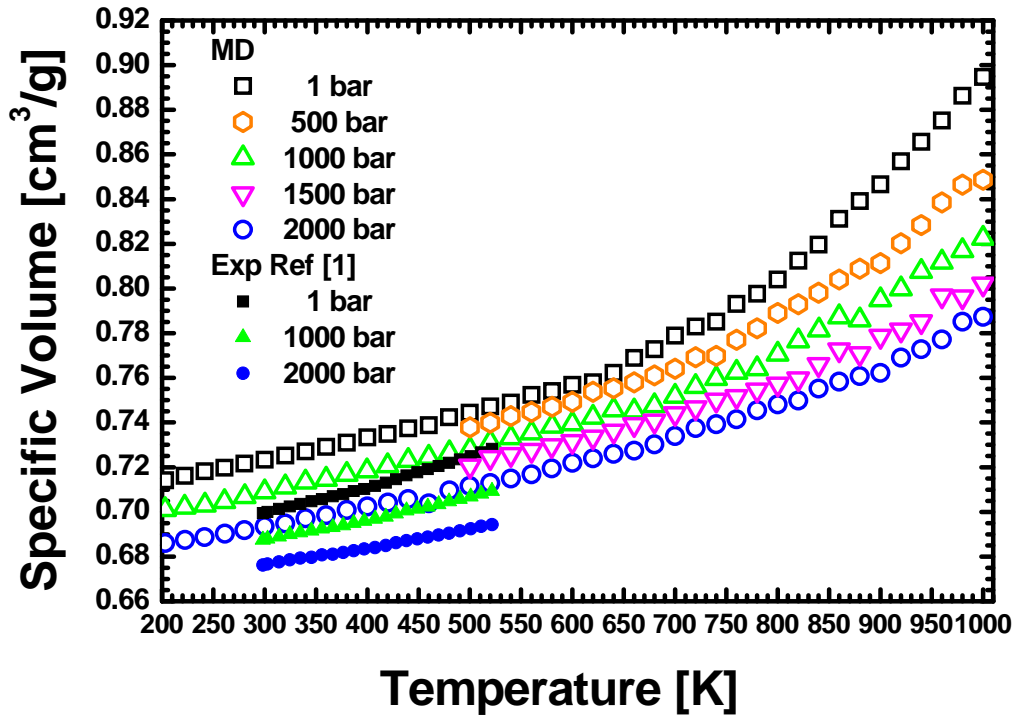
Figure 4. Specific volume vs. temperature for Kapton packing models at all pressure values in comparison to experimental data points [1]. Presented values are averaged over three packing models.

As for PEI, also for Kapton two values of the thermal expansion coefficient can be clearly distinguished at atmospheric pressure, a lower value up to about 650 K, representing the glassy range, and a higher value at T> 800 K representing the rubbery range. Also for Kapton, the simulated specific volumes in the glassy range are a bit higher than the experimental values (about 3%). Once again, the very fast cooling, due to short time scale of the molecular modeling, produces a polymer packed at higher free volume with respect to the one of the "real" structure. The same trend is also seen for the higher pressure of p= 1000 bar and p= 2000 bar. It should be noted that the specific volume data in the rubbery range present a real prediction. To obtain further pVT data in the rubbery range, additional simulations have been performed at p= 500 bar and p= 1500 bar in the t-range of 500 K to 1000 K. Also these data are presented in Figure. 4.

Matrimid: Isobaric curves at different pressures have been simulated in a NpT ensemble ranging from 200 K up to 1000 K. Figure 5 summarizes the simulated specific volume data as function of temperature for the Matrimid models at pressure values ranging from 1 bar up to 2000 bar.
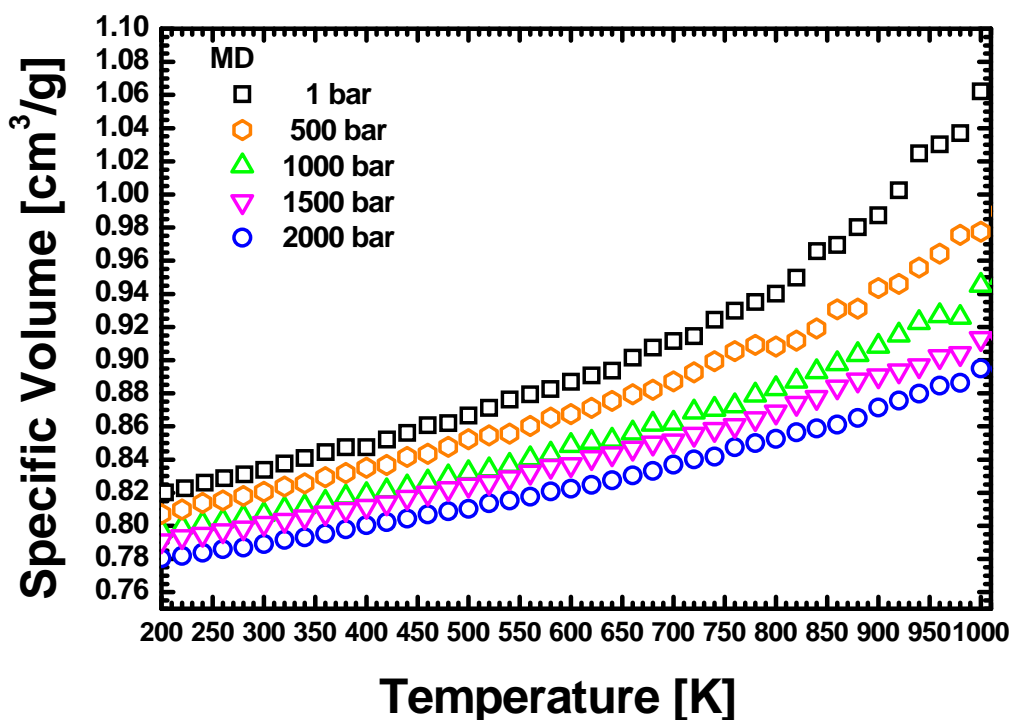

Figure 5. Simulated specific volume vs. temperature for Matrimid at all pressure values, 1, 500, 1000, 1500, 2000 bar. Reported values are averaged over the three packing models.

The "cooling curve" was calculated from T = 1000 K, temperature at which the packing model was created, stepwise ($\Delta T = 20$ K) with NpT-MD simulations using the pressure control method after Andersen. The temperature was controlled with a Berendsen thermostat. A temperature step was composed as before out of a 20 ps NVT-simulation, followed by a 100 ps NpT simulation at the new temperature, and a final 100 ps NpT-

production run at the same temperature. In case of Matrimid, a reduction of the usual integration time step (of 1 fs) was necessary in order to simulate the molecular mechanics of the macromolecules, likely due to its very rigid backbone. Hence, 0.5 fs was the value employed as time step; higher values often produced system instability of the Matrimid packing models, the volume rescaling algorithm of the barostat was not able to follow the dynamics of the systems, leading to very enlarged systems with a lack of physical meaning.

The simulated specific volumes at p = 1 bar for Matrimid polyimide in the temperature range 200-1000 K as calculated from molecular simulations on the three packing models shows that an almost linear trend exists up to approximately 600 K that represents the behavior of the polymer in the glassy state. The resulting thermal expansion coefficient $(1.4 \times 10^{-6} \text{ K}^{-1})$ is in line with what reported for many glassy polymers and in the same order of magnitude of the value of Matrimid declared by the supplier $(0.84 \times 10^{-6} \text{ K}^{-1})$. Raising further the temperature, a second order transition is clearly observable and can be estimated at approximately 650 K (very similar to the value of 610 K reported by many authors). At very high temperatures (T> 800 K) the behavior is clearly not linear, and a concave trend is apparent; this is often observed for many polymeric systems well above their glass transition. At p = 1bar a standard deviation of data was estimated to about 0.5%, whereas it is slightly higher at higher temperature, but it is still in the order of 1%. Analogous trends were then observed at the other investigated pressure values, namely 500, 1000, 1500, and 2000 bar. It should be noted that for Matrimid practically no experimental pVT-data exist, except some density values at room temperature in the glassy range.

PCL. PCL is a semicrystalline polymer with a rubbery amorphous phase at room conditions. PCL shows a glass transition at 213 K and has a melting point of 332-337 K. The MD simulations were performed in a T-range from 500 K to room temperature (300 K), because the applied molecular dynamics technique does not allow to model any crystallization phenomena, and the glass transition temperature of PCL is too low to be interesting. Figure 6 presents the simulated high-temperature pressure-volume-temperature (pVT) data from the MD simulations for all investigated pressure values in

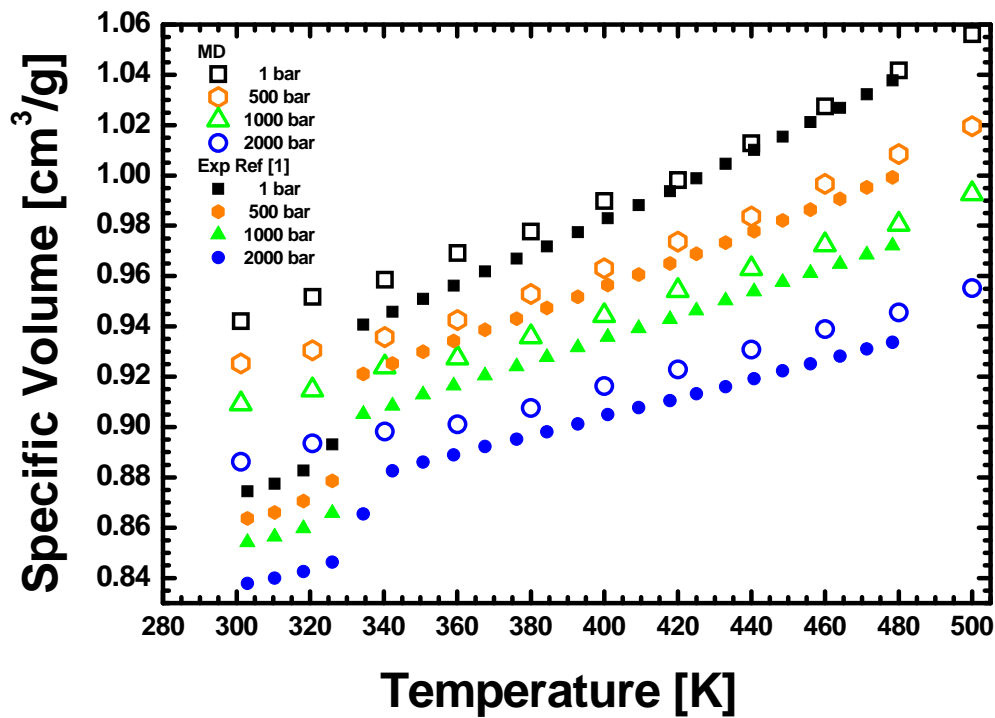comparison to experimental data. Presented data points are the average out of three packing models.

Figure 6 . Simulated specific volume vs. temperature for PCL at all pressure values, 1, 500, 1000, 2000 bar. Reported values are averaged over the three packing models.

For every pressure, the three single packing models showed a standard deviation below 0.3 %. The cooling curves at all the pressure values show a change in the slope as a glass transition is occurring; this happens at approximately 370 K that is too high for PCL, even considering a very fast cooling rate, (the experimental PCL glass transition temperature is about 210 K).

The agreement with experimental data points is excellent at p = 1 bar above 370 K, i.e. in the rubbery range of the simulated PCL. Very good agreement is also found for higher pressures in this temperature range. For all pressure values, the slope of simulated data

agrees very well with experimental one. Between 320 K and 340 K, the experimental specific volume data indicate by a pronounced step the melting transition of the semi-crystalline PCL. This step is of course not reproduced by the simulated PCL packing models which represent only an amorphous phase.

Conclusion

NpT Molecular Dynamics simulations were used to calculate the pressure-volume-temperature data above T_g, that are seldom available for high T_g polymers. The high temperature values of the simulation ensured for the three investigated polyimides a successful creation of packing models and fast relaxation of the chains. In the case of PEI, the simulated pVT behavior is consistent with the experimental data above Tg, available only for this polymer.

Also for the amorphous phase of PCL, it is possible to simulate pVT behavior in good agreement with experimental data.

References

[1]   P. Zoller, D. Walsh, Standard Pressure-Volume-Temperature Data for Polymers, Technomic, Lancaster, 1995.

[2]   M. Heuchel, D. Hofmann, P. Pullumbi, Macromolecules 37 (2004) 201-214.