

海外特別研究員最終報告書

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(氏名は必ず自署すること)

海外特別研究員としての派遣期間を終了しましたので、下記のとおり報告いたします。

なお、下記及び別紙記載の内容については相違ありません。

記

1. 用務地（派遣先国名）用務地：イサカ市コーネル大学（国名：アメリカ合衆国）2. 研究課題名（和文）※研究課題名は申請時のものと変わらないように記載すること。メソ秩序構造の分解・組み換えによる再構築3. 派遣期間：平成 29 年 4 月 24 日 ～ 平成 31 年 4 月 23 日

4. 受入機関名及び部局名

Cornell University, Material Science and Engineering Department5. 所期の目的の遂行状況及び成果…書式任意 **書式任意 (A4 判相当 3 ページ以上、英語で記入も可)**

(研究・調査実施状況及びその成果の発表・関係学会への参加状況等)

(注)「6. 研究発表」以降については様式 10－別紙 1～4 に記入の上、併せて提出すること。

The originally proposed project was designed to establish the methodology to construct meso-ordered structures via decomposition and re-construction of self-assembled block-copolymers (BCPs). To achieve this, it was essential to control the spatial distribution of constituent BCPs in blended BCP films. This requirement arises from the fact that the relative position of constituent BCPs needs to be precisely defined to give designed structures. Although some works were reported for controlling spatial distribution of BCPs by selective surface-segregation of one particular constituent of blended films/membranes, most of them require harsh conditions on thermal annealing and/or give rise to imperfect control on spatial distribution.

During my two years research, we found new method to accomplish almost-perfect surface segregation of BCP over other polymeric components, and yet it requires no special treatments besides casting the solution of blended BCP/homo-polymers. We figured out surface segregation is caused when two kinds of solvents with different surface energies are employed,

each of which is selective for different polymeric component respectively. We believe the polymeric species preferentially absorbing the lower surface energy solvent comes up to surface, though the detailed mechanism has not been elucidated yet. In fact, we achieved almost-perfect surface coverage with ordered BCP layer over entire membrane by carefully designing solvent system in consideration of solvent surface energies and solvent-polymer interaction parameters ($\chi_{\text{solvent-polymer}}$). We used this new technique to prepare bilayer SNIPS (self-assembled and non-solvent induced phase separation) membrane, where only the membrane surface is composed of BCP to ensure periodically arrayed meso-pores and the substructure is composed of homopolymers, establishing high resolution and flux in water application yet reasonable production cost by minimum usage of expensive BCP.

We started our investigation with the combination of BCP of polystyrene-*b*-poly(4-vinylpyridine) (SV: molecular weight is 200 kDa and monomer composition is styrene : 4-vinylpyridine = 82 : 18) and polysulfone (PSf: 20 kDa). The cast solution was prepared by following procedure: SV was dissolved in 1,4-dioxane (DOX)/N-methyl-2-pyrrolidone (NMP) = 9/1 at 18wt% and blended with PSf in NMP (20wt%) so that the blending ratio between SV:PSf is 10:90 to 2:98. After casting the solution, evaporation time was given for 40 s, and then entire membrane was immersed into water bath. The SEM observation of resultant membrane surfaces shows hexagonally arrayed meso-pores even at blending ratio of 2:98 (SV:PSf). Also, XPS (X-ray photoelectron spectroscopy) revealed that there was only negligible sulfur on the surface. These results clearly showed that the membrane surface was perfectly covered with SV by surface segregation. We also confirmed this perfect surface coverage happens only when binary solvent systems were employed, where each solvent is selective to each polymeric component respectively and whose surface energies are remarkably different; DOX is polystyrene selective and relatively low surface energy (34 mJ/m²) whereas NMP is PSf selective and relatively high surface energy (41 mJ/m²). The unary solvent system of NMP nor DOX did not give rise to surface segregation. Moreover, the binary solvent system of which surface energies are close each other, *e.g.* DOX (34 mJ/m²) and DMF (37 mJ/m²), did not cause surface segregation of BCP. These results show that selective solvents are preferentially absorbed by specific polymeric

components respectively and the difference of surface energy of solvents cause the surface segregation, *i. e.* the polymeric component swollen by the solvent with lower surface energy comes up to surface. This phenomenon is not limited to combination of BCP of SV and PSf, but other BCPs like polystyrene-*b*-poly(acrylic acid) also shows similar surface segregation with appropriate binary solvent system. Also, the homopolymer-homopolymer combination with almost same surface energy like polystyrene (41 mJ/m²) and PSf (41 mJ/m²) showed perfect surface segregation when DOX/NMP binary solvents were used, which exclude the possibility that this BCP-micelle surface segregation is not entropically driven as already known.

To design such solvent-BCP interaction, comprehensive understanding of the self-assembled structures of BCP in the solution is very important. The BCPs frequently used for SNIPS membranes are composed of major hydrophobic blocks, *e.g.* polystyrene, and minor hydrophilic blocks, *e.g.* poly(4-vinylpyridine) or poly(acrylic acid). Such amphiphilic BCPs are known to make micelles in relatively hydrophilic organic solvents like binary solvents of tetrahydrofuran (THF) and N,N-dimethylformamide (DMF). However, the micellar structures, *i.e.* which block is core and which block is corona, or the solvents distribution difference between inside and outside of micelles, are highly nontrivial, and those structural parameter seriously affect the solvent-polymer interaction because corona block should be the dominant block to determine micelle-solvent interaction as compared to core block. So far, a number of studies about the micelle structure in particular for SV in THF/DMF mixture were reported based on various experiments techniques, *e.g.* small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), cryo-electron microscopic techniques and atomic forced microscopy (AFM), and yet remained unsolved. We newly approached this issue via relaxation time analysis on ¹H nuclei magnetic resonance (NMR). Based on the dynamics of polymer chains and solvents, we could conclude that polystyrene is the corona forming block and poly(4-vinylpyridine) is the core-forming block in THF/DMF=9/1 (weight ratio) with the BCP monomer composition of styrene : 4-vinylpyridine = 82 : 18 with molecular weight of 200 kDa. This was accomplished by measuring spin-spin relaxation time (*T*₂) with a wide range of the BCP concentration from 0.1wt% to 20wt%. At the critical micelle concentration elucidated by

diffusion ordered spectroscopy (DOSY) (around 4wt%), the T_2 of poly(4-vinylpyridine) dropped more quickly than that of polystyrene while increasing the BCP concentration. This indicates poly(4-vinylpyridine) is the core-forming block, and thus the movement is more constrained than corona-forming polystyrene. Moreover, we figured out that beyond the CMC, the chemical exchange rate of DMF homo hydrogen-bond, *i. e.* bonding between the formyl proton and the amide oxygen/nitrogen of DMF molecules and cross- hydrogen-bonding between the formyl proton and pyridine moieties of poly(4-vinylpyridine) increased. At the concentration range lower than 4wt% of BCP concentration, the correlation time of hydrogen-bonding exchange is about 2 ms, and similar to pure solvents of THF/DMF=9/1. In contrast, over 8 wt% correlation time decreased to 1.5 ms, which is similar length as to pure DMF. At the concentration of 18wt%, the correlation time dropped down to 0.9 ms, which is almost same time length as one of unary DMF solvent with 20wt% homo poly(4-vinylpyridine). This indicates that the environments surrounding DMF molecules in DMF/THF=1/9 with 18wt% BCPs of the SV is very similar to the environments of unary DMF solvents with 20wt% homo poly(4-vinylpyridine) which is in concentrated range with chain entanglement. This means the BCP make micelles with cores of poly(4-vinylpyridine) swollen by DMF, which is localized inside core and separated from major solvent of THF to some extent. Although to conduct more quantitative analysis SANS experiment in BCP/deuterated DMF/protonated THF could be necessary, this qualitative understanding that solvents distribution is not homogeneous and DMF is localized in micellar core gave important sights for us to design the systems giving rise to controlled distribution of BCP in blended membrane as mentioned above.