



materials design

Studies of the Molecular Weight Dependence of the Glass Transition Temperature of Oligomers

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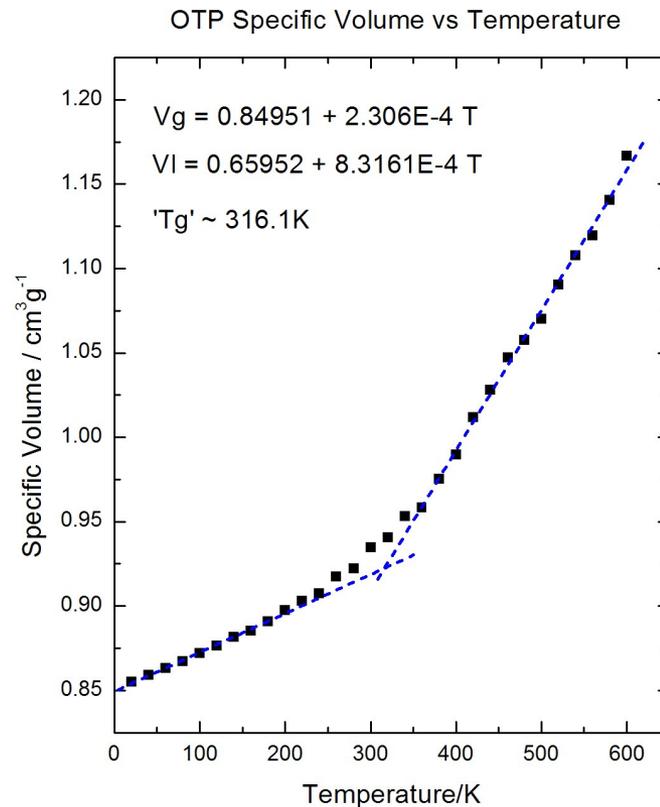
Background

- History
 - First MD studies of glass formation for simple LJ systems:
 - Clarke – J. Chem. Soc. Faraday II **75**, 1371 (1979)
 - Andersen et al – J. Phys. Chem. **88**, 4019 (1984)
 - Analogous studies on united atom flexible chain molecules:
 - Roe et al – J. Chem. Phys. **87**, 7285 (1987)
- Most commonly applied approach to locate T_g is based on identifying location of discontinuity of slope in volume-temperature curves, at constant P (i.e. analogous to dilatometry studies)
- Quantitative comparison with experimental T_g not attempted in earliest studies. Later studies of a variety of systems initially reported T_g higher than experiment, e.g.
 - Boyd et al – Macromolecules **27**, 7781 (1994)
- Explained by effective cooling rates in simulations orders of magnitude faster than experiments (i.e. simulations are essentially measuring an ultra high frequency T_g for which $T_g > T_g(1\text{Hz})$)
- Some published results report almost exact agreement with experiment, (even with force fields known to give poor prediction of PVT behavior)



Typical V-T Curves - OTP

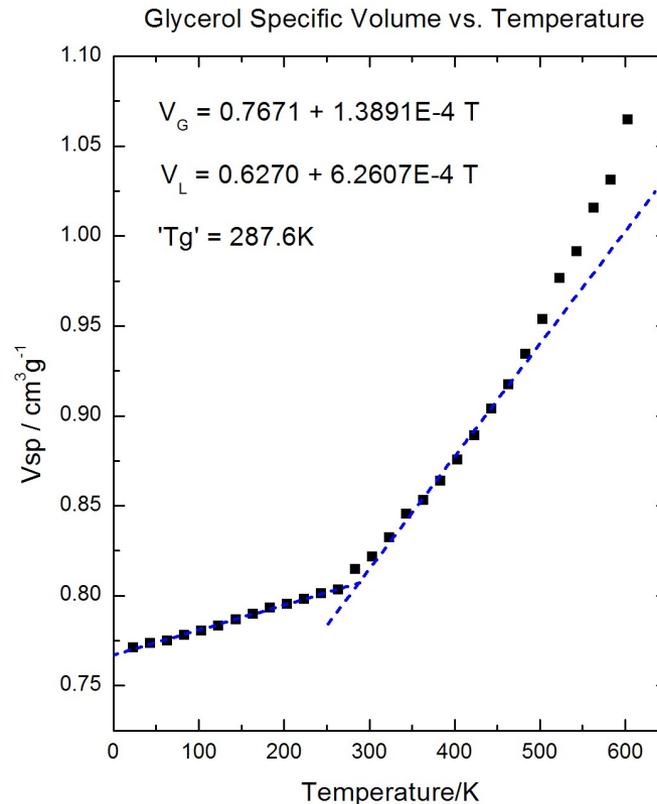
Ortho-Terphenyl is experimentally one of the most widely studied model glass forming systems. Typical simulation results with a good force field (COMPASS) give $T_g \sim 73$ degrees higher than experiment:





Typical V-T Curves - Glycerol

With glycerol, more extensive curvature is observed at high temperatures. However, the Tg can be estimated to be not less than 287.6K, at least 90 deg higher than experiment



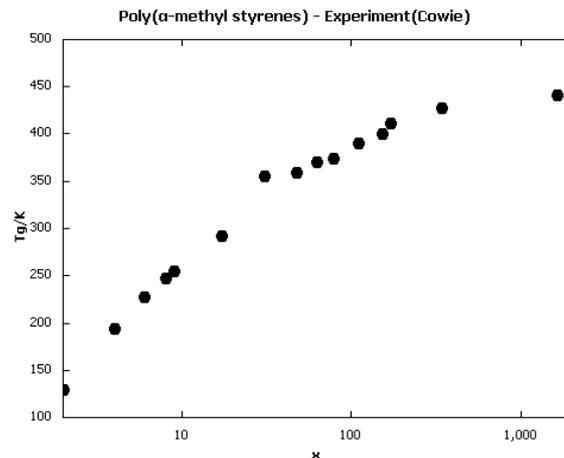


Some Tg Simulation Issues

- Factors that can potentially affect apparent Tg determined from simulations:
 - Methodology: V-T curves from simulations often do not show well-defined linear low and high temperature regions
 - Cooling rate effects can be evident
 - Force field absolute accuracy needs to be high
- Other issues arise, especially for chain molecule systems:
 - Variations in molecular architecture, such as stereoregularity/tacticity, repeat unit orientation, isomer composition (as in vinyl content of dienes etc) can in principle sometimes affect the actual Tg
 - Slow volume relaxation on the simulation time scale can shift and distort simulation curves
 - Commercial polymers are often polydisperse
- A deeper understanding of simulations (leading to routine and accurate Tg prediction) requires further, ideally systematic, studies...

Opportunities for Systematic Studies

- Tg of oligomers of a given polymer are known in some cases to vary widely, spanning a range of as much as 200 degrees before reaching the high molecular weight limit characteristic of the polymer of interest
- Although extensive experimental data sets exist for only a few polymers, fortunately good data exist for some of the simpler systems, such as polystyrene and poly(α -methyl styrene), e.g. from Cowie & Toporowski, Eur. Polym. J. **4**, 621 (1968):



- From a simulation perspective:
 - Some good force fields are available for predicting EOS behavior
 - Experimentally, tacticity effects are known to be minor



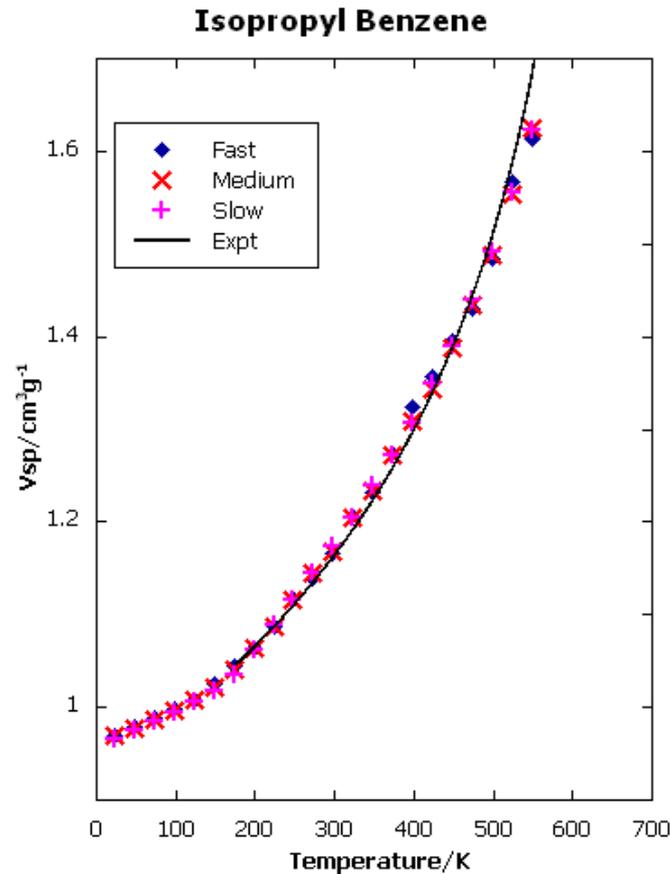
Tg Studies – This Work

- Study poly(α -methyl styrene) with degree of polymerization (DP) = 1, 2, 3, 4, 5, 6, 9, 15, 20, 80. Molecular weight = 118, 236, 354, 472, 590, 708, 1062, 1770, 2360, 9440
- Perform stepwise cooling NPT simulations using LAMMPS:
 - 25 degree intervals from typically 623K to 23K
 - Use 100ps, 500ps, 2500ps NPT simulation at each temperature
 - Study both isotactic and atactic chains
 - Use refined version of pcff force field from LAMMPS distribution



Results – Rate Effects DP=1

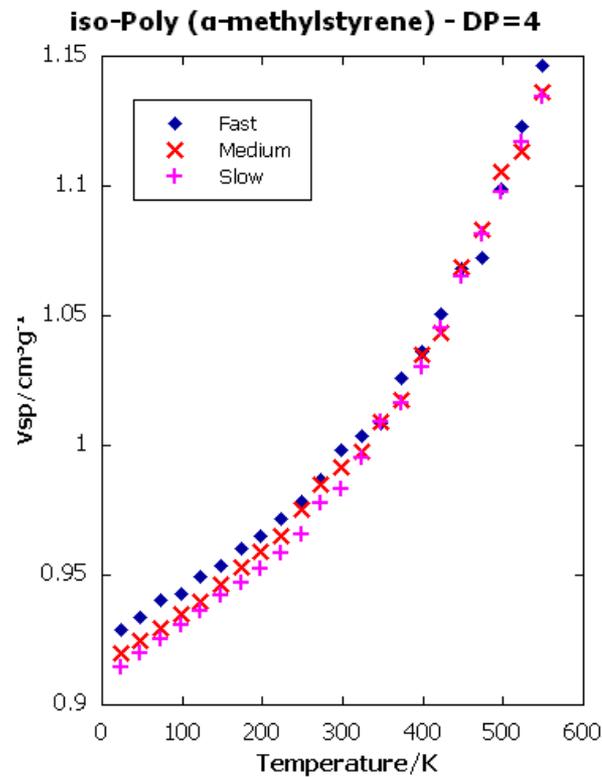
- Poly(α -methyl styrene) with DP=1 (isopropyl benzene) shows little evidence of cooling rate effects on V-T curves:





Results – Rate Effects DP=4

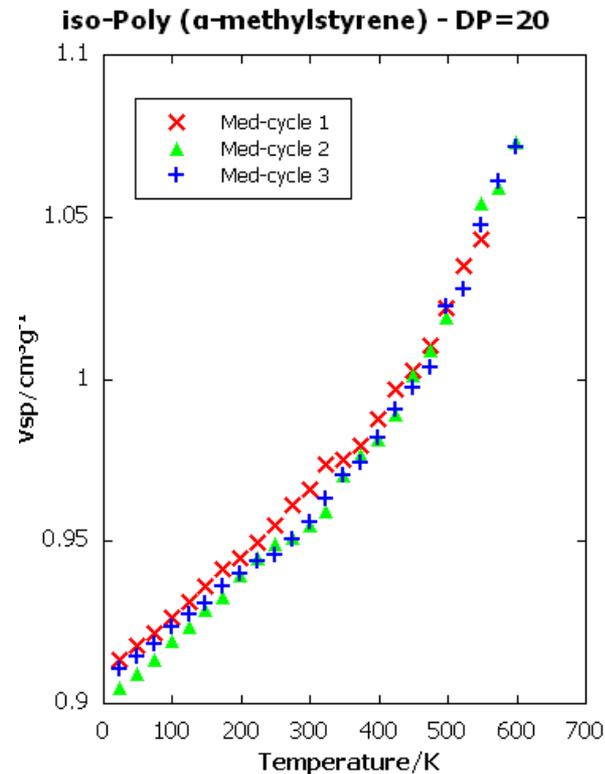
- Some cooling rate effects become evident for poly(α -methyl styrene) with DP>4





Results – Relaxation Effects

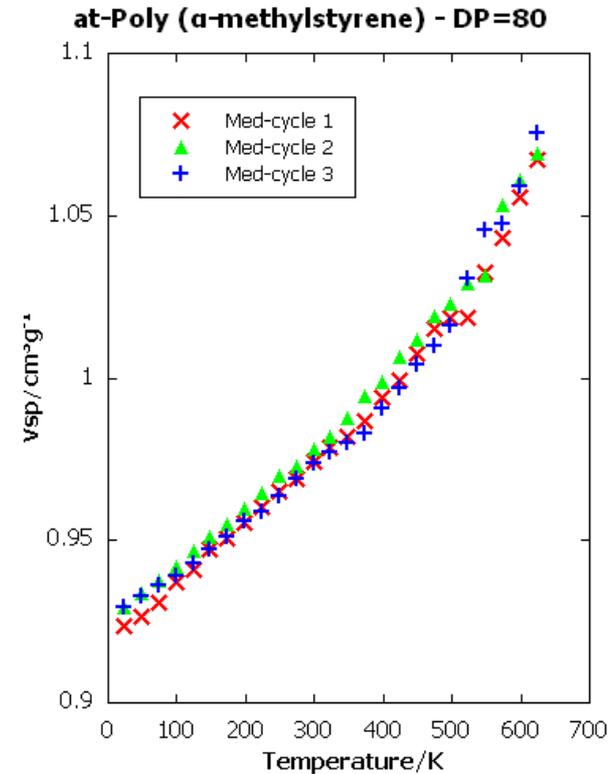
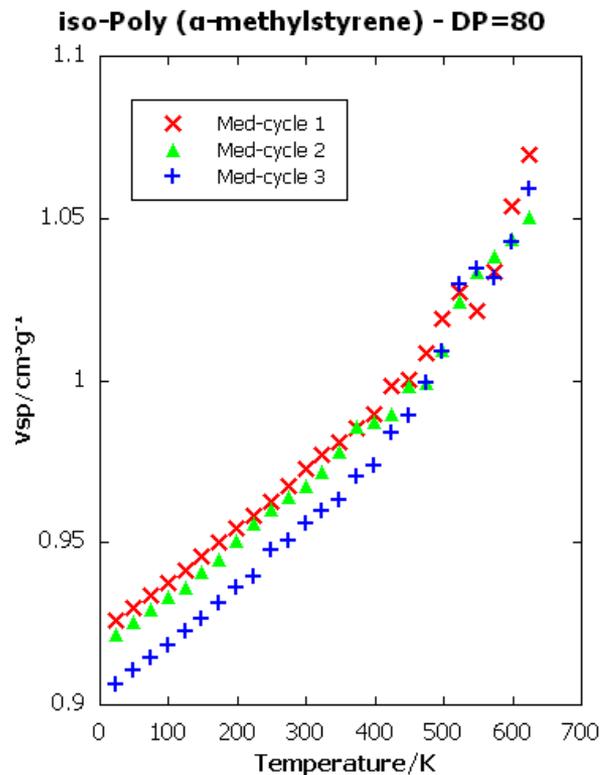
- Relaxation effects eventually become apparent on repeating stepwise cooling cycles multiple times, e.g. for DP=20:





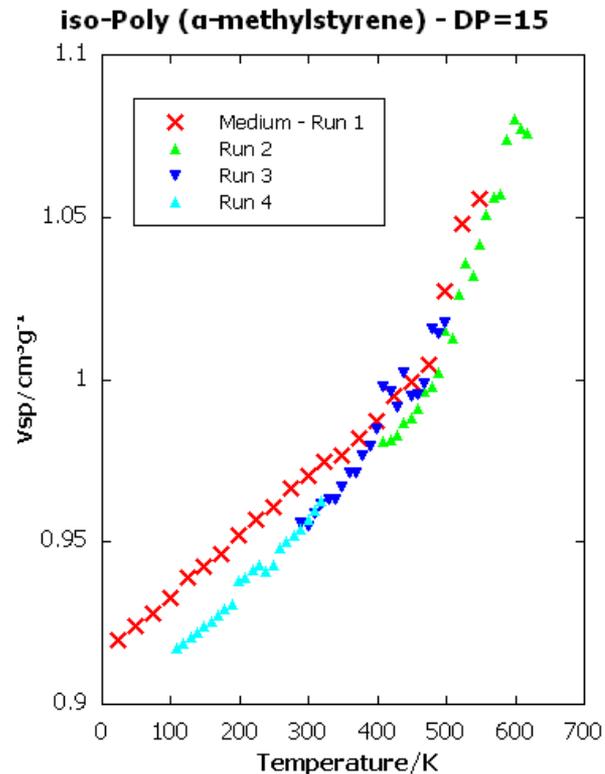
Results – Tacticity Effects

- Relaxation effects make comparisons difficult, but tacticity effects may be minor (?), e.g. at DP=80:



Results – Anomalies

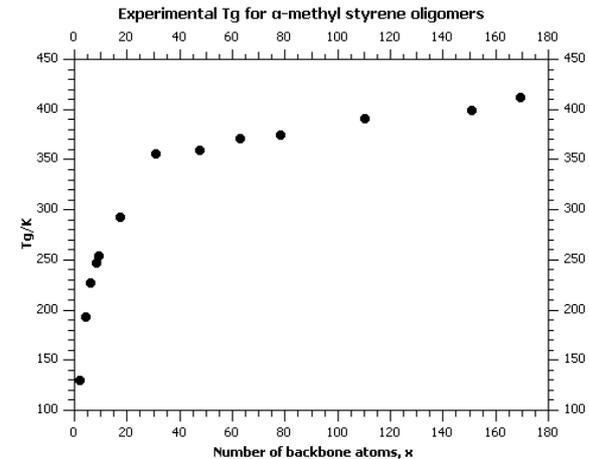
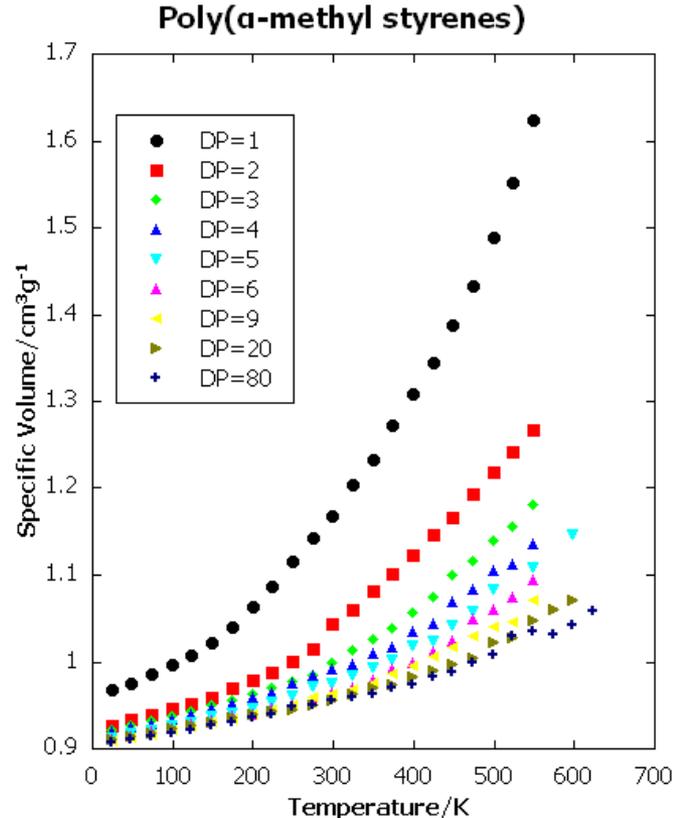
- Working with a crystallizable polymer can sometimes lead to unusual behavior, e.g. isotactic poly(α -methyl styrene), for which $T_m = 441\text{K}$, showed the following:





Results – All Oligomers

- Comparison of V-T curves for poly(α -methyl styrene) oligomers with DP=1-80. All samples are isotactic, and cooling rates of 500ps per 25K interval are used. The plot on the right shows the experimental data of Cowie at al for chain lengths up to DP=90:





Summary & Ongoing Work

- Calculations on low molar mass model compounds relevant to polystyrenes show excellent agreement with experimental PVT behavior
- Differences in thermal expansion behavior, and its systematic shifting to higher temperatures as chain length increases is visible, but:
 - Precise identification of high and low temperature regions remains difficult
 - Cooling rate effects and slow relaxation of the system have the potential to distort the results
- Need to investigate 'smoothing out' of high temperature melt data for longer chains by simulating , e.g., 10x larger systems
- Investigation of curve fitting to determine transition between low and high temperature behaviors for comparison with experimental T_g
- Parallel series of calculations with polystyrene underway
- Possible extension to other systems such as polybutadienes
- Summary planned at 2011 AIChE Annual Meeting in Minneapolis