DoDyNet Final Conference on Double Dynamics Networks
24-27 May 2022

Linear Viscoelasticity of Unentangled Associative Polymer: Theory and Simulation

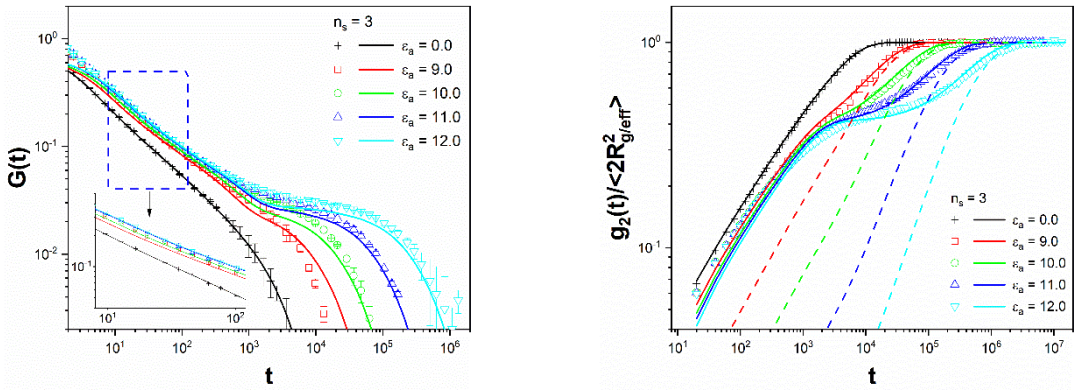
Nuofei Jiang, Hongdong Zhang, Yuliang Yang, Ping Tang[a]

[a]*State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433,*
Correspondence Author address: pingtang@fudan.edu.cn

Polymers bearing associative groups (APs) are characterized by their fantastic viscoelastic behaviors. The dynamics of unentangled AP melts in the linear regime is often referred as “sticky Rouse”. Here we propose a new framework of sticky Rouse model (SRM), which considers stickers as beads suffering additional frictional force and relaxing in a homogeneous medium [1]. Based on this concept, the linear viscoelastic properties of AP are derived from a modified Rouse equation of motion, with an effective frictional parameter representing the strength of associative interaction. Theoretical results show this friction-based SRM predicts gelation transition and a typical sticky Rouse relaxation time spectrum, which are consistent with previous theories and experimental findings. In addition, some characteristic molecular motions in AP are also predicted, which has not been pointed out by previous theories.

Inspired by the predictions of the SRM, molecular dynamics simulation on unentangled AP melt is designed [2]. The values of the effective frictional parameter are obtained from diffusion constants, and they are found to be directly linked to the association relaxation time. The linear relaxation modulus and segmental relaxation functions are then predicted from SRM without free parameters, and found to be quantitatively consistent with simulation results, as shown in Fig. 1.

Our results show the SRM proposed here can provide a deeper understanding on the dynamics of AP from the molecular level. Recently the basic idea of this model has been successfully extended to described duel polymer networks [3].



(a) (b)

Fig. 1. Comparison between theory and simulation on (a) linear relaxation modulus and (b) segmental relaxation function.

Acknowledgments: The authors acknowledge the National Natural Science Foundation of China (NNSFC) (Grant Nos. 21774027, 21973017, and 21534002) for financial support.

[1] Jiang, N.; Zhang, H.; Tang, P.; Yang, Y., *Macromolecules* **2020**, 53 (9), 3438-3451.
[2] Jiang, N.; Zhang, H.; Yang, Y.; Tang, P., *J. Rheol.* **2021**, 65 (4), 527-547.
[3] Shao, J.; Jiang, N.; Zhang, H.; Yang, Y.; Tang, P., *Macromolecules* **2022**, 55 (2), 535-549.