Self-Assembly in Drying Film of Methylcellulose gel

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メチルセルロース水溶液は低温でゾル、高温でゲルを示す物理ゲルであり、さらにLCST型相挙動を示す。このメチルセルロース水溶液をガラス基板上に滴下し、ゲル相を保つ温度で乾燥膜を作製したところ、偏光顕微鏡で観察すると、膜全体は負の球晶の色づきを示し、膜中心には微結晶が生じるという興味深い結果が得られた。そこで、この乾燥膜の構造および結晶形態を明らかにするために広角X線散乱測定などを行うとともに、このような自己組織化膜が形成される機構を検討するため、相状態の違い、および分子量の違いがどのように影響するかを検討している。

1 Introduction

Methylcellulose(MC) aqueous solution is an interesting material, which forms physical gel and shows a inverse temperature dependence on sol-gel transition of a gelatin. We have derived phase diagrams for MC aqueous solution by DSC, SAXS and visual inspection (Figure 1) [1]. Based on the phase diagrams, we investigate a drying process of the MC aqueous solution keeping a gel phase, and a crystalline morphology of these dried films. MC is a kind of an amphiphilc molecule since its monomer contains the hydrophobic and hydrophilic residues. The film therefore might reflect the amphihilic property in the aggregation process.

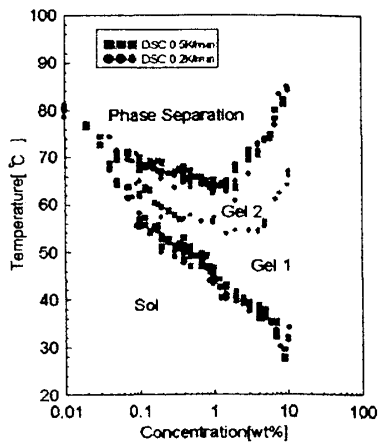

Figure 1: Phase diagram of MC-4

2 Experimental

2.1 Samples

The molecular structure of MC is shown in Figure 2. We used MC polymer powder whose molecular weights are polydisprese but whose DSs are almost fixed 1.75-1.79. We used mainly MC-4($\overline{M}w = 9.36 \times 10^5$), and we also used MC-1($\overline{M}w = 1.24 \times 10^5$) in order to examine the influence of the molecular weight for aggregation process.

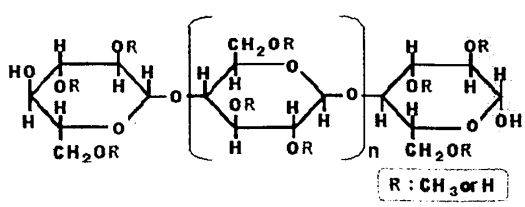

Figure 2: Molecular structure of MC

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Figure 3 shows the schematic diagram of solvent evaporation, MC aqueous solution dropped to on a glass substrate is placed on hot stage which has been set at a certain temperature to keep gel phase.

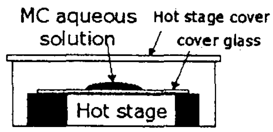

Figure 3: Schematic diagram of solvent evaporation

2.2 Measurements

Drying process and dried films were inspected under crossed polarizers using a Nikon Optiphoto2-pol optical microscope (OM). To study of the crystalline morphology of dried films, X-ray diffraction patterns were measured by a Rigaku X-ray Diffractometer Rint-1500 and a PSPC-MDG.

3 Results and Discussion

Figure 4 shows the process of evaporating of solvent by OM inspection. During the solvents are evaporating, dried area grow up from the circumference to the center of the film (Figure 4a). After the solvent seems completely evaporate (Figure 4b), a crystalline domain has appeared at the center of the film (Figure 4c). The dried film indicates the Maltese cross and the birefringent pattern like negative spherulite. A negative spherulite indicates orientation of optically uniaxial crystal (see figure 5), and a crystal of MC is regarded as an optically uniaxial crystal and the molecular chain of MC corresponds to the long axis of the optically uniaxial crystal. Therefore, the film's pattern suggests that the molecular chains of MC are orientated perpendicular direction to radial axis of the circular film.

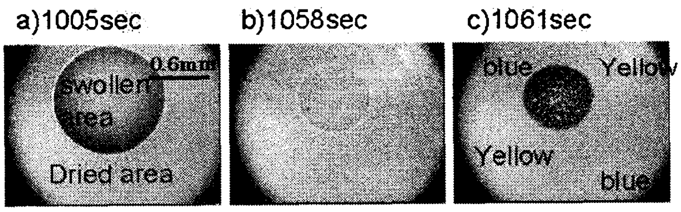

Figure 4: The process of evaporating of solvent by OM inspection (insert of sensitive color plate)

X-ray diffraction pattern of the crystalline domain of the film was measured by MDG-WAXS. They predict that folding chains like lamellar are organized at the center of the film. Furthermore, X-ray diffraction pattern of the whole of the film measured by WAXS predicts a certain lattice plane orientation, thus we are analyzing the crystalline morphology of the MC films. On the other hand, since the most important factor in formed a self-assembly film has not been clarified, we make films by different condition, for example, sol phase and another molecular weights of MC.

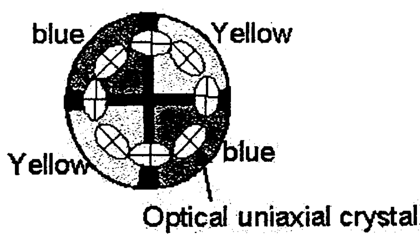

Figure 5: Schematic diagram of negative spherulite

References

1) M. Takahashi, M. Shimazaki, J. Yamamoto: *J. Polym. Sci. Part B* **39**,91-100(2001)