

Structure and dynamics of silica nanoparticles in liquid crystal investigated with synchrotron x-ray radiation

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1. Introduction

Self-assembled anisotropic structures [1, 2] can be formed when particles are dispersed into nematic liquid crystal (NLC). This offers a promising method to fabricate new anisotropic composites. To achieve this, investigation is necessary to study structures and dynamics of these composites. So far, the samples are studied under optical microscope, which requires the samples to be thin and transparent with low volume fractions of particles.

In this study, we aimed to surpass the limitation of optical microscope by introducing x-ray scattering to study thicker and higher volume fraction samples to further investigate the formed structure of colloidal particles. Besides, few studies focus on structure of NLC dispersed with particles or dynamics of dispersed particles. To solve this, we also aimed to study the structure of surrounding NLC and the dynamics of dispersed nematic colloids. We hope to further understand these self-assembled anisotropic composites through this study.

Small angle x-ray scattering (SAXS) is a widely utilized method to reveal the information of nanoparticles including surface, shape, size and interparticle structures. X-ray photon correlation spectroscopy (XPCS) is a powerful method to investigate the dynamics of colloids, polymers and liquid surface, based on the principle that under the coherent x-ray, fluctuation of nanoparticles will result in the fluctuation of scattering intensity. By analyzing the correlation of sequential intensity, some dynamics

of the samples can be revealed.

In this study, SAXS and XPCS were utilized to investigate structure and dynamics of nanoparticles dispersed in NLC, while scanning microbeam wide angle x-ray scattering (microbeam WAXS) was used to investigate the structure of NLC molecules after being dispersed with nanoparticles. Dependence of nanoparticles' structure and dynamics as well as dependence of NLC molecular orientation on volume fraction of nanoparticles was focused on.

2. Experiment

Silica nanoparticles with diameter around 100 nm were coated with Tween 60 (Polyethylene glycol sorbitan monostearate, a nonionic surfactant) by dispersing nanoparticles into a mixture of Tween 60 (3.5 wt%) and water, then nanoparticles were cleaned by distilled water and dried. Coated particles were dispersed into 5CB (4'-Pentyl-biphenyl-4-carbonitrile, NLC, nematic to isotropic transition temperature is around 36 °C) using supersonic at 45 °C. The dispersed samples were then injected into cells and taken into the experimental station. The volume fractions of silica ϕ were from 0.3 % to 10.0 %.

SAXS was performed at SPring-8 BL03XU. Microbeam WAXS was performed at Photon Factory (PF) BL-4A with a beam size focused to 5 μm \times 5 μm . XPCS was performed at SPring-8 BL40XU. For XPCS, two pinholes with diameter 5 μm and 35 μm were installed to produce partially coherent x-ray [3]. Details of experiments are shown in table 1.

Table. 1 Introduction of experiments

Experiment	Beam line	X-ray energy	Camera length	Detector
SAXS	SPring-8 BL03XU	8.3 keV	3 m	PILATUS
Microbeam WAXS	PF BL-4A	11 keV	12 cm	CCD +Image intensifier [4]
XPCS	SPring-8 BL40XU	10.5 keV	3 m	CCD +Image intensifier

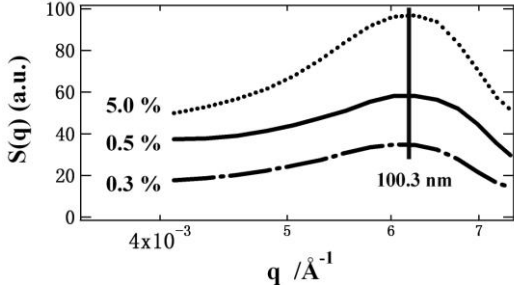


Fig. 1 Dependence of $S(q)$ on q with ϕ of 0.3 %, 0.5 % and 5.0 %.

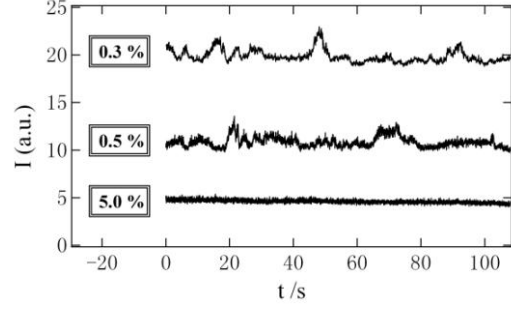


Fig.3 Intensity fluctuation at a pixel with q of 0.3 %, 0.5 % and 5.0 % at 29 °C.

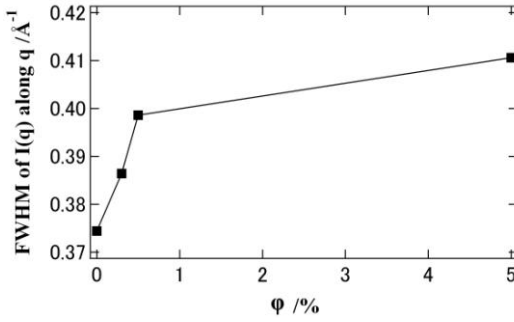


Fig.2 Dependence of FWHM of $I(q)$ on ϕ .

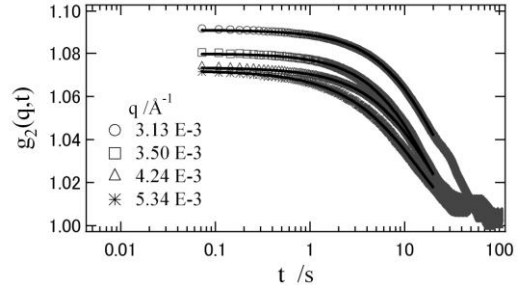


Fig. 4 Dependence of $g_2(q,t)$ on correlation time t for 0.5 % sample at 29 °C (Line: fitted data).

3. Results and Discussion

Form SAXS result, structure factor $F(q)$ can be obtained through the relation $S(q)=I(q)/F(q)$, where $I(q)$ is scattering intensity and $F(q)$ is form factor. $S(q)$ can reveal interparticle distance d based on the relation $d=2\pi/q$, where q is scattering vector at which $S(q)$ shows a peak. Figure 1 shows the dependence of $S(q)$ on q for samples with ϕ equal to 0.3 %, 0.5 % and 5.0 %. These three samples all show a peak at the same q , which is equal to 0.0063 \AA^{-1} . The average distance between neighboring nanoparticles is estimated to be 100.3 nm, which is of the same order as the diameter of nanoparticles. Form SAXS, it can be seen that silica nanoparticles are forced to contact with each other.

Microbeam WAXS shows that 5CB becomes less oriented with increasing ϕ . X-ray peak broadening was observed to become more significant with increasing ϕ as figure 2 shows. Two aspects are generally considered to result in x-ray peak broadening, one of which is grain refinement, while the other is the existence of microstress. We think

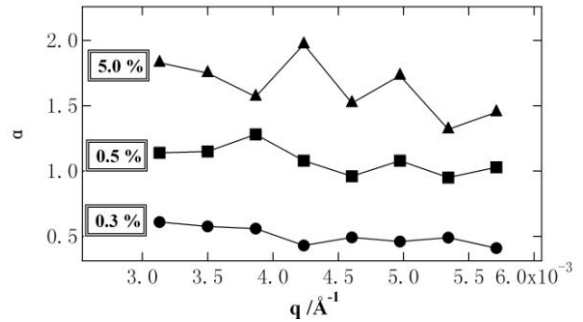


Fig. 5 Dependence of exponent α on q .

that these two aspects are both reasonable for x-ray peak broadening observed.

Figure 3 shows the intensity fluctuation pattern at a pixel with the same q for samples with ϕ of 0.3 %, 0.5 % and 5.0 %, respectively, measured at 29 °C. The intensity fluctuation can be obviously seen and the fluctuation rate decreases when ϕ equals to 5.0 %.

XPCS data are analyzed with normalized intensity autocorrelation function $g_2(q,t)$ as

$$g_2(q,t) = \frac{\langle I(q,t')I(q,t'+t) \rangle}{\langle I(q,t') \rangle^2} \quad (1)$$

where t is correlation time.

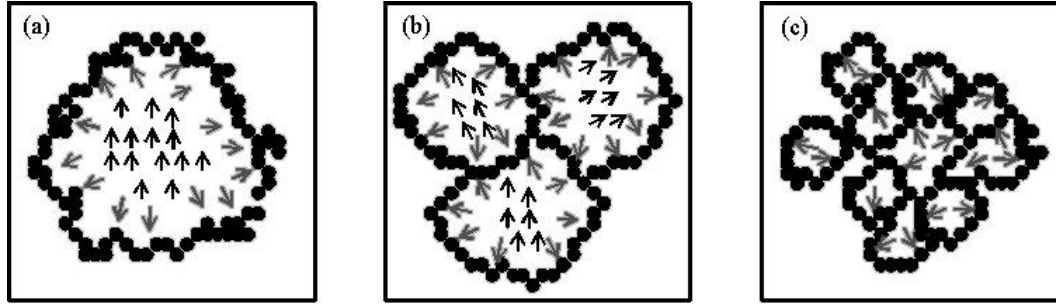


Fig. 6 Schematics of silica nanoparticles dispersed in 5CB. (a) 0.3 %, (b) 0.5 % and (c) 5.0 %.

In this study, $g_2(q,t)$ can be fitted by an exponential equation

$$g_2(q,t) = 1 + \beta \exp \left[-2 \left(\frac{t}{\tau} \right)^\alpha \right] \quad (2)$$

where β is contrast, τ is relaxation time and α is exponent.

Figure 4 shows $g_2(q,t)$ for the sample with ϕ of 0.5 % measured at 29 °C. Experimental data can be well fitted by Eq. 2 as the black line shows.

Dependence of exponent α on q for samples with different ϕ is shown in figure 5. A transition from stretched exponential relaxation mode to compressed exponential relaxation mode was observed. For 0.3 % sample, α is less than unity, indicating a stretched exponential behavior, which results from formation of nanoparticle aggregation. For 0.5 % sample, α is around unity, similar to a diffusive behavior. While for 5.0 % sample, α is larger than unity, indicating a compressed exponential behavior, which results from microstress between silica nanoparticles and 5CB molecules.

NLC has anisotropic viscosities along different directions. If the nanoparticles were homogeneously dispersed in 5CB, we can expect some tendency of relaxation time on azimuthal angles. $g_2(q,t)$ was calculated along different azimuthal directions and relaxation times obtained from various azimuth angles intercross with each other, without obvious dependence on the azimuth angles.

Based on experimental results, a possible model for a thin layer of sample can be given here as figure 6 shows. Silica nanoparticles are dispersed in 5CB as black spheres show. The matrix is 5CB with gray arrows indicating the director field around particles

and black arrows indicating director field of oriented 5CB away from nanoparticles. With increasing ϕ , the cellular structures become more condensed, which generates more interfaces and more microstress. Based on this model, all the experimental data can be interpreted reasonably.

4. Summary and Prospect

SAXS, microbeam WAXS and XPCS were performed to investigate structure and dynamics of silica nanoparticles dispersed in 5CB as well as the structure of 5CB after being dispersed with silica nanoparticles. Based on experimental results, a model that silica nanoparticles form cellular structures in 5CB matrix is proposed.

For prospect, it is important to confirm the mechanism underlying the transition from stretched exponential behavior to compressed exponential behavior, to investigate exactly the structure of dispersed silica nanoparticles, and to clarify the relation between structure and dynamics of nematic liquid crystal colloids.

References

- [1] I. Musevic et al., Science **313**, 954 (2006).
- [2] P. Poulin et al., Science **275**, 1770 (1997).
- [3] Y. Shinohara et al., Jpn. J. Appl. Phys. **46**, 13, L300 (2007).
- [4] Y. Amemiya et al, Rev. Sci. Instrum., **66**, 2290 (1995).

Presentation

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