187b Rheological and Structural Studies of Linear Polyethylene Melts under Planar Elongational Flow Using Nonequilibrium Molecular Dynamics Simulations

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1. Introduction

Nonequilibrium molecular dynamics (NEMD) simulations play a significant role in our understanding of rheological and structural behaviors of polymeric materials in flowing systems, which is important not only in practical polymer processing, but also in advancing our knowledge of fundamental characteristics of chain molecules, *i.e.*, viscoelasticity.[1,2] While numerous data of shear flow as an important standard flow in the study of rheology have been accumulated not only by real experiments but also by computer simulations, there have been only few experimental data of elongational flow due to the difficulty in performing experiment. More seriously, NEMD simulation of elongational flow has been fraught with its limited simulation time, which could be easily exceeded by the intrinsic relaxation time of physical system even with short chain molecules. This difficulty has been partially, i.e., only for planar elongational flow (PEF), resolved by Kraynik and Reinelt's[3] discovery of the temporal and spatial periodicity of lattice vectors in PEF, and therefore we could, in principle, continue NEMD simulations without any limit. Recently, however, Todd and Daivis[4] have reported an aphysical phenomenon in their NEMD simulations of PEF for a simple fluid especially at low elongation rates when using the so-called SLLOD algorithm, which has been the most widely used NEMD algorithm. Very recently, all such problems have been resolved by the present authors[5] using the so-called proper-SLLOD (or p-SLLOD) algorithm implemented with their simulation strategy. Furthermore, more recently using the p-SLLOD algorithm, the present authors[6] have performed for the first time NEMD simulations of PEF for systems composed of short-chain alkanes. Many interesting results have been observed there. All the results reported therein were shown to be physically reasonable, and their physical interpretations of numerous different phenomena appeared to be physically plausible and consistent with each other. Those work appeared to further demonstrate the fundamental correctness of the p-SLLOD algorithm for elogational flow (in fact, for arbitrary flow).

In this study, we extend our NEMD simulations of PEF to more complex linear polyethylene melts of $C_{50}H_{102}$ up to $C_{128}H_{258}$. **2. Technical approach**

In our previous work,[6] we studied quite extensively the rheological and structural properties of three short-chain alkanes such as $C_{10}H_{22}$ (decane), $C_{16}H_{34}$ (hexadecane) and $C_{24}H_{50}$ (tetracosane), under PEF using NEMD simulations by the p-SLLOD algorithm. In the present work, we explore more complex systems comprising polyethylene melts of $C_{50}H_{102}$, $C_{78}H_{158}$ and $C_{128}H_{258}$. This choice of chain length may be considered a crossover from the Rouse regime to the reptation regime.[7] The same temperature, T=450 K, was used for all the systems. Different density, however, was employed for each system: r=0.7426 g/cm^3 for $C_{50}H_{102}$, r=0.7640 g/cm^3 for $C_{78}H_{158}$, and r=0.7754 g/cm^3 for $C_{128}H_{258}$. Due to the fully stretched conformation of molecules at high elongation, we used fairly big systems (but still not enough for high elongation rates), in particular for $C_{128}H_{258}$. Specifically, we employed 96 molecules for $C_{50}H_{102}$ (total 4800 interaction sites), 192 molecules for $C_{78}H_{158}$ (total 14976 interaction sites), and 416 molecules for $C_{128}H_{258}$ (total 53248 interaction sites). The reduced elongation rate employed in this study ranges from =0.0001 to 0.2. The highest elongation was limited by =0.2 in order to avoid any artificial effect due to the small system size, whose effect, in fact, was observed using the present simulation box size at higher elongation rates. **3. Results and Discussion**

The longest relaxation time, the so-called Rouse time t_{Rouse}, were determined by the time correlation function of the end-to-end vector of chains using equilibrium MD simulations: t_{Rouse}=500 ps for $C_{50}H_{102}$, t_{Rouse} =1.4 ns for $C_{78}H_{158}$, and t_{Rouse} =5.5 ns for $C_{128}H_{258}$. The corresponding reduced critical elongation rates are found to be =0.0047 for $C_{50}H_{102}$, =0.0016 for $C_{78}H_{158}$, and =0.00043 for $C_{78}H_{158}$. Approximately, above the critical elongation rate for each system, two elongational viscosities, h_1 and h_2 showed tension-thinning behavior as elongation rate increased for all the systems in this study. As in our previous work with short-chain alkanes, it was observed that h_1 and h_2 are, in general, not equal to each other, indicating that there are two independent material functions in PEF. The minimum behavior in the hydrostatic pressure was also observed for all the systems, as clearly reported in NEMD simulations of shear flow for $C_{100}H_{202}$ by Moore *et al.*.[8] This behavior appeared to originate from the change in the intermolecular LJ potential energy with elongation rate through two competing factors of chain alignment (static factor) and intermolecular collision (dynamic factor). As for two important structural quantities, the mean square end-to-end distance of chains, $<R_{ete}^{2}>$, and the mean square radius of gyration of chains, $<R_{g}^{2}>$, it was observed that at low elongation rates both $<R_{ete}^{2}>$ and $<R_{g}^{2}>$ increase with increasing elongation rate because the molecules are elongated due to the field, and in the intermediate range of elongation rate the intermolecular collisions between molecules become stronger and is likely to disrupt their full elongation, which leads to a plateau value. Further details of chain conformation have been represented well by investigating the conformation tensor, which is considered one of the most important physical quantities in polymer rheology. **4. References**

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