§21. Molecular Dynamics of Strongly Coupled Multichain Coulomb Polymers

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Polyampholytes (PA) are the polymers that comprise of both positively and negatively charged monomers (molecules), for which the electrostatic coupling constant is of order or even greater than unity at room temperature and normal pressure,

$$\Gamma = e^2/\epsilon a T > 1. \qquad (1)$$

The importance of this study consists both in the fundamental processes of plasma physics, and its methodology of molecular dynamics which can be applied to materials R&D needed in fusion programs.

In the fiscal year 1998 by following a previous work for the single-chain PA [1], we revealed with the use of molecular dynamics simulations the multichain effect and also the effect of added salt on randomly co-polymerized charged polymers in a Langevin fluid [2,3]. The monomers of opposite signs tend to form loose complexes, which makes the Coulomb force attractive on average. With multichain polyampholytes, the typical state at high temperature is a container-bound one-phase state of separated chains with a substantial void among them (Fig.1(a)). The association and dissociation processes occur repeatedly, with the former process a few times faster than the latter. A glass transition occurs when temperature is lowered, at the filling index $\xi = 1$ as shown in Fig.2. A compact and glassy globule in a segregated phase of Fig.1(c), which resembles that of a single-chain polyampholyte, is a typical state at low temperature due to the Coulomb force. It was proven that the probability of losing this state is as low as, $P_{dis} \sim \exp(-N^{3/2})$, with N the number of monomers. The critical temperature defined by overlapping of the chains increases with molecular weight and stiffness of the chains, and is less sensitive to the number of the chains. An alternate charge sequence makes a difference only when its block size is quite small. The addition of salt suppresses the formation of a dense globule by shielding the electric field; however, this is not effective when the salt ions are not allowed to penetrate well into the globule.

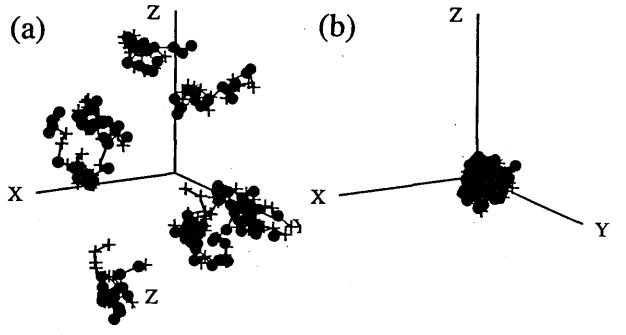

Fig. 1. Typical relaxed conformations of multichain polyampholyte for high and low temperatures in (a) and (b), respectively. A morphological change occurs via glass transition between them.

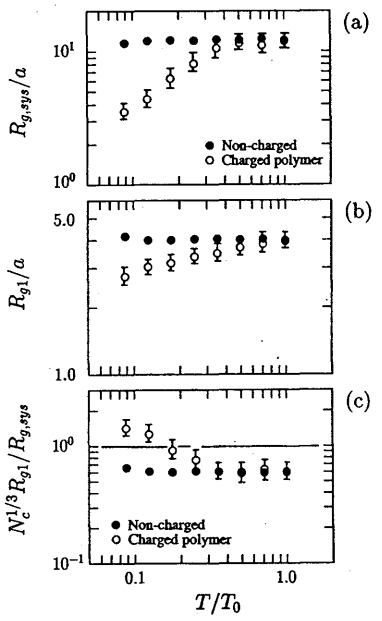

Fig. 2. Effect of the Coulomb force, as seen in differences between the non-charged polymers and charged polymers. The figure shows the system and individual gyration radii in (a) and (b), respectively, and (c) the filling index which indicates chain overlapping for $\xi \geq 1$.

References
[1] M. Tanaka, A.Yu Grosberg, V.S. Pande, and T. Tanaka, *Phys.Review, E56*, 5798 (1997).
[2] M.Tanaka, A.Yu Grosberg, and T.Tanaka, in *Slow Dynamics in Complex Systems* (edited by M.Tokuyama and I.Oppenheim, AIP Conference Series, CP469, 1999).
[3] M. Tanaka, A.Yu Grosberg, and T. Tanaka, *J. Chemical Phys.*, 110, 8176 (1999).