STRUCTURAL ANISOTROPY OF SILICA HYDROGELS PREPARED UNDER MAGNETIC FIELD

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Introduction

Gels are regarded as a typical random system. Therefore, it is hardly considered that gels become ordered by applying magnetic field. When we carried out a crystal growth experiment using silica gels as medium which we prepared in a magnetic field, we got a result to suggest [1][2]. Regarding polymer gels, if the unit structure of the gel network has a magnetic sensitivity, we can imagine that the network aligned parallel or perpendicular to the magnetic field does form.

In a case the silica gels were prepared with addition of lead (II) bromide, an aggregate of crystallites with their crystallographic axes aligned to the direction of magnetic field is observed [1][2]. When $Pb(NO_3)_2$-doped silica gels prepared in a magnetic field were used, an aggregate of crystallites was observed even if no magnetic field was applied during the crystal growth. Therefore, we ca conclude that structural anisotropy occurs in the silica gels during the preparation in the magnetic field. Unlike polymer gels, the silica gels do not have unit structure with a magnetic sensitivity. Therefore, we cannot imagine the mechanism of the alignment due to the magnetic field intuitively. It is an issue to elucidate this mechanism and the structural anisotropy in silica gels.

We considered that it is a key that silica gels are doped with a lead (II) ion. In case we prepared the samples without doped lead (II) ions, no birefringence was exhibited [3]. Thus, we speculate that a loop, which a network of the silica forms, and the lead (II) ions form together a certain complex structure, and that structure aligned with respect to the magnetic field. Because of a large amount of water between the networks, the cross-link density of hydrogels is low. The structure that another silica atom connected to four all of the oxygen atom connecting to a silica atom is rare, and it is expected that one or two oxygen atoms connected to most of Si atoms are terminated by a hydrogen atom. In case a side-chain group prefers the parallel alignment, the polymer chain aligns perpendicularly to the magnetic field because the side-chain group is basically normal to the main chain [4][5]. If one of such groups contains a conjugate π electron, a typical example is a benzene ring, a ring current can be induced. In such case the loop prefers to the perpendicular alignment to the magnetic field. On the other hand, in case a group has magnetic moment, the part including such a group prefers to the parallel alignment [6]. Such a mechanism may occur on a closed loop of the silica hydrogels.

Experiment

The samples were prepared in the same way as described in [1][2], except for the strength of the magnetic field. Sodium metasilicate was dissolved in distilled water by starting for 2 hrs. After that, acetic acid and aqueous solution of $Pb(NO_3)_2$ were added and then stirred for 2 hrs. This solution was settled for 7 days under various magnetic fields (0, 3, 5, 7, 9 and 10T) which were applied normal to the long axis of vessels at a 298K. The vessels used have a square cross-section with a side being 10.0 mm. Glass and quartz cells were used as the vessels. We estimated the sample thickness for this measurement to be d=10.00±0.09 mm.

Method of Birefringence Measurement

The Sénarmont method was employed for the birefringence measurement. We utilized together a spectrometer to evaluate the intensity of the light transmitted the analyzer as a function of the rotation angle of the analyzer [3]. In a usual Sénarmont method the rotation angle of the analyzer, which is a polarizer located after quarter wave plate (the Sénarmont compensator), where the transmitted light disappears is evaluated by eyes. If no sample, the transmitted light vanishes for the configuration of the crossed polarizers. If a birefringent sample is inserted with the axis pointing 45° with respect to the transmitting axis of the polarizer, the rotation angle of the analyzer at which the transmitted light disappears changes. Instead of detection by eyes, we fit the intensity as a function of the rotation angle, θ, of the analyzer by $I=A\cos(2\theta-\delta)+B$ to determine the retardation $\delta=2\pi\Gamma/\lambda$ with Γ and λ being the optical path difference and the wavelength of light source (commonly a mercury light, whose λ being 546 nm, is used). Photons were counted per 100 ms for a few minutes to obtain the intensities I (averaged) and the standard deviations were also calculated. The measure of birefringence, Δn, is obtained from $\Gamma=\Delta nd$. Note that Δn here is defined as $\Delta n=n_{\|}-n_{//}$ with the optic axis being as parallel (‖) to the direction of the magnetic field.

Results and Discussion

Results Δn for magnetic fields of 0-10T are shown in

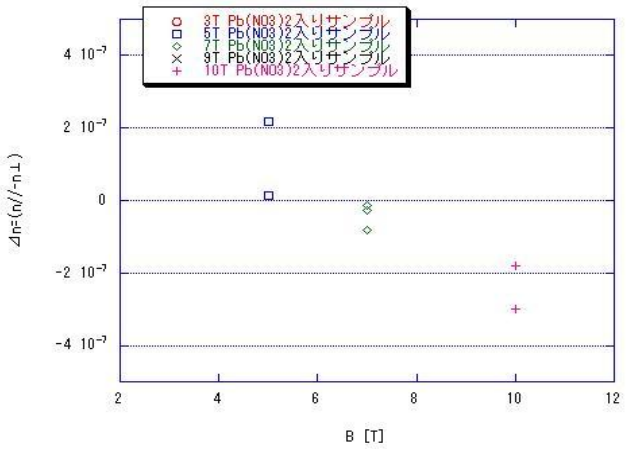

Fig.1 Δ*n* v.s. *B* for samples prepared in glass cells.

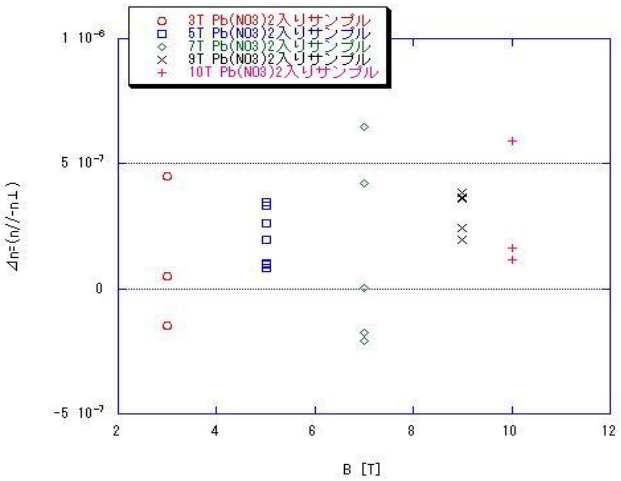

Fig.2 Δ*n* v.s. *B* for samples prepared in quartz cells.

Figs.1 and 2 for glass cells and quartz cells, respectively. We have used the cells, which exhibited results of Sénarmont measurement of Γ/d being of the order of 10^{-8}.

In Fig.1 we have confirmed that a "bistability" regime around 5T, as expected, and negative birefringence of $\Delta n \sim -3\times10^{-7}$ at magnetic fields higher than this value. Here, the bistability means that there are two Δn's with respect to one magnetic fields. Below the bistability regime there exists one Δn corresponding to a less alignment phase of and above this regime there exists one Δn corresponding to a there is one Δn which corresponds to a phase of a well alignment phase.

In Fig.2 positive birefringence is shown as opposed to an expectation. We could not identify the bistability regime such as the case of the glass cell, but we observe that Δn tends to increase weakly as the magnetic field.

Because the difference of the materials of the cells leads such difference in the results, we speculate that there exist some differences in the structure between a cell-wall affected region and the bulk part. The affections of the glass and quartz cells to the structure of the gels must differ with each other.

Let us discuss on the result in a framework of the Frederiks transition [7]. First of all let us assume oblate groups such as close loops like disco-like cylinder with a magnetic sensitivity parallel to the group, i.e., if the groups align a negative birefringence appears with the optic axis being as the cylindrical axis, which corresponds to the director of a nematic liquid crystal. The surfaces of the vessels are classified into two with respect to the anchoring of the "molecules": homogeneous anchoring and homeotropic one. In case of the oblate molecule in the former the groups tend to align normal to the wall and in the latter parallel in absence of the external field. We can understand the a positive birefringence for glass-cell samples in absence of the magnetic field with the optic axis being as the direction of the magnetic field (normal to the side walls) by assuming the homeotropic anchoring. In this case the groups apart from the wall align their axes along the magnetic field if the field exceeding the critical value is applied and the sample tends to be of a negative birefringence.

On the other hand, even if we assume the homogenous anchoring for the quartz cells as opposed to the glass cells, we cannot successfully understand the results (this assumption is based on a speculation that the surfaces of the quartz cells are prepared so as to have no specific structure). The groups align along the wall in absence of the external field and then the samples are of negative birefringence. And under the external field the alignment of the groups is enhanced, so that the magnitude of the birefringence increases. This conjecture is opposite to the results. The speculation is opposite; the surfaces of the quartz cells have a specific structure so that the birefringence of the cell vanishes and this structure prefers the homeotropic anchoring and the magnetic field enhances this effect.

Concluding Remarks

Δ*n* v.s. *B* for the glass cells was consistent to the earlier result [3]. However, the result for quartz cells were as poised to the expectation that the samples are of the negative birefringence. We can understand the results for the glass cells by assuming the homeotripic anchoring. However, we failed to understand the results for the quartz cells. We speculate that there exist some differences in the structure between a cell-wall affected region and the bulk part. We may confirm the structure by changing the thickness of the bulk part of the measurement direction.

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