

## Fixation of self-assembled structure induced by vaporization of volatile solvents in polymer solutions containing nanoparticles

Hiroyuki Takeno<sup>1\*</sup>, Kunimitsu Kikuchi<sup>1</sup>, Toshiaki Dobashi<sup>1</sup>

and

Masahiro Nobe<sup>2</sup> and Atsumi Wakabayashi<sup>2</sup>

<sup>1</sup>Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan

Fax: +81-277-30-1409, e-mail: takeno@bce.gunma-u.ac.jp

\* Author to whom correspondence should be addressed.

<sup>2</sup> Advanced Materials Division, Sumitomo Osaka Cement Co. Ltd., 585, Toyotomi-cho, Funabashi, Chiba 274-8601

Self-assembly of polymer solutions containing zirconium oxide nanoparticles in mixtures of organic solvents and water in the course of vaporization of the solvents is interesting as one of preparation methods to obtain photonic crystals. In the preceding paper, we reported that the water droplets formed by nucleation were regularly arranged and then collapsed due to aggregation and coalescence of the droplets during the vaporization. In this study we tried to fix the self-assembled structure with keeping the regularity in the following two methods; (i) freezing of the self-assembled structure due to vitrification of the polymer and (ii) fixation of structures arising from photo-crosslink due to ultra-violet (UV) irradiation. We succeeded in freezing of the regular structures in the former method, while in the latter method the regular structures were collapsed due to viscoelastic effects of phase-separated structures induced by the UV irradiation.

keyword: fixation, self-assembly, nanoparticle, vitrification, photo-crosslink

### INTRODUCTION

Recently, studies on self-assembly of nanoparticles have attracted many researchers from both scientific and technological aspect. From the latter point of view, regular structure like colloidal crystals is important for fabrication of materials with high performance, e.g., regular array of nanoparticles with spacing of scale of micrometers can be utilized as optical devices such as photonic crystals [1]. On the other hand, it has been shown by many researchers that honeycomb structures can be formed by casting a kind of polymer solutions under a flow of moist gas [2-5]. Hence, it is expected that the self-assembly of polymer solutions containing nanoparticles enables us to fabricate a regular structure of nanoparticles. For this purpose, we investigated the self-assembly of polymer solutions containing nanoparticles in mixed solvents of water and 2-butanone in a previous study [6]. At 20 °C, the mixture of water and 2-butanone is in the single-phase state in the range of concentration larger than 90 wt% 2-butanone or lower than 23 wt% 2-butanone,

while it is in the two-phase state [7]. Therefore, if the mixture with much butanone-richer concentrations enough to form homogeneous solution is exposed to the condition where solvents evaporate, it starts to phase-separate at a certain time because 2-butanone is much more volatile than water. Our previous study showed that a regular array of droplets was formed during vaporization of solvents from poly(vinyl methyl ether) solution containing zirconium oxide particles [6]. The regular array, however, collapsed with further evaporation of solvents, and finally the structures disappeared [6]. It is necessary to fix the regular structures in the course of the self-assembling process in order to fabricate materials with high performance. In this study, we try to fix the regular structures in two methods; (i) to freeze structures by vitrification of polymers and (ii) to fix them by photo-crosslink induced by ultra-violet (UV) irradiation.

### EXPERIMENT

The preparation and characteristics of

zirconium oxide ( $ZrO_2$ ) particles (average size 75 nm) were described elsewhere [6]. Two kinds of polymers were used in this study: One is poly(methyl methacrylate) (PMMA) with molecular weight of ca. 120,000 (commercial value), which was purchased from Aldrich Co., while the other is poly(vinyl ethyl ether) (PVEE) with molecular weight of 120,000 (commercial value) purchased from Scientific Polymer Products Co. The preparation of the cast samples is as follows. First we prepared polymer solutions by dissolving a polymer in 2-butanone at desired concentration. A small amount of distilled water and aqueous  $ZrO_2$  suspension was added into the polymer solution. Moreover, a small amount of ethanol was added to make a homogeneous solution. For vitrification, we used the solution without any further addition. For ultra-violet (UV) curing, we used a urethane-acrylate oligomer and a photo-crosslink initiator (IRGACURE 500 from Ciba Specialty Chemicals Co.). UV ray with wavelength of 254 nm (CSL-100C, Cosmo Bio Co. Ltd.) was irradiated at  $3400 \mu W/cm^2$  for the solution containing both the urethane-acrylate oligomer and the photo-crosslink initiator at desired time to fix the structure. We observed the time-evolutions of the self-assembled structures induced by evaporation of solvents from the solutions using optical microscopy (OM), after 500  $\mu l$  of the solutions were poured into a petri dish with 30 mm diameter. All the measurements were carried out at room temperature.

#### RESULTS AND DISCUSSION

First let us show self-assembling process for mixtures containing PMMA and  $ZrO_2$  particles. Figure 1 shows optical microscopy images of self-assembling structures at different times for the polymer solution with concentration of 89 wt% 2-butanone, 4.0 wt % PMMA and 0.03 wt%  $ZrO_2$  particles (The concentration represents one before evaporation of solvents). At the initial stage the mixture is homogeneous and hence no structures are visible in the length scale of optical microscopy. As solvents evaporate, droplets suddenly appear by nucleation from the homogeneous solution in a microscopy field. Afterwards, the droplet size becomes larger with time and the interdroplet distance gets close to each other with time as shown in Figure 1a (droplets with black color represent ones at a location of different focal depth). Moreover, as solvents evaporate more and more, the droplets are regularly arranged with keeping an almost constant spacing (Figure 1b). At this stage, the growth of the droplet size becomes slower due to interactions between the droplets. These behaviors are similar to that for poly(vinyl methyl ether) (PVME) solution added with  $ZrO_2$  particles as reported in our previous paper. Considering from the concentration of water and 2-butanone, it is expected that the droplet phase

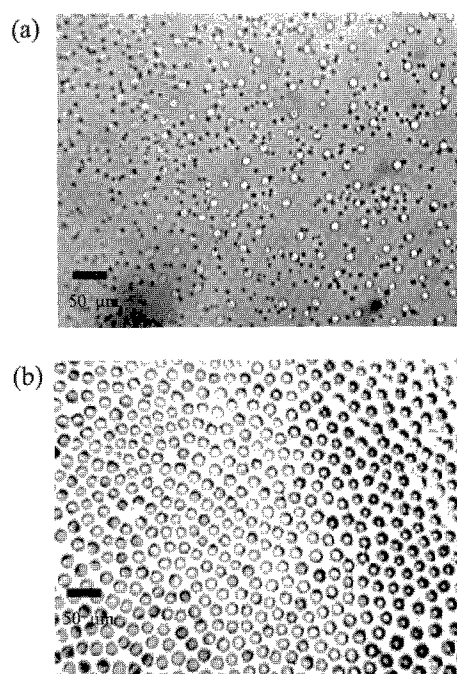


Fig. 1 Optical microscopy images of self-assembling structures for PMMA solution containing  $ZrO_2$  particles at 1228 s (a) and 2366 s (b).

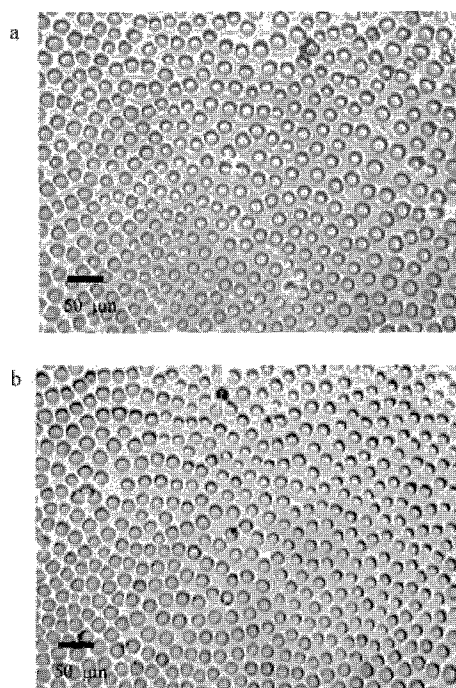


Fig. 2 Optical microscopy images of self-assembled structures after 4 days (a) and 14 days (b) for the above sample.

is water-rich, while the matrix phase is 2-butanone-rich (The details of the self-assembled structures were discussed in the previous paper [6]). After that, even as evaporation of solvents proceeds further, the

structures do not change with time, i.e., the structures are frozen, in contrast that for PVME solution with  $ZrO_2$  particles the regular array of droplets finally collapsed and they coalesced with others. This results form the difference in glass transition temperatures ( $T_g$ 's) of the two polymers. According to the literature [8],  $T_g$ 's of PVME and PMMA are  $-31$  and  $105$  °C, respectively. Therefore, in the case of PMMA system when the amount of solvents decreases with time, the matrix phase is frozen, because it is expected that PMMA is mainly dissolved in matrix phase due to insolubility of PMMA with water. As a consequence of freezing of matrix phase, droplets also become immobile. The frozen structures were unchanged at least for more than two weeks as shown in Figure 2 [9]. We estimated the average diameter of the droplets  $D$  from optical microscopy images. Figure 3 shows double logarithmic plot of the diameter of the droplets against time for PMMA solution containing  $ZrO_2$ . Growth of the droplet size is separated into two regimes. In regime (I), the nucleated droplets grow with time  $t$  at a large rate. In this regime, the droplets grow due to diffusion of water in the matrix phase into the droplet phase. After further evaporation of solvents (after ca 1800 sec), growth of the droplets is pinned due to vitrification of matrix phase in regime (II).

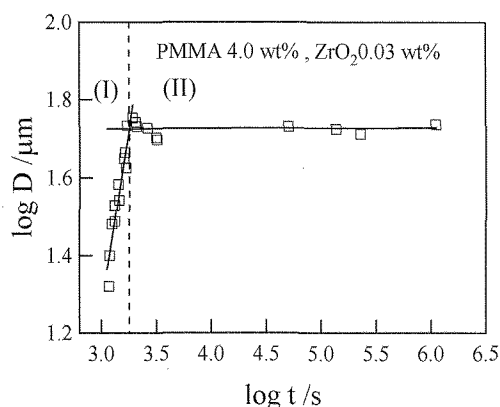


Figure 3 Time change in droplets size of self-assembled structures.

Next let us show photo-crosslink effect on the self-assembling process. In the photo-crosslink experiments, we divided the prepared solution into some, one of which was used as the reference without UV irradiation and the residuals of which were irradiated at different doses. All these samples were simultaneously poured into petri dishes and cast. First we observed the self-assembling process of the reference sample without irradiation under OM and as soon as the droplets are nucleated, we started UV-irradiation for the other samples. Figure 4 shows the optical microscopy images of the self-assembled structures for 4.6 wt% PVEE solution (88 wt% 2-butanone) containing 0.02 wt%  $ZrO_2$  particles

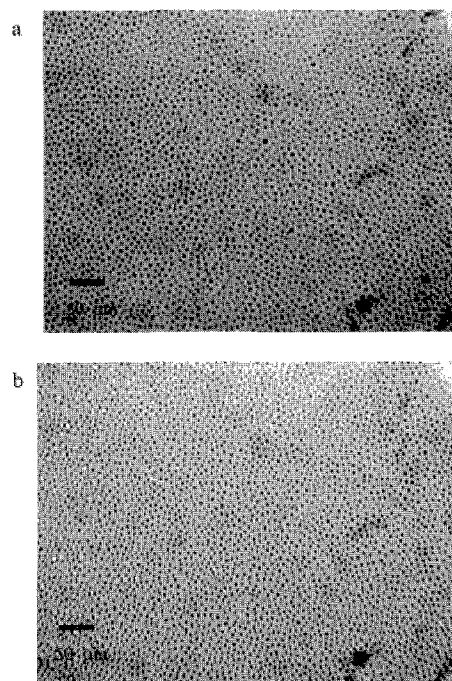


Figure 4 Optical microscopy images of self-assembled structures at 2190 s (a) and 3950 s (b) after onset of evaporation of solvents for 4.6 wt% of PVEE solution containing 0.02 wt% of  $ZrO_2$  and 1.9 wt% of urethane-acrylate oligomer without UV irradiation.

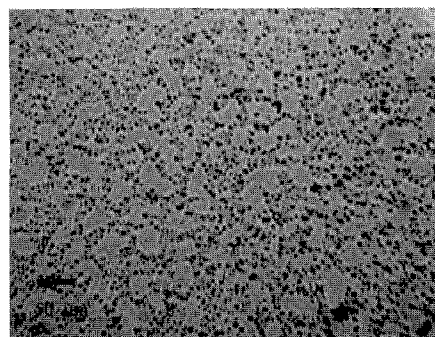


Figure 5 Optical microscopy image of the self-assembled structure after UV irradiation for 10 min. The composition of the sample is the same as that of Figure 4.

and 1.9 wt% urethane-acrylate oligomer without UV irradiation (reference sample) at  $t = 2190$  s and 3950 s (b) after the onset of evaporation of solvents. In Figure 4, it is shown that the droplets have roughly equal size and interestingly do not grow at least  $t > 30$  min. Thus, the urethane-acrylate oligomer has an effect to stabilize the droplets. The stabilization of the droplets was, however, not realized for the mixture with the urethane-acrylate oligomer but without PVEE. Therefore, it is expected that an

addition of polymer or urethane-acrylate oligomer has a multiplier effect to stabilize the droplets. Figure 5 presents the OM image of the self-assembled structure after UV irradiation for 10 min. As shown in the figure, the droplets collapsed to form network-like structures. This behavior attributed to the viscoelastic or elastic effect arising from photo-crosslink. The network-like structure is very similar to that shown by Tanaka, a pioneer in the works of viscoelastic phase separation [10]. The structures irradiated for different times were more or less network-like (not shown). Thus, UV irradiation collapse regular array of the droplets and fixation of the structures with keeping regularity lead to failure.

#### CONCLUSION

We tried to fix the regular self-assembled structures induced by evaporation of solvents for polymer solutions containing nanoparticles in mixed solvents of 2-butanone and water. Use of a polymer with high glass transition temperature successfully lead to freezing of the structures with keeping regularity, while photo-crosslink with UV ray results in collapse of regular array of droplets due to viscoelastic effect on phase-separated structures.

#### REFERENCES and NOTES

- [1] C. M. Bowden, J. P. Dowling, H. O. Everitt *J. Opt. Soc. Am. B* 10,280 (1993).
- [2] G. Widawaski, B. Rawiso, B. François, *Nature* 369, 387-389 (1994).
- [3] O. Pitois and B. Francois, *Eur. Phys. J. B8*, 225-231 (1999).
- [4] M. Srinivasarao, D. Collings, A. Phillips and S. Patel. *Science* 292, 79-83 (2001). Type
- [5] O. Karthaus, N. Maruyama, X. Cieren, M. Shimomura, H. Hasegawa and T. Hashimoto, 16, 6071-6076.
- [6] H. Takeno, S. Nakazato, T. Dobashi, M. Nobe and A. Wakabayashi, *Colloid Polym. Sci.*, accepted .
- [7] *Kagaku binran*, in Japanese.
- [8] *Polymer Handbook*, 3rd edition.
- [9] Visual fields for these optical microscopy images may be somewhat different. Slight difference in theses images is due to difference of visual fields.
- [10] H. Tanaka, *Macromolecules*, 25, 6377-6380 (1992).

(Received December 25, 2006; Accepted January 19, 2007)