Why Many Polymers are so Fragile: The Final Answer?

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If fragility of molecular liquids is usually limited to m~80-100, many polymers exhibit fragility m~150 and even higher. The mechanism of this unusually steep temperature dependence of structural relaxation (high fragility) in polymers still remains a puzzle [1]. To reveal additional hints for understanding the underlying mechanism, we analyzed molecular weight (MW) dependence of chain and segmental dynamics in several polymers. While fragility of segmental dynamics in many polymers increases sharply with MW, fragility of chain dynamics appears to be essentially independent of MW and comparable to fragility of small molecular liquids. Our surprising discovery is that the temperature dependence of the chain relaxation in polystyrene follows well the Adam-Gibbs relationship, which fails in the case of segmental relaxation [2]. Moreover, many correlations that fail for segmental dynamics fragility work well for chain fragility [2]. These results suggest that the molecular level relaxation (chain relaxation) follows the behavior usual for small molecules even in polymers. It is the segmental relaxation that has the unusually high fragility. We suggest that many polymers cannot reach an ergodic state on the time scale of segmental dynamics due to chain connectivity and rigidity. This leads to a sharper decrease in accessible configurational entropy upon cooling, and results in steeper temperature dependence of segmental relaxation. The proposed scenario provides a new important insight in specifics of polymer dynamics: the role of ergodicity time and length scale.

References

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2. C. Dalle-Ferrier, et al., **J. Chem. Phys. 145**, 154901(2016).