高等学校化学学报 2007 , 28 (5): 992—995 ISSN: 0251-0790 CN: 22-1131/O6

研究论文

受限状态聚合物熔体的分子动力学模拟

李奕杰[1,2], 魏东山[1,2], 金熹高[1], 韩志超[1], 廖琦[1]

1. 中国科学院化学研究所, 高分子物理与化学国家重点实验室, 高分子科学与材料联合实验室, 北京 100080;
2. 中国科学院研究生院, 北京 100039

收稿日期 2006-6-30 修回日期 网络版发布日期 2007-4-25 接受日期

摘要 用粗粒化的分子动力学(MD)模拟方法从分子层次研究了受限于粗糙壁内的聚合物熔体的动力学性质. 结果表明, 对于链长较短的受限聚合物熔体体系, 随着膜厚的增加, 体系内部高分子链的松弛时间逐渐减少; 然而对于链长较长的受限体系, 聚合物链的松弛时间随着膜厚的增加先减少后增加. 推测这种由于链长的变化所引起的动力学性质的差异源自受限熔体内聚合物链聚集状态的改变, 并且通过考察交叠参数对这种改变进行了分析. 结果表明, 在膜厚增加的过程中, 决定受限状态高分子长链松弛机理的因素逐渐从受限效应转变成为链间的缠结效应.

关键词 分子动力学模拟 聚合物熔体 受限状态 松弛时间

分类号 0631

Molecular Dynamics Simulation of Confined Polymer Melts

LI Yi-Jie[1, 2], WEI Dong-Shan[1, 2], JIN Xi-Gao[1], Han Charles C.[1], LIAO Qi[1]*

1. Joint Laboratory of Polymer Science and Materials, State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China;
2. Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

Abstract We present the results of molecular dynamics simulations of polymer melts confined between two rough walls. Simulations were performed for the coarse-grained bead-spring chains of Lennard-Jones particles. The results show that, the longest relaxation time decreases with increasing the film thickness for the confined polymer melt systems with relative short chains; while for the confined systems with longer chains, the relaxation time decreases first and then increases to the bulk value when increasing the film thickness. We speculate on the origin of this unique phenomenon and conclude that longer chains in the confined systems change from the entangled state in three-dimensional space to the segregated state in nearly two-dimensional space with the decrease of film thickness. The overlap parameter is used to interpret this transitional process. We find that, for the longer polymer chains, entanglement effect determines the relaxation time in thicker films, while confinement effect dominates the relaxation in thinner films.

Key words Molecular dynamics simulation Polymer melt Confinement state Relaxation time

DOI:

通讯作者 廖琦 qiliao@iccas.ac.cn