MAR13-2012-001179

Dynamics and thermodynamics of polymer glasses

DANIELE CANGIALOSI, CSIC

The dynamics and thermodynamics of glass-forming systems have been the subject of intense research in the last decades. Among the variety of aspects that have been analyzed, the following can be included: i) the dramatic slowing down of the dynamics when decreasing temperature often described by a Vogel-Fulcher-Tammann (VFT) law; ii) the possible connection between such slowing down and the thermodynamics of the glass-former. These aspects have been deeply investigated above the laboratory glass transition temperature (T_g). It has been speculated that mere extrapolation of the dynamics and thermodynamics to low temperatures produces a singularity at a finite temperature. In particular, extrapolating the behavior above T_g to low temperatures would imply that: (i) the relaxation time associated to the glassy dynamics shows a divergence; (ii) the entropy of the glass equals that of the crystal. Experimental as well as theoretical efforts in the sub-T_g regime are required to clarify whether this scenario really exists. Recent experimental studies indicate deviations of the relaxation time from the VFT behavior to a milder temperature dependence [1,2] and several theoretical approaches provide a rationale to such deviations [3-7]. In this contribution the temperature range of dynamics and thermodynamics is extended to 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. Interestingly, a double stage recovery is observed for $T < T_g- 10$ K. In all cases the enthalpy recovered after the two-stage decay approximately equals that extrapolated from the melt. Time-temperature superposition close to each plateau in the enthalpy delivers shift factors containing information on the dynamics below T_g. The following scenario emerges analyzing the temperature dependence of the shift factors: i) In both stages of recovery, Arrhenius temperature dependence of the shift factor is observed; ii) The shift factor corresponding to the first stage recovery exhibits relatively low activation energy (several times smaller than that of the α process at T_g); iii) The second stage exhibits activation energy similar to that of the polymer α relaxation at T_g. These results indicate that divergence of the relaxation time at a finite temperature is likely avoided, whereas the question of a thermodynamic singularity remains open.

[1] P. O'Connell and G. B. McKenna, J. Chem. Phys. **110**, 11054 (1999).
[2] S. Simon, J. Sobieski, and D. Plazek, Polymer **42**, 2555 (2001).
[3] I. Avramov and A. Milchev, J. Non-Cryst. Solids **104**, 253 (1988).
[4] K. S. Schweizer and E. Saltzman, J. Chem. Phys. **119**, 1181 (2003).
[5] T. Hecksher, A. I. Nielsen, N. B. Olsen, and J. C. Dyre, Nat. Phys. **4**, 737 (2008).
[6] J. C. Mauro, Y. Yue, A. J. Ellison, P. K. Gupta, and D. C. Allan, Proc. Natl. Acad. Sci. U. S. A. **106**, 19780 (2009).
[7] Y. S. Elmatad, D. Chandler, and J. P. Garrahan, J. Phys. Chem. B **113**, 5563 (2009).