Self-assembling in gelation processes of NIPAAM gel

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ポリ N-イソプロピルアクリルアミド(NIPAAM)／水系は曇点を 32℃に持つ LCST 型の相図を有する。その為に NIPAAM ゲルの形成過程は合成温度に強く依存する事が予想される。例えば合成温度が 32℃より高い時には、NIPAAM ゲルはマクロ相分離とゾルーゲル転移が競合しながら形成されるため、ゲルの内部構造はマクロ相分離構造を内包した階層構造を取ると予想される。本研究では様々な合成温度における NIPAAM ゲルの合成過程における内部構造の形成機構を、時分割超小角 X 線散乱法(USAXS 法)および時分割小角 X 線散乱法(SAXS 法)により調べた結果について報告する。

INTRODUCTION

N-Isopropylacrylamide (NIPAAM) gel is an chemical gel and exhibits volume phase transition at 32°C[1]. The dynamics of the volume phase transition is affected by the internal structure in the gels and the formation process of the internal structure is very important. The internal structures or inhomogeneity of NIPA gels strongly depends on the gelation temperature since the polyNIPA/water system has a lower critical solution temperature type phase diagram with theta temperature being 30.5°C[2] so that the macrophase separation is involved during the gelation process at higher temperature.

In this study, we investigated the gelation process of NIPA after the onset of temperature-jump by using time-resolved small-angle X-ray scattering (SAXS). We shall present the how the temperature affects the internal structure formation.

EXPERIMENTAL

Materials and Method. NIPAAM (monomers, 1.47M), *N,N'*-methylene-bis(acrylamide) (crosslinker, 63.4mM), and *N,N',N',N'*-tetramethyl ethylenediamine (accelerator, 17.8mM) were dissolved into water purged with nitrogen. After addition of 17.5mM anmonium peroxodisulfate (AP) solution to the monomer solution with the monomer solution/ the AP solution =25/75 (v/v), the monomer solution was quickly transferred into a cell. Then the cell was put into the heater block for SAXS experiments. SAXS experiments were conducted at the BL45XU, Spring-8. We used the CCD camera with Image-Intensifier. After the onset of the pressure jump, we measured the time changes in the scattered intensity with the scan rate being 10s/scan. All scattered intensity profiles were corrected for background and then circularly averaged for further analyses.

RESULTS AND DISCUSSION

Figure 1 shows the time change in the scattered intensity I(q,t) as a function of the magnitude of scattering vector q [=$(4\pi/\lambda)\sin(\theta/2)$, with θ being the scattering angle] after the onset of temperature jump to 35.0C, where the turbid gel was formed. At time t>145s, I(q) show q^{-4} dependence and obeys Porod law, indicating that the macroscopic phase separation have already occur before the completion of the gelation. We found that the scattered intensity during the gelation process can well described by the following equation:

$$I(q) = Aq^{-4} + \frac{I(0)}{1+q^2\xi^2}, \qquad (1)$$

where A is proportional to interfacial area density and the square of the amplitude of the concentration between two phases, I(0) represents the osmotic compressibility of the gel network, and ξ is the correlation length of the gel network corresponding to the mesh size of the network. Fig.2 shows the time changes of A, I(0), and ξ. From the time changes in these parameters, The gelation process at 35.0C can be divided into the following two regions:

(i)Region I, t<295s : In this region, all parameters increase with time, indicating that the macrophase separation progresses and the macrophase separation is accelerated by the increase of molecular weight of NIPA gel.

(ii) Region II, 295s<t : In this region, A becomes constant whereas I(0) and ξ decreases with time. Invariance of A is due to the fact that the macrophase separation has been pinned down by gelation. The decrease in I(0) and ξ is caused by the fact that the networks becomes dense associating with the progress of the gelation

The results of the gelation process at 19.7C will be discussed in the meeting.

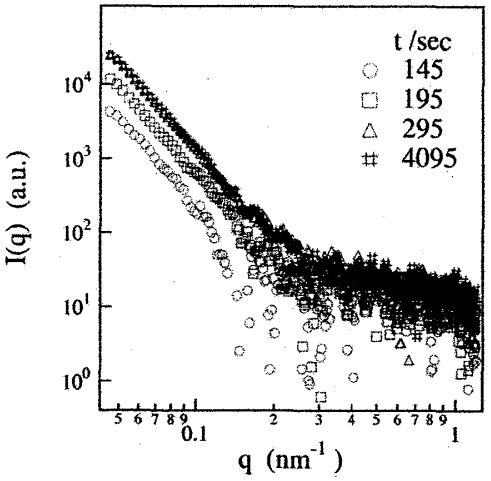

Figure 1. The time changes in the scattered intensity plotted as a function of q during the gelation processes at 33.0C.

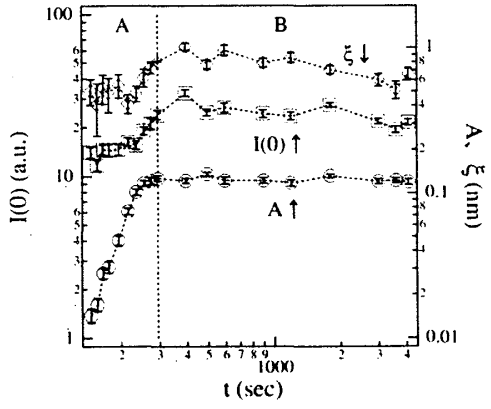

Figure 2. Time changes in A, I(0), and ξ at 35.0C.

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