論 文 の 内 容 の 要 旨

論文題目　Creation of surface-grafted gels and evaluation of skin layer formation ability
（表面グラフトゲルの創製およびスキン層形成能の評価）

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In this research, the novel functional hydrogel whose only surface polymer network is precisely designed was created. Recently, biomimetic or bioinspired materials are vigorously researched to realize the superior functions which animals and plants have. Most of the functions have not only spatial but also temporal orders derived from dissipative structure in non-equilibrium open system. Especially, metamorphosis is very attractive from the view point of biomimetic and bioinspired materials because this phenomenon has long time-scale, from days to years, and functions significantly change through it. However, this attractive phenomenon has not been targeted in this field. To achieve “artificial metamorphosis,” the pupal state, which is peculiar to complete metamorphosis, is focused on, and this research first aims the creation of pupal shell utilizing skin layer. In more detail, to utilize skin layer with arbitrary polymer composition, the surface-grafted gel which has grafted polymers only in the surface region of the gel is designed based on the idea of comb-type polymer network which enables fast shrinkage of network.

In Chapter 2, thermoresponsive surface-grafted gels were successfully synthesized by immobilization of ATRP initiators only in the surface region of the gels and subsequent ARGET ATRP of grafted polymers. The VPTT of base polymer network and the LCST of grafted polymers was 41 °C and 34 °C, respectively. Fine wrinkle pattern on the surface was observed in equilibrium swollen state due to the mismatch between the swelling ratio of inside and outside of the gels. The surface-grafted gels also exhibit unique shrinking pattern called

“bubble pattern” around volume phase transition temperature. In addition, during shrinking process in response to temperature increase, the period of constant volume was observed. As for swelling behavior, the speed of swelling is affected by this design, i.e., the speed is lowered. These results indicate that the formation of skin layer was successfully induced by the introduction of surface-grafted polymers, and the bulk properties are critically dominated the physical design of surface network.

In Chapter 3, the graft density of surface-grafted gels was controlled by reacting ATRP initiators and structurally analogous non-initiators at a certain ratio simultaneously to the gels. The pattern of wrinkles on their surface was correlated to graft density. The enhancement of homogeneity of surface polymer network was confirmed caused by the introduction of grafted polymers. Young’s modulus of the surface was lower with higher graft density. These static properties affected the dynamic volume change properties. The permeability of skin layer during shrining process decreased and the speed of swelling also decreased as the graft density increased. It was revealed that the graft density is a critical parameter for the properties of surface-grafted gels, and the properties are now arbitrarily controllable.

In Chapter 4, the surface-grafted gels which is composed of hydrophilic polymer network and thermoresponsive surface-grafted polymers were successfully synthesized. The fine wrinkle patterns were also observed on their surface. Though the gels did not show the volume phase transition in response to temperature change, the speed of swelling from dried state to equilibrium swollen state was much lower at high temperature above the LCST of grafted polymers than at low temperature below LCST. From these results, it is suggested that the control of permeability of the surface of gels is possible only by the conformational change of grafted polymers rather than the formation of skin layer.

In summary, functional hydrogels which have novel physical structure of polymer network called surface-grafted hydrogels have been created. Note that the surface-grafted gels have unique properties which conventional hydrogels do not have; i.e., (1) only the surface network is precisely designed, (2) a dense skin layer can be formed in response to temperature change, and (3) the permeability of the surface can be arbitrarily controlled with arbitrary composition of polymer network. The essences of this research can be described as follows; (a) the focus on the surface of gels of bulk size, (2) the design methods and strategies for synthesis of gels, and (3) discussion about the relationship between static “surface” properties and dynamic “bulk” properties of gels.