Comment on "Resolving the Mystery of the Chain Friction Mechanism in Polymer Liquids"

In a recent Letter to this journal, Sokolov and Schweizer (SS) [1] offered an explanation for the length-scale dependence of the friction mechanism in polymers. This dependence gives rise to different temperature dependences for the local segmental and global chain modes, which in turn underlies the well-known breakdown of time-temperature superpositioning in the glass transition zone of polymers. In consideration of the issues enumerated below, we believe it is problematic to describe the explanation proffered by SS as "resolving the mystery of the chain friction mechanism in polymer liquids" [1].

(i) The interpretation of SS rests on the assumption that the decoupling of translational and reorientational motions in nonpolymeric liquids is due to heterogeneity of the local dynamics. However, for three well-known cases of such decoupling, *o*-terphenyl [2], tris(naphthyl)benzene [3–5], and sucrose benzoate [6], the distribution of relaxation times is unchanged with variation in temperature over the range of T/T_g from about 1.02 to 1.2. As pointed out by Mapes *et al.* [7], "The dielectric relaxation and photon correlation spectroscopy results imply a relaxation time distribution whose shape is too temperature independent to cause [translational-rotational decoupling], at least within the framework of current approaches." The role of dynamic heterogeneity remains to be fully understood and there is another explanation for the decoupling that does not invoke heterogeneity [8]. The point is that it is premature to explain a second phenomenon using an explanation that does not account for the first phenomenon.

(ii) Decoupling of the viscosity and self-diffusion is known in entangled polymers, these quantities having different activation energies and incompatible molecular weight dependences [9]. Since both involve global chain modes, it is not obvious how this decoupling can be accounted for by heterogeneous dynamics. The inference is that the temperature dependence of the chain dynamics cannot arise simply from temporal and spatial averaging of the heterogeneous segmental dynamics, which would just give the same friction factor as that of the segmental dynamics.

(iii) SS support their ansatz by its consistency with "the almost universal behavior of the temperature dependence of chain relaxation" [1]. This universal behavior is the putative equivalence of the T_g-normalized temperature dependence (fragility) of the viscosity, η, or global relaxation time, τ_c, for all polymers. However, with the exception of polystyrenes of different molecular weights (wherein temperature dependences of low molecular weight samples reflect contributions from a changing compliance and the sub-Rouse modes, in addition to the usual friction factor [10]), the fragility of the chain dynamics of polymers differ substantially [11]. Averaging of T_g-normalized temperature dependences can yield single curves with large error bars (Figure 3b in Ref. [1]), but the data points *per se* exhibit substantial deviations. For example, the ordinate value of a fragility plot of τ_c for polyvinylethylene is more than twice that for polymethylphenylsiloxane at $T_g/T \sim 0.92$; there is a similar difference between polyisobutylene and polystyrene at $T_g/T \sim 0.95$ [11]. Other examples can be cited; there is no universal behavior.

(iv) In evaluating the temperature dependence of the chain dynamics, η and τ_c should not be used interchangeably. The viscosity is given by the product of τ_c and the recoverable equilibrium compliance, J_e. The latter strongly decreases upon cooling towards T_g [12–14], introducing an additional effect of T on η. As a result, depending on the molecular weight of the polymer and its proximity to the glass transition, the T dependence of the viscosity can be the same as or stronger than that of τ_c [10]; consequently, fragility plots combining η and τ_c cannot show universal behavior. Moreover, this strong decrease of J_e as T_g is approached cannot be a consequence of temporal and spatial averaging of the heterogeneous segmental dynamics.

K. L. Ngai,[1] D. J. Plazek,[2] and C. M. Roland[1]
[1]Naval Research Laboratory
Washington D.C. 20375-5342, USA
[2]University of Pittsburgh
Pittsburgh, Pennsylvania 15261, USA

Received 8 July 2009; published 5 October 2009
DOI: 10.1103/PhysRevLett.103.159801
PACS numbers: 83.80.Sg, 64.70.P−

[1] A. P. Sokolov and K. S. Schweizer, Phys. Rev. Lett. **102**, 248301 (2009).
[2] R. Richert, J. Chem. Phys. **123**, 154502 (2005).
[3] R. Richert, K. Duvvuri, and L.-T. Duong, J. Chem. Phys. **118**, 1828 (2003).
[4] X. R. Zhu and C. H. Wang, J. Chem. Phys. **84**, 6086 (1986).
[5] K. Zemke, K. Schmidt-Rohr, J. H. Magill, H. Sillescu, and H. W. Spiess, Mol. Phys. **80**, 1317 (1993).
[6] J. R. Rajian, W. Huang, R. Richert, and E. L. Quitevis, J. Chem. Phys. **124**, 014510 (2006).
[7] M. K. Mapes, S. F. Swallen, and M. D. Ediger, J. Phys. Chem. B **110**, 507 (2006).
[8] K. L. Ngai, Philos. Mag. **87**, 357 (2007).
[9] G. B. McKenna, K. L. Ngai, and D. J. Plazek, Polymer **26**, 1651 (1985).
[10] C. M. Roland, K. L. Ngai, and D. J. Plazek, Macromolecules **37**, 7051 (2004).
[11] K. L. Ngai, D. J. Plazek, and C. M. Roland, Macromolecules **41**, 3925 (2008).
[12] D. J. Plazek and V. M. O'Rourke, J. Polym. Sci. A **9**, 209 (1971).
[13] K. L. Ngai and D. J. Plazek, Rubber Chem. Technol. **68**, 376 (1995).
[14] P. G. Santangelo and C. M. Roland, J. Rheol. **45**, 583 (2001).