

Analysis of Internal Structures in Poly(N-isopropylacrylamide) Gel by Scattering Methods

Takuya Okamoto¹, Yoshitsugu Hirokawa¹, Kohtaro Kimishima¹,
Hiroshi Jinnai¹, Satoshi Koizumi², and Takeji Hashimoto^{1,3}

¹*Hashimoto Polymer Phasing Project, ERATO, JST, 15 Morimoto-cho,
Shimogamo Sakyo-ku, Kyoto 606-0805, Japan*

²*Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan*

³*Division of Polymer Chemistry, Graduate School of Engineering,
Kyoto University, Kyoto 606-8501, Japan*

Abstract: The internal structures of poly(N-isopropylacrylamide) (PNIPAAm) gel were investigated by means of laser light scattering (LS) and small angle neutron scattering (SANS). LS curve showed a maximum corresponding to 12 μm in spacing between the dense (or sparse) polymer network domains. The fine structures in the dense polymer network domain was found to be composed of the microgels connected with loose polymer network by the analysis of the SANS curve. The results of LS and SANS analysis indicated that the gel had the hierarchical structures.

Introduction

Gel consists of a three-dimensionally cross-linked polymer network and a fluid. The network structure influenced by the gelation conditions affect the characteristics of the gels such as optical, mechanical, and swelling properties. Many studies on the gel have been made so far, however, there are not so many reports relating to the internal structures and inhomogeneities of the gel. In order to understand the characteristics of the gel, it is important to study the internal structures. We have been studying the internal structures of PNIPAAm gels by laser scanning

confocal microscope (LSCM). The results indicated that the gels had the three dimensional bicontinuous structures consisting of dense and sparse polymer network domains at the length scale of μm order. We further investigated the fine internal structures in the gel by means of LS and SANS. In this report, we present the analysis of the internal fine structures in the gel over the length scale of μm to nm.

Experiments

Sample preparation

NIPAAm monomer was purified by recrystallization. N,N'-methylene-bis(acrylamide) (BIS) (cross-linker), N,N,N',N'-tetramethylethylenediamine (TEMEDA) (accelerator), and ammonium peroxodisulfate (AP) (initiator) were used as received. PNIPAAm gels were prepared by free radical polymerization in the presence of BIS. A pregel solution was first prepared by dissolving NIPAAm monomers, BIS, and TEMEDA in pure water. After addition of 0.4 wt.% AP solution, the pregel solution was quickly transferred into a cell and the cell was immersed in the temperature controlled water bath for 1hr for gelation. The concentrations of NIPAAm monomer, BIS, and TEMEDA were 1.33 M, 10 mM, and 21 mM, respectively. For the preparation of sample for SANS sample deuterated water was used instead of pure water.

LS and SANS experiments

The observation of the internal structures of the gels was carried out at room temperature by LS and SANS. The laser source of LS was a He-Ne laser operated at 632.8 nm. SANS measurement was performed on the SANS (wavelength 6.6 Å) facility at Japan Atomic Energy Research Institute.

Results and Discussion

In order to investigate the internal structures of the gel, LS measurement was carried out. Figure 1 shows the double logarithmic plot of the scattered intensity as a function of the wave

number q for the gel prepared at 24.5 °C.

The profile showed a maximum at $q=q_m \sim 0.0005 \text{ nm}^{-1}$, which corresponded to 12 μm in spacing D between the dense (or sparse) polymer network domains ($D=2\pi/q_m$). The spacing agreed well with that found by the LSCM.

Moreover, the LS profile in Figure 1 showed a straight line with a slope of ca-2.5 over the q range from 0.001 nm^{-1} to 0.01 nm^{-1} , elucidating a fractal-like structure with mass fractal dimension of 2.5.

Further fine structures in the dense polymer network domain were investigated by means of SANS. Figure 2 shows the double logarithmic plot of the scattered intensity as a function of the wave number q for the gel prepared at 24.5 °C. The slope in the q ranging from 0.03 nm^{-1} to 0.07 nm^{-1} was found to be expressed by a q^{-4} dependence. This indicates the presence of a clear surface of microgels according to the Porod's law. For the analysis, we

speculated the model of fine structure in the gel as shown in Figure 3 on the basis of the high magnification image of LSCM. The observed scattering curve was analyzed to be the summation of the intensities scattered from the interface of the microgels, highly cross-linked polymer network in the microgels and the loose network connecting the microgels.

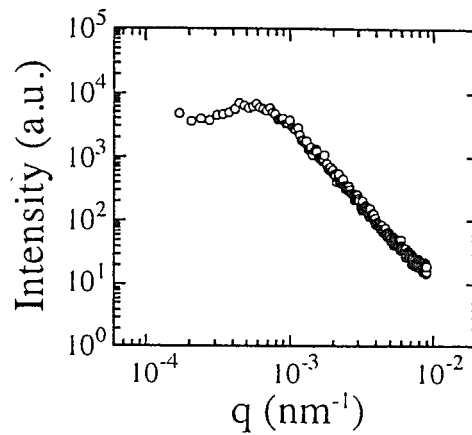


Figure 1. LS profile of PNIPAAm gel prepared at 24.5°C. q is magnitude of the scattering vector defined by $q=(4\pi/\lambda)\sin(\vartheta/2)$ with ϑ and λ being the scattering angle and wavelength of the incident beam in the medium.

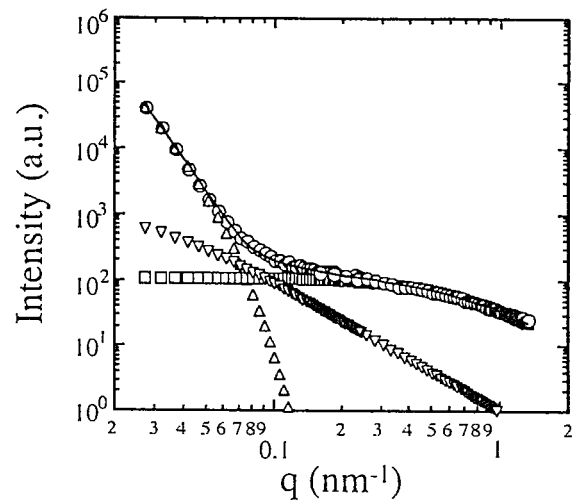


Figure 2. SANS scattering curve and its analysis. (○): SANS scattering curve, (△): Surface of microgel, (□): Highly cross-linked polymer network in microgel, (▽): Loose polymer network.

Conclusion

The internal structures of PNIPAAm gel were investigated by means of LS and SANS. LS and SANS results indicated that the gel had the hierarchical structures: The macroscopically homogeneous gel had the bicontinuous domain structure composed of regions rich in polymer concentration and regions poor in polymer concentration. The fine structures in dense polymer



Figure 3. Speculated internal fine structures of PNIPAAm gel.

network domain had the fractal-like structures which consisted of the microgels connected with the loose polymer networks.

References

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