

DF 23: Glasses and Glass Transition I (Joint Session with CPP and DY)

Time: Thursday 11:45–12:45

Location: ZEU 114

Invited Talk

DF 23.1 Thu 11:45 ZEU 114

Dynamics and thermodynamics of glassy polymers below the glass transition temperature — •DANIELE CANGIALOSI — Paseo M Lardizabal 5, 20080 San Sebastian, Spain

Glass-forming systems constitute an important class of materials. Among different aspects, the dramatic slowing down of the dynamics when decreasing temperature and the possible connection between such slowing down and the thermodynamics of the glass-former have been intensively studied. It has been speculated that mere extrapolation of the dynamics and thermodynamics to temperatures below the glass transition temperature (T_g) produces a singularity at a finite temperature, with divergent relaxation time and vanishing configurational entropy. Here the dynamics and thermodynamics are studied at temperatures as low as $T_g - 40$ K by performing enthalpy recovery experiments on glassy polymers for times up to 10^7 - 10^8 seconds. We find a single stage recovery behavior for temperatures larger than about $T_g - 10$ K. A double stage recovery is observed for $T < T_g - 10$ K. The enthalpy recovered after the two-stage decay equals that extrapolated from the melt, whereas partial enthalpy recovery occurs in the first decay. From the analysis of the time to reach each equilibrium it is found that the equilibration time corresponding to the first stage recovery exhibits relatively low activation energy, whereas the second one exhibits activation energy similar to that of the polymer segmental relaxation. These results indicate a complex scenario of the dynamics and thermodynamics below T_g with multiple equilibration steps and leave open the question the finite temperature singularity.

DF 23.2 Thu 12:15 ZEU 114

Excess heat capacity and fictive temperature of polystyrene in a wide range of cooling and heating rates — •GUNNAR SCHULZ¹, TIMUR VASILIEVICH TROPIN², YEONG ZEN CHUA¹, JÜRN W. P. SCHMELZER¹, and CHRISTOPH SCHICK¹ — ¹Institut für Physik, AG Polymerphysik, Universität Rostock, Rostock, Germany — ²Frank Laboratory of Neutron Physics, Joint Institut for Nuclear Research, Dubna, Moscow region, Russia

The physical characteristics of polystyrene allow straightforward and reproducible measurements of heat capacity, C_p , glass transition temperature, T_g , and other properties. The possibility to reuse one sample

for numerous cooling and heating cycles permits the investigation of the influence of the cooling and heating rates on C_p and T_g .

In our research, we conduct the cooling phases with various (constant) cooling rates, but the respectively following heating phases with only one heating rate. The comparison of the heat capacities observed after different cooling rates results in an excess C_p , which we also calculate by means of a model.

Our measurements furthermore yield the fictive temperature in the cooling rate range from 10^{-4} K s⁻¹ to 10^4 K s⁻¹. We compare these results with the dynamic T_g observed by means of temperature-modulated differential scanning calorimetry (TMDSC). The dependence of the fictive T_g on the cooling rate and the dependence of T_g on the modulation frequency turn out to be closely related.

DF 23.3 Thu 12:30 ZEU 114

Glassy dynamics and physical aging in fucose saccharides as studied by Infrared- and Broadband Dielectric Spectroscopy — •WILHELM KOSSACK¹, KAROLINA ADRJANOWICZ², MAGDALENA TARNACKA¹, WYCLIFFE KIPROP KIPNUSU¹, MATEUSZ DULSKI², EMANUEL URANDU MAPESA¹, KAMIL KAMINSKI², SEBASTIAN PAWLUS², MARIAN PALUCH², and FRIEDRICH KREMER¹ — ¹Universität Leipzig, Linnestr.5, Molekülphysik, 04103 Leipzig, Germany — ²Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland

Fourier Transform InfraRed (FTIR) and Broadband Dielectric Spectroscopy (BDS) are combined to study both, the intra- and intermolecular dynamics for two isomers of glass forming fucose, far below and above the calorimetric glass transition temperature, T_g . It is shown, that the various IR-active vibrations exhibit in their spectral position and oscillator strength quite different temperature dependencies, proving their specific signature in the course of densification and glass formation. The coupling between intra- and inter-molecular dynamics is exemplified by distinct changes of IR active ring vibrations far above the calorimetric glass transition temperature at about $1.16T_g$, where the dynamic glass transition (α relaxation) and the secondary β relaxation merge. — For samples physically annealed below T_g slower isothermal relaxation times than extrapolated from liquid state are observed.