<div align="center">論文の内容の要旨</div>

論文題目　　　**Swelling Behaviors of Polyelectrolytes Gels with Alternating Neutral/Highly Charged Sequences under Various Environmental Conditions**
（中性/高電荷シーケンスを交互に導入した高分子電解質ゲルの多様な環境下での膨潤特性）

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Polyelectrolyte gels comprise fixed ions on the polymer strands and contain a solvent with mobile ions. In contrast with electrically neutral gels, polyelectrolyte gels often exhibit significant swelling ability, depending on the external solution conditions. Such behaviors can be explained using the Flory–Rehner model that considers the Donnan equilibrium (F-R-D model), in which the equilibrium state of polyelectrolyte gel is determined by three energetic contributions to the swelling pressure of the system, i.e. (i) contribution of the elastic free energy accompanied by the swelling of the network strands, Π_{el}; (ii) contribution of the free energy derived from the mixing of polymer segments with solvent molecules, Π_{mix}; and (iii) contribution of the osmotic free energy originating from the imbalanced distribution of the counterions inside and outside the gel, Π_{ion}. However, this model assumes a homogeneous distribution for fixed ions; therefore, its applicability to the case of heterogeneous distributions of fixed ions remains unclear.

Conventionally, polyelectrolyte gels are prepared via the random radical copolymerization of charged and neutral monomers with crosslinkers. The charged monomers are expected to localize on a strand, owing to the differences in the reactivities of the monomer, with areas of dense and sparse fixed ions. The local potential wells are formed in the relatively highly charged polymer-rich regions, in which some of the

counterions are entrapped. As a result, this kind of inhomogeneity distribution of fixed ions can result in the generation of osmotically passive counterions. However, it is impossible to evaluate the heterogeneous distribution of charges within conventional polyelectrolyte gel system; thus, the validation of the associated theories is often inhibited. To fully understand the swelling behaviors of polyelectrolyte gels, it is important to study the polyelectrolyte gels with well-controlled block structures.

In 2008, we fabricated a polymer gel with a well-controlled network structure via an AB-type crosslinking between two tetra-armed polyethylene glycols (known as the Tetra-PEG gel). As the tetra-armed building blocks were precisely synthesized via anionic polymerization, the resultant networks were expected to have a regular network structure with tetra-functional crosslinking points and a uniform strand length. As elucidated in our previous reports, the controllability of the network structures was confirmed using ^{1}H multiple-quantum nuclear magnetic resonance, Fourier transform infrared spectroscopy, and mechanical tests. Thus, the fabrication method of the Tetra-PEG gels is expected to be a reasonable method to fabricate polymer gels with well-controlled block structures. Recently, Oshima et al. successfully synthesized Tetra-armed polyacrylic acid (Tetra-PAA) and Tetra-functional PAA gels using the end-linking of Tetra-PAAs via click chemistry. According to small-angle neutron scattering and small-angel X-ray scattering studies, Tetra-PAA gel in the uncharged state had a similar concentration fluctuation as that in an uncrosslinked solution, suggesting that the heterogeneous distribution of polymer segments was highly suppressed, similar to the case of conventional Tetra-PEG gels.

In my thesis, the neutral and charged segments are composed of polyethylene glycol (PEG) and PAA, respectively. The PEG and PAA segments are coupled by click chemistry between the maleimide and thiol groups to create the network formation. I utilize the regular polyelectrolyte gels with alternating neutral/highly–charged sequences (the Tetra-PAA-PEG gel), and investigate the effect of the heterogeneous distribution of fixed ions on the swelling behaviors.

Chapter 1 is the general introduction, where I introduced the historical background for the conventional researches in polyelectrolyte gels, and its problems.

In Chapter 2, I discussed the fabrication and structural homogeneity of Tetra-PAA-PEG gel, and the swelling behaviors of Tetra-PAA-PEG gel in monovalent salt (i.e. NaCl) solution. I prepared Tetra-PAA-PEG gel with different pH buffer solution to alter the gelation rate. I optimized the gelation condition to obtain the transparent gels. To understand the network homogeneity, mechanical and spectroscopic measurements were performed, the results suggested Tetra-PAA-PEG gel have a regular network structure composed of uniform network strands and can be applied as an excellent model for investigating the swelling behavior of polyelectrolyte gel. Then, I investigated the swelling behaviors of Tetra-PAA-PEG gel in monovalent salt solutions with various pH and ionic strengths. The swelling ratio Q increased with an increasing pH. In contrast, the swelling ratio decreased with the increase of the ionic strength. When we compared experiment swelling ratios with predicted swelling ratios by the F-R-D model, the deviation was extremely large. Normally, the F-R-D model worked well for predicting the swelling behavior of polyelectrolyte only under the weakly charged condition. In the case of highly charged condition, ion-ion interaction exceed the thermal fluctuation, a portion of counterions condense on the fixed ions and significantly decreasing the osmotic pressure. In Tetra-PAA-PEG gel system, the counterion condensation is predicted to occur when pH > 5.6. By considering additionally counterion condensation in the polyacrylic acid units (F-R-D-M model), the swelling behaviors of Tetra-PAA-PEG gel under the highly charged condition can be well explained. These results indicate that the ionic interactions within the length scale of the network strand can determine the counterion condensation and that it is vital to estimate accurately the distance between neighboring fixed ions for predicting the swelling behaviors of polyelectrolyte gels.

In Chapter 3, I discussed the effect of nonlinear elasticity on the swelling behaviors of Tetra-PAA-PEG gel in monovalent salt solution. First, I designed and fabricated a series of Tetra-PAA-PEG gels with tuned elastic modulus by changing the neutral

segments lengths, while the crosslink density and initial fixed ions concentration were maintained. I investigated the swelling behaviors of Tetra-PAA-PEG gels in monovalent salt solutions with various pH and ionic strengths. The swelling ratio was well reproduced by the F-R-D-M model in the moderate swelling regime ($Q < 10$). However, in the high swelling regime ($Q > 10$), the F-R-D-M model overestimated the Q compared to the experimental results. When I introduced the finite extensibility to the elastic free energy in the F-R-D-M model, the swelling behavior was successfully reproduced even in the high swelling regime. My results reveal that finite extensibility is one of the factors determining the swelling equilibrium of highly charged polyelectrolyte gels. The modified F-R-D-M model reproduces well the swelling behavior of a wide range of polyelectrolyte gels.

In Chapter 4, I discussed the swelling behavior of Tetra-PAA-PEG gel in divalent salt (i.e. $CaCl_2$) solution. The swelling ratios can be well reproduced by the modified F-R-D-M model in 0.1 mM $CaCl_2$ solution. However, in the 100 mM $CaCl_2$ solution, the modified F-R-D-M model overestimated the Q compared to the experimental results. Then, I investigated the salt concentration dependence of the swelling ratios. The gap between the predictions and experimental results increased with increasing the salt concentration. To understand the reason for the deviation, I performed the rheological measurement. I found the experimental shear modulus can be well reproduced by the predictions by the Flory's model in 0.1 mM $CaCl_2$ solution but deviated from the predictions in 100 mM $CaCl_2$ solution, which indicated the formation of aggregation that contributed to the elasticity of the gel. The small angle X-ray scattering (SAXS) measurement was performed to prove the existence of the aggregation structure, the results suggested the deviation in 100 mM $CaCl_2$ solution can be attributed to the enhancement of the elasticity or the decrease of the mixing pressure through the formation of aggregation structure.

Chapter 5 is the conclusion. I summarized all the results and propose the universal guideline for the design of polyelectrolyte gels.