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KEYNOTE

Nanopattern Formation of a Block Copolymer by Water as a Non-Solvent

Shigeru Okamoto

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan.

okamoto.shigeru@nitech.ac.jp

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Abstract. We demonstrate how to obtain a highly ordered nanopattern of a block copolymer (BCP). We investigated a pattern formation via microphase separation and order-order transition of a BCP with an ultra-high-molecular-weight (UHMW). UHMW-BCPs have so high viscosity that they do not reach equilibrated structure when they form nanopatterns because of the large number of entanglements per chains. We enhanced the chain mobility by adding to a BCP a neutral solvent, i.e., a miscible solvent to all the components of the BCP (a semi-dilute solution). However, the nanopattern had a low degree of order or disappeared because the segregation power was also extremely shielded due to the dilution effect. Here, we found that addition of a "differentiating non-solvent" (ex. water) in the semi-dilute solution enhances the segregation power and the resulting nanopatterns are highly ordered. The patterns were successfully applied to non-linear optical materials such as photonic crystals.

1. Introduction

A block copolymer (BCP) is a polymer in which different polymers are connected mostly by covalent bonds; here, constituent polymers are called block chains or simply blocks. As different polymers generally phase separate, constituent block chains phase separate from each other. However, there is an important thing to mention about structures resulting from the phase separation. In a blend of different polymers, they macroscopically phase separate just as in a water/oil system. To the contrary, block chains does not macroscopically phase separate but just on the order of nanometers or their molecular sizes because of the connectivity between the blocks; a minor component (shorter blocks) forms so-called microdomains in the matrix of a major component (longer blocks). As a consequence, they form one-, two- or three-dimensional self-assembled periodic nanopatterns with a variety of morphologies depending on the volume fractions of constituent block chains such as alternating lamellae, hexagonally-packed cylinders, spheres on a body-centered cubic lattice and some network structures. These structures are expected to be applicable to non-linear optical materials such as a photonic crystal.

The period of a nanopattern or the spacing of microdomains is dependent on the molecular size of a BCP. In order to apply them to visible light, the period should be on the order of hundred nanometers; the molecular weight should be as big as ca. 10^6. Here, we have a big problem caused by this ultra-high molecular weight; it exceedingly increases the viscosity because of the large number of entanglements per chain. In other words, the relaxation time of the chain mobility becomes so long that the nanopatterns made of such ultra-high-molecular-weight BCPs (hereinafter UHMW-BCPs) are virtually frozen and thus suffer from defects. Here, I discuss how to obtain an equilibrated nanopatterns with the so high degree of order that they can be applied to optical devices.

2. Formation of a Highly Ordered Nanopattern

2.1 Enhancement of Chain Mobility

A neat BCP, i.e., a bulk material without a solvent has a much higher viscosity because of a large number of entanglements per chain than a BCP solution. In the case of an UHMW-BCP, the viscosity is too high for a resulting nanopattern to reach the equilibrated state as mentioned above. Fig. 1 shows a typical example of a film of an UHMW-BCP cast from its solution. The grains have different colors (blue, green, yellow, etc.) according to their orientation; the nanopattern consist of the multi grains with random orientation and the wide distribution of the period.

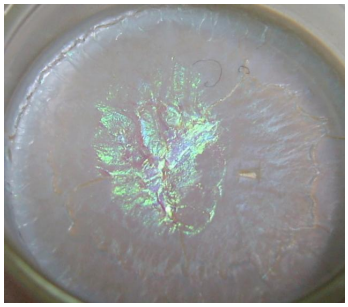

Fig. 1 an example of a nanopattern formed in a film showing the low degree of order.

In order to reduce the viscosity, we added a neutral solvent to a BCP. Note that a neutral solvent is a solvent that is miscible with all the components of the BCP blocks. The dilution increases the chain mobility and we expected the system becomes closer and closer to the equilibrated state, i.e., the degree of order increases. Actually, we found the peak width in the reflection spectrum of the nanopattern became smaller and smaller with the increase of a neutral solvent; the distribution of the period became narrower. However, the systems went into disordered state, as seen in the typical example of polystyren-*b*-polymethylmethacrylate / tetrahydrofuran (PS-*b*-PMMA / THF) in Fig. 2, before obtaining the reflection peak sharp enough to be used as a photonic crystal. This is because the segregation power between the constituent blocks was too much shielded by the neutral solvent, THF. Here, we have found microphase separation can be induced by the addition of non-solvent, water, to a solution at a very low concentration on the order of several percent (semi-dilute). The system showed iridescent colors, attributed to the Bragg reflection from the periodic microphase-separated structures [1, 2, 3] (Fig. 2); besides, the colour showed red shift indicating that the segregation power increased with non-solvent. Hereinafter, we call this kind of non-solvent a “differentiating non-solvent”. In these low-concentration solutions, BCPs can easily reach structural equilibrium with high order because of the high mobility. As a consequence, in the vicinity of the lyotropic phase boundary of order-disorder transition, large grains with the size of centimeters were formed as seen in Fig. 3. The large grains gave a spot-like ultra-small-angle x-ray scattering (USAXS) pattern.

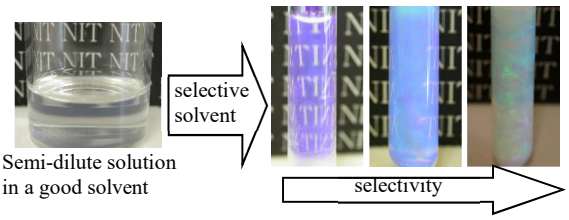

Fig. 2 Microphase separation induced by selective solvent.

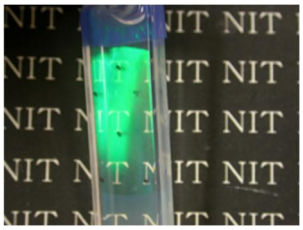

Fig. 3 a giant grain in a solution of a block copoymer

2.2 Spatial Distribution of Solvent Molecules

In the previous section, water, a differentiating non-solvent, played a very important role in the formation of the highly ordered nanopattern. Thus, it is interesting to reveal the mechanism; here, we performed SANS contrast variation measurements in order to investigate the distribution of the BCP and the solvent molecules in the semi-dilute solution [1]. This method allows us to determine the concentrations of the components in each phase by changing scattering contrast with combinations of

the protonated and deuterated solvents. In this experiment, A polystyrene-*block*-poly (*tert*-butyl methacrylate) (PS-*b*-P*t*BuMA) diblock copolymer was employed. The weight-averaged molecular weight, M_w, and the polydispersity index of M_w were estimated to be 8.2×10^5 g/mol and 1.2, respectively. The volume fraction of polystyrene, φ_{PS} was evaluated to be 0.43 by ^{1}H-NMR. The value of the scattering length density of PS ($\rho_{h\text{-}PS} = 1.34 \times 10^{10}\,cm^{-2}$) is higher than that of P*t*BuMA ($\rho_{h\text{-}PtBuMA} = 0.537\times 10^{10}\ cm^{-2}$). Fig. 4 shows the scattering intensity profile of the solutions at the water content, φ_w, of 9.1 vol %. The scattering profiles of the red, yellow, green and blue colors indicate that the solvent mixture consists of deuterated THF and D_2O (designated as "d-THF = 1 and D_2O = 1"), deuterated THF and H_2O (d-THF = 1 and D_2O = 0), protonated THF and D_2O (d-THF = 0 and D_2O = 0), and protonated THF and H_2O (d-THF = 0 and D_2O = 1), respectively. The red scattering profiles for "d-THF = 1 and D_2O = 1" showed the multiple scattering maxima, which indicates well-ordered microdomain structures were formed. These combinations of the solvents varies the scattering intensity; the deuterated solvents have bigger scattering lengths density for neutron while they do not change the chemical property, i.e., the nanopattern is not altered with the combination. The scattering intensity is proportional to the square of scattering length density difference, $\Delta\rho$, between the PS and the P*t*BuMA phases. The composition of each component in each phase was determined from the intensity variation in Fig. 4 as shown in Table 1. The values of φ_{water_PtBuMA} and φ_{THF_PtBuMA} at φ_w = 9.1 vol % are 11.0 and 84.6 vol %, respectively, and greater than the average values (9.1 and 81.2 vol %, respectively), while φ_{water_PS} and φ_{THF_PS} are smaller than the averages. Thus φ_{PS_PS} is greater than the average (9.7 vol %) and φ_{PtBuMA_PtBuMA} is smaller than that (9.7 vol %). Note that both of φ_{PS_PS} and φ_{PtBuMA_PtBuMA} should be 9.7 vol % if the solvents uniformly distribute over the whole system. These results mean that the ratio of the water content to that of THF was kept almost constant and both of water and THF moved from the PS phase into the P*t*BuMA phase by the addition of water. Therefore we consider that water and THF distribute together as a single solvent.

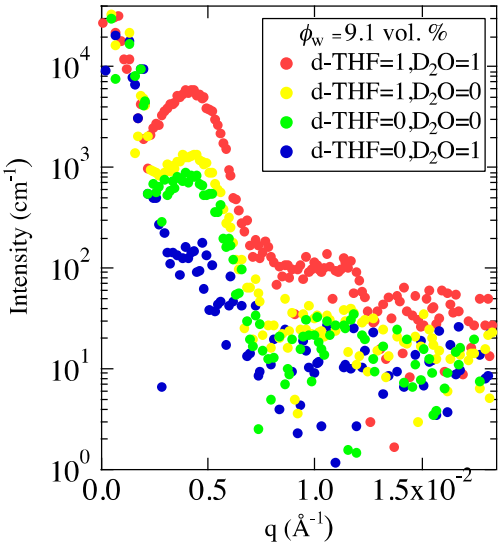

Fig. 4. 1-D SANS profiles at f_w = 9.1 vol %. This Figure was reproduced from Figure 7 of Reference 1.

Table 1. Composition of each component in each phase[a].

	ϕ_w = 9.1 vol %	
	PS phase	P*t*BuMA phase
PS	19.0	0
P*t*BuMA	0	4.40
THF	75.2	84.6
water	5.80	11.0

[a] This table was reproduced from Table 4 of Reference1.

This feature was well depicted by the computer simulation based on the self-consistent field (SCF) theory. With the software, SUSHI, in the OCTA system [4], we calculated spatial concentration distribution, φ, of K-type segments at the equilibrium taking the chain conformation into account using the path integral formalism. Fig. 5 shows the

calculated composition profiles of the four components, PS, P*t*BuMA, THF and water, at ϕ_P =9.7 vol % and ϕ_w =9.1 vol %. The left axis indicates the concentrations of PS, P*t*BuMA and water (designated as ϕ_{PS}, ϕ_{PtBuMA} and ϕ_w, respectively) and the right axis indicates the concentration of THF (designated as ϕ_{THF}) and the bottom axis indicates the spatial axis, x. The red, green, purple and blue colors indicate the components of St, *t*BuMA, THF and water, respectively. For the simplicity, the profiles were shown over one period with the x-axis normalized by the domain periodicity, D = 13.1 pixels. All the components periodically fluctuate around their average compositions, i.e., the system is in the ordered state by the selectivity of THF/water prompted by the addition of enough amount of water. Here it is worthy noting that the neutral solvent, THF, gathers in the vicinity of the phase boundary between PS and P*t*BuMA. This shields the unfavorable contact between the two components at the interface. It should be also noted that the water molecules locate in the middle of the P*t*BuMA, i.e., away from the interface, which also decreases the unfavorable contact with PS. We defined PS and P*t*BuMA phases as the regions where the concentrations are higher than their average values, from which the volume fractions of the phases were measured and in good agreement with the SANS result. Surprisingly, THF behaved as a selective solvent in the presence of water. The major amount of THF and water locate in the P*t*BuMA phase. This is qualitatively rationalized as follows; in order to let THF uniformly distribute over the whole system and water selectively introduced into the P*t*BuMA phase, the macrophase separation between THF and water is required. However, this segregation brings about a huge entropy loss because the majority of the components (90.7 vol.% by volume or over 99 mol% by the numbers) consist of the small molecules, THF and water. Thus, the macroscopic segregation is energetically unfavorable. The non-uniform distribution of the solvents well explained the SANS result in the previous chapter.

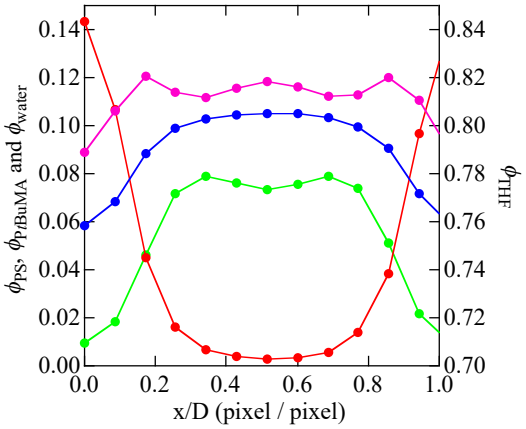

Fig. 5 Spatial distribution of all the components at ϕ_w = 13 vol %. This Figure was reproduced from Figure 4 of Reference 1.

3. Application to a non-linear optical material

The nanopatterns fabricated in the semi-dilute solutions have such a high degree of order that they can confine and control the flow of light. We applied the semi-dilute solutions to optical devices, such as a laser resonator, an optical switch, a wavelength-tunable photonic crystal [5, 6], etc. We also succeeded in enhancement of nonlinear optical property of gold nanoparticles by the periodic nanopattern [8]. Furthermore, we fixed a photonic nanopattern in a solution by gelation [3]. We also found the technique is not limited to the selectivity change of solvent compositions but also applicable to a temperature dependence of solvent selectivity [7].

3. Conclusion

The novel technique to highly order nanopatterns formed by block copolymers was demonstrated using some model specimens. Water is generally a non-solvent to most of polymers except hydrophilic polymers. However, it stimulated ordering when mixed with a neutral solvents miscible for all the component of a block copolymer used; it enhanced the segregation power in a semi-dilute solution where the segregation power was too much shielded by the neutral solvent and hence triggered the microphase separation at such a low concentration. As a consequence, the nanopattern formed had a small number of defects and the high degree of order owing to such a low viscosity.

The solvent mixture of a non-solvent and a neutral solvent (ex. Water and THF) behaved just as a single selective solvent as revealed by the SANS contrast variation measurements and the computer simulation based on the SCF theory using "SUSHI" in the OCTA system. This selectivity is the point to obtain a highly ordered structure. The technique was applied to fabricate non-linear optical materials such as photonic crystals.

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The SANS experiments were conducted at SANS-J with the approval of the Japan Atomic Energy Agency (JAEA) (Proposal No. 2008B-A12 and 2009A-A70.)

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