## §36. Analysis of the Polymer Chain Dynamics in the Poly-ion Complex

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The physics of non-equilibrium system, such as the plasma confinement has been attracts much interest. Particularly, the investigation of the formation process of self-organized structure and symmetric order in the non-equilibrium and non-linear system has becomes important. In order to explorer the understanding of the universal property of the self-organization, we investigate sol-gel transition in the mixed complex of polymers containing a large number of cations and anions by using the theoretical method of statistical physics.

Some of mixed complexes which consist of macromolecules are known to cause sol-gel transition. In recent experimental study, it is found that poly-ion complexes (PIC) which contains small amounts of poly-anion (PA) and poly-cation (PC) causes sol-gel transition by application of the shearing vibration. This property is called dilatancy of which mechanism we investigate theoretically.

We adopt transient network theory[1]. In figure 1, we show two configurations of the micelles formation in the complex which consists of telechelic associated polymer (PC) and poly-functional polymer (PA). One is the flower micelles in which the paired end of loop chain of PC and anion in PA are combined, the other is a micelle that has a large-scale structure in which PC treat as bridge chain and make crosslinks among the flower micelles. The phase which mainly contains the flower micelles is considered to be the sol phase, whereas the phase which contains the large-scale structure of micelles is considered to be the gel phase. We consider that sol-gel transition accompanies the reorganization of micelles according to the relocation of the PC chain among the flower micelles.

We investigate sol-gel transition specifically considering the dynamics of PC chain in flowing solution. As it is shown in figure 2, PC in the flower micelles make loops at the anions in the PA chains. Because formation probability of a PC loop would be reduced in accordance with the increase of the flow velocity in solution, the formation probability of a flower micelle in sol phase is reduced by shearing vibration. Then the disturbance of the flower micelles by shearing of solution induces the formation of the crosslinked micelles, so that the shearing induces sol-gel transition. In order to evaluate the loop formation probability, we adopt Rouse model (Free-draining model) which is the theoretical model of polymer chain that is composed of globules and connecting spring. The configuration of Rouse model is shown in figure 3. First, we obtain the distribution function of the globules in the polymer chain in the mixed complex by solving the Fokker-Plank equation. Evaluating the formation probability of a closed loop of PC (the formation probability of a flower micelles) by using distribution function, we can theoretically prove that the formation probability of a PC loop (a flower micelle) is reduced in accordance with the increase of the flow velocity.

In our past experimental and theoretical study of dilatancy, we find that the phase boundary of sol-gel transition depends on the mixture ratio of PC and PA. Our present study provides a theoretical understanding of the phase boundary dependence. Present result shows the dependency of the formation probability of a PC loop (a flower micelle) on the flow velocity of solution and suggests the dilatancy of PIC i.e. sol-gel transition of the mixed complex induced by the shearing disturbance.

1) Fumihiko Tanaka: Polymer Physics, (Cambrudge University press, 2011).

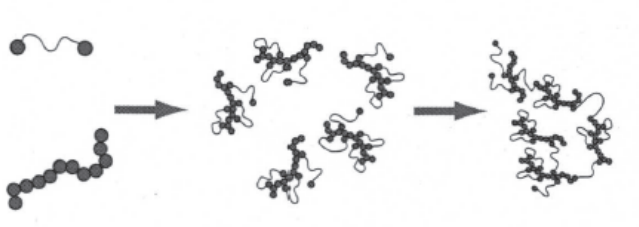

Fig.1 Internal reorganization of the transient network induced by a macroscopic disturbance.

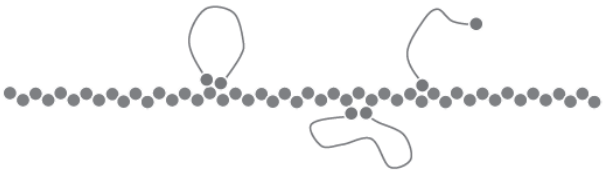

Fig. 2 Configuration of formation of a flower micelle which is composed of PC and PA.

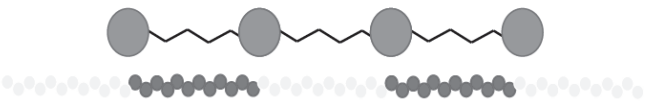

Fig. 3 Configuration of a PC polymer chain in Rouse model. PC polymer is composed of globules and connecting spring.