Although conformational relaxation of individual polymers in entangled state has been extensively investigated by direct observation in experiments, evaluation of molecular measures to adequately describe the individual polymer dynamics has not been established yet. In this study, relaxation behavior was discussed, on the basis of the primitive chain network simulations, for a measure for individual polymer conformation employed in some experiments. As the molecular measure, the maximum distance in between segments contained in a given polymer chain, which is often referred to as chain extension and usually nomenclated by $x$ was mainly examined following some experiments with fluorescent microscopy of DNA. The relaxation behavior was discussed in terms of auto-correlation function obtained in quiescent state. It was found that the relaxation obtained as ensemble average of the auto-correlation functions of individual polymers is significantly different from neither stress relaxation nor dielectric relaxation of the normal mode, while the power-law exponent of the longest relaxation time against chain length for the relaxation functions of stress and the measure $x$ is close to each other.

1. INTRODUCTION

Several researchers following the landmark study by Perkins et al. have performed observation of individual DNA molecules with fluorescent microscopy, assuming that DNA exhibits the universal polymer motion. Indeed, although DNA is known as a rigid polyelectrolyte, under some conditions with a high ionic strength it has been reported that the observed DNA diffusion can be explained by the established models for flexible and neutral synthetic polymers. Recently rheological data have been reported for the entangled solutions used in the observation has been reported and consistency between microscopic and macroscopic relaxation times has been confirmed for the examined solutions.

However, available data on the relaxation functions or spectra of the observed individual polymer motion in entangled solutions has not been reported. It is due to uncertainty of the measures for individual molecular relaxation behavior in microscopic experiments. In the experiments, DNA is stained uniformly along its contour and observed through 2D images projected to the high sensitive fluorescence detector. Because of the nature of this method, measures obtained from the fluorescent intensity matrix on the detected 2D images have been reported and consistency between microscopic and macroscopic relaxation times has been confirmed for the examined solutions.

In this study we performed primitive chain network simulations and compared relaxation functions obtained for macroscopic measures and measures for individual molecules including the measure $x$ used in the fluorescent microscopy experiments. Comparison among relaxation functions and effects of possible artifacts on average calculations shall be discussed.

2. MODEL AND SIMULATIONS

We used the primitive chain network model that has been already reported in several publications. In the model a network composed of nodes and strands represents an entangled polymer system. Consecutive strands in the network represent polymer chain. Each node has four converging strands consistently with the binary assumption of the entanglement, and the node position is determined by force balance among the tension of the converging strands, friction force against medium, osmotic force generated by local density fluctuations, and thermal agitation. Transport of monomers along the polymer chain occurs through the node and the monomer number assigned to each strand is determined by kinetic equation accounting for the same physico-chemical forces with the node dynamics. In addition entanglement and disentanglement among chains by reptation are realized by creation and destruction of the network nodes at the chain ends.

Simulations were performed with monodisperse linear chains consisting of 9.6 and 19.2 strands dispersed in simulation box of $12^3$ with usual periodic boundary condition. Segment density in the box was set to 10.

![Image](https://example.com/fig1.png)

Fig. 1 A typical snapshot of the simulation shown as (a) 3D structure and its projection onto 2D plane, (b) intensity matrix constructed from the 2D projection
3. MEASURES

For discussions on the measure for the chain extension employed in the DNA experiments, we obtained the measure in the simulations as shown in Figs 1 in some different ways. Fig 1 (a) indicates chain conformation in 3D space, and from the conformation we can obtain the measure as the maximum separation in between the nodes in 3D space from the actual position of each node. Fig 1 (a) also shows the 2D projection of the 3D conformation on the x-y plane lying on the bottom, and similarly to the case of 3D conformation, we can obtain the measure for the maximum node separation in 2D. In Fig 1 (b), onto the 2D projection we include the effect of the detector cell as a mimic of the high-sensitive CCD camera used in the DNA experiments. Setting a spatial resolution we assumed square mesh on the detector lying on x-y plane, counted number of the chain nodes located on each detector cell, and obtained an intensity matrix. From the intensity matrix we calculated the maximum separation between the cells having the signal from the chain.

The relaxation functions of the measures under equilibrium were obtained as auto-correlation functions based on the Green-Kubo formula. The relaxation functions for the bulk measures, e.g., stress and electrical polarization, are calculated from the time development of the measures recorded for time period being more than 1000 times longer than the observed longest relaxation time. The relaxation functions for individual chains are calculated as ensemble average of the auto-correlation functions of 100 chains. The auto-correlation of each chain was calculated from time development of the individual chain measures for time period being 20 times longer than the longest relaxation time. Note that the x relaxations presented in the following sections were calculated for the measure x obtained with the cell detector with the cell dimension of 1 x 1.

4. RESULTS AND DISCUSSION

Figure 2 shows relaxation functions for the measure x compared with relaxations of shear stress and electrical polarization. The relaxation functions of the measure x is similar to neither the stress relaxation nor the dielectric relaxation. This result is not trivial because the x relaxation and the dielectric relaxation are calculated from similar measures for the global polymer segments is similar to neither stress relaxation nor dielectric relaxation, while the longest relaxation time obeys a similar scaling behavior against molecular weight. For further discussion the individual chain measure under flow and deformation has been being examined and the results will be reported elsewhere.

5. CONCLUSION

Since it is apparent from Figure 2 that the relaxation functions can be described by a single exponential function in the long time region, the longest relaxation time was extracted by the least square fitting. Figure 3 shows the molecular weight dependence of the relaxation time for the x relaxation. The relaxation time for the stress relaxation is also plotted for comparison. It is indicated that the scaling behavior for the relaxation time against the molecular weight is similar to that for the stress. This means that the x relaxation is not dominated by fast relaxation modes of polymer dynamics such like Rouse relaxation, though the relation in between the relaxation functions is unknown.

REFERENCES