

Dynamic Crossover in Polymers, Role of Molecular Weight

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1. Introduction

One of the most characteristic features of glass-forming liquids is the sharp slowing down of relaxation times, τ , upon cooling. In these materials relaxation dynamics exhibit a non-Arrhenius temperature dependence usually described by Vogel-Fulcher-Tamman (VFT) relation [1]. However, for majority of glassforming liquids it is impossible to fit data in the entire temperature range with a single set of VFT parameters. Above some characteristic temperature it is necessary to use another set of VFT parameters. Existence of this dynamic crossover was predicted by the mode-coupling theory (MCT) [2]. The theory predicts a transition from a liquidlike to a solidlike dynamics on a molecular time and length scale at some specific temperature, T_C , above the glass transition temperature T_g . The dynamic crossover becomes even more evident with the use of derivative analysis proposed by Stickel *et al* [3] $\phi_T = \left(\frac{d \log x}{dT}\right)^{-1/2}$, where x is the relaxation time or frequency. If

τ follows the VFT equation, ϕ_T should vary linear with T . This is the so-called Stickel plot. In this plot, a change in the dynamics appears as a break in the linear dependence and the crossover temperature, T_B , can be clearly identified. In most cases $T_C \sim T_B$. Novikov and Sokolov check literature data for existence of crossover phenomena in different materials [4]. They found that T_B strongly depends on material whereas the relaxation time at the crossover temperature, τ_C , seems to have a rather universal value, $\tau \sim 10^{-7 \pm 1}$ sec, for the majority of materials.

An important feature of supercooled liquids is also degree of departure of relaxation times from Arrhenius temperature dependence. Angell proposed classification of the liquids according to this deviation from activation behavior. He used the slope of the temperature dependence of relaxation times, presented vs T_g/T , to estimate the so called "steepness index" or "fragility", m [5]. According to this classification parameter, m increases with increasing deviation from Arrhenius-like behavior. It has to be emphasized, that ratio T_B/T_g , correlates with the fragility of the system: the lower value of the ratio, the higher is the fragility.

2. Dynamic crossover in polymers

Polymers present an interesting example: one can change properties of these materials by changing only the chain length with no change in chemical structure. For some polymers,

like siloxanes, change of molecular weight has weak influence on relaxation dynamics [6]. For another group of polymers such as Polystyrene (PS) increasing molecular weight leads to significant changes of T_g and m [7]. It has been shown that polymers also exhibit a kind of dynamic crossover. Moreover, it seems that temperature dependences of chain and segmental relaxation dynamics becomes different at $T < T_C$. However, there is no study of molecular weight dependence of T_g .

We address this problem by investigations of Polyisoprene (PIP) and PS with different molecular weights using broadband dielectric spectroscopy (DS) and depolarized light scattering (LS).

In both polymers a dynamic crossover has been identified at temperatures significantly above their T_g 's. Moreover, the crossover temperature estimated from Stickel plot, T_B , and critical temperature obtained from the MCT analysis, T_C , are similar. The results show that increasing molecular weight leads to increases in the crossover temperature.

It has to be emphasized that the relaxation time at which crossover is observed remains independent of molecular weight and similar in both polymers. It is almost the same universal relaxation time, $\tau \sim 10^{-7 \pm 1}$ sec that has been reported for most of the non-polymeric systems.

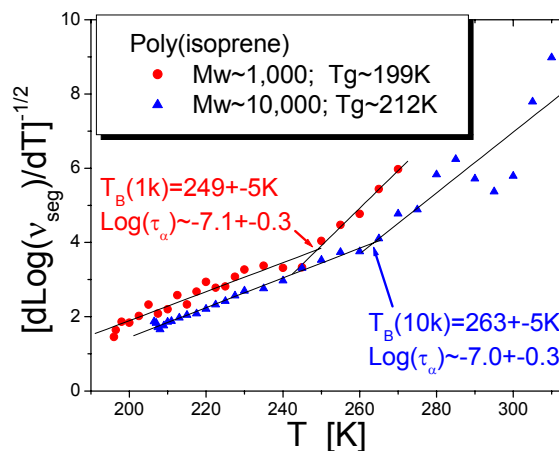


Fig. 1: Stickel plot of data for PIP. Straight lines represent result of Stickel analysis of VFT fits.

References

- [1] H. Vogel, J. Phys. Z. **22**, 645 (1921); G. S. Fulcher, J. Am. Ceram. Soc. **8**, 339 (1925); G. Tamman and W. Hesse, Z. Anorg. Allg. Chem. **156**, 245 (1926);
- [2] W. Gotze and L. Sjogren, Rep. Prog. Phys. **55**, 241 (1992);
- [3] F. Stickel, E. W. Fischer and R. Richert, J. Chem. Phys. **102**, 6251 (1995);;
- [4] V. N. Novikov and A. P. Sokolov, Phys. Rev. E **67**, 031507 (2003);
- [5] C. A. Angell, *Relaxation in Complex Systems*, edited by K. Ngai and G. B. Wright, National Technical Information Service, U. S. Department of Commerce, Springfield, VA 22161 (1985), p. 1;
- [6] S. Pawlus, S. J. Rzoska, J. Ziolo, M. Paluch, C. M. Roland, Rub. Chem. Tech. **76**, 1106 (2003);
- [7] P. G. Santangelo and C. M. Roland, Macromolecules **31**, 4581 (1998);