Large Scale Supramolecular Self-Assembly of Graft-Copolymers Prepared by Rapid Evaporation of Organic Solvents

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Large scale supramolecular self-assembly was prepared by using poly(ethylene glycol) (PEG) macromonomer -g-poly(styrene) (PSt) copolymers. The ordered structure of mesh- and crater-like morphologies were obtained depending on St/macromonomer ratio and the solution concentration.

Most of self-assembly have been prepared from a variety of synthetic amphiphilic compounds. Such molecules are comprised of polar head groups and hydrophobic alkyl chains, and this amphiphilic property is believed to be essential to their self-organization. Based on this hypothesis, a lot of novel amphiphiles were synthesized and used to prove self-assembly.[1-3] The other studies reported that polymeric self-assembled monolayers show better thermal and mechanical stability than that of the self-assembled monolayer made by small molecules.[4-8] Recently, Zhang et al. showed that the ordered self-organizing films of amphiphilic polymers could be obtained by the slow evaporation of solvents.[7] Those self-assembles consisted of polymers are expected to have a unique properties. As novel self-assemblies, we decided to explore the formation of large scale self-assemblies. For this purpose, we introduced a novel amphiphilic polymer prepared by the macromonomer method.

The macromonomer method was developed as the preparation method for monodispersed polymeric microspheres.[9] The copolymerization system of macromonomer method is a kind of inhomogeneous system,[10] so the resulting copolymers contains the block-like-structured copolymer, which means that the graft copolymer consists of a macromonomer-rich-segment(brush like part; hydrophilic moiety) and a styrene-rich-segment(tail like part; hydrophobic moiety). So, the graft copolymer could be thought as a large amphiphile as a whole. The poly(ethylene glycol) (PEG) macromonomer-g-styrene (St) copolymers,[11] which were formed as nanosphere, were dissolved into chloroform at various concentrations, and dip-coated onto the PET surface.[12]

The obtained thin film was observed using a scanning electron microscope(Hitachi 7010A, Tokyo, Japan). Figure 1 shows SEM images of self-assembling films. It was clear that mesh- and crater-type ordered structures were observed. The sizes of the structures were in micrometer order (1 to 10 μm). Table 1 summarized the results of the self-assembling film formation of various graft copolymers in various conditions. It becomes clear that the formation of an ordered structure depends on the St/macromonomer ratio rather than on molecular weight of macromonomer. The ordered structure (mesh and crater) was obtained when the St/macromonomer ratio was higher than 80. The differences in structure of each self-assemblies are due to the hydrophilic/hydrophobic balance of the graft copolymer. During solvent evaporation, PEG- and PSt-rich sequences tend to aggregate, respectively, and the topical concentrations increase. As chloroform was removed, aggregates of graft copolymer were relocated to minimize surface free energy, and finally they form ordered-structured self-assemblies. When the films of graft copolymers were prepared by the slow evaporation method, smooth and homogeneous films were obtained. Therefore, the ordered structure obtained here was regarded as one of the metastable state. The solvent evaporation rate is one of the key factors for forming these ordered structures. Shimomura et al. reported the preparation of the ordered self-assembly of nanosize polystyrene aggregates on mica.[13] In that study, they pointed out that the concentration of the solution and the evaporation rate of the solvent were essential factors for controlling the size and structure of self-assembly. While our scale and materials were different from theirs, the same principles are present in this study.

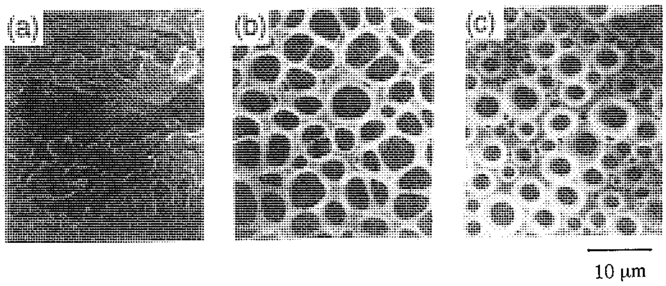

Figure 1. Scanning electron micrographs of self-assembling films. All copolymer solution were 1 wt%. (a) sample **1** (amorphous), (b) sample **2** (mesh), (c) sample **3** (crater).

Table 1. Morphology of cast film of PEG/PSt graft copolymers[a]

No.	PEG macromonomer Mn	graft copolymer[b] St/macromonomer	soln. conc. / % 0.1	0.2	0.5	1.0
1	1740	20	A	A	A	A
2	1740	80	A	A	M	M
3	1740	220	C	C	C	C
4	1740	400	C	C	C	C
5	4250	70	A	A	A	A
6	4250	600	C	C	C	C

[a] A: amorphous, C: crater, M: mesh.
[b] Molar ratio.

ESCA analysis (Shimadzu ESCA 1000, Kyoto, Japan) of the obtained film was done to confirm the above hypothesis. C1s spectra of samples **1**, **2**, **3** and PET were shown in Figure 2. The peaks of C-O bonding (at 287 eV, assigned to the PEG unit) were decreased with decreasing PEG content in the copolymers. For sample **2** and **3**, the peak ratios of the C-O bonding and the C-C and/or C=C bonding (at 285 eV, assigned to the styrene unit) were relatively low as compared to the theoretical one. It

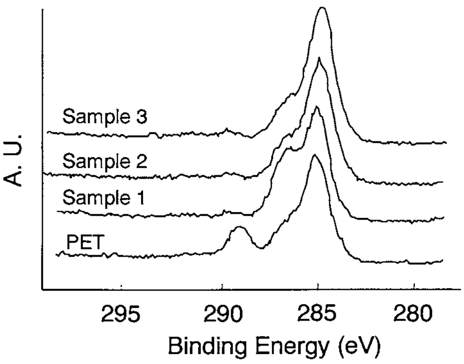

Figure 2. ESCA spectra of C1s for the cast films. Sample codes are referred to Table 1.

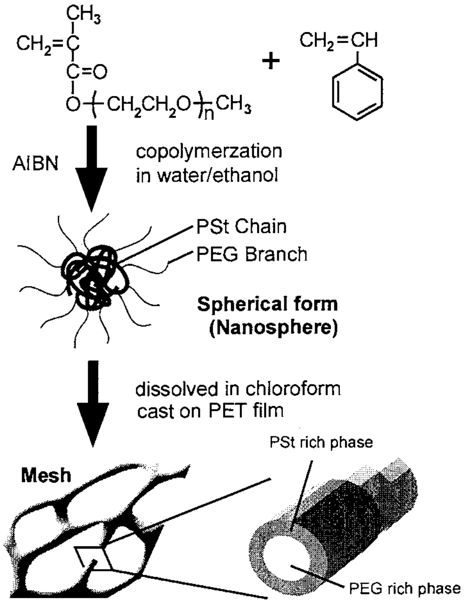

Figure 3. Schematic representation of the preparation of large scale self-assembly by graft copolymers.

means that the surfaces of the mesh or crator-structre were covered with PSt segment. The wettability of those films was also measured by the sessile drop method. The water contact angles of samples **2**, **3**, **4** and **6** were higher than 100 degrees. These water repellency of the samples were maintained after longer contact with water droplets. This result suggested that the outermost surface of those samples were fully covered by PSt segment. The self-assemblies obtained here were very stable against the boiling water treatment, the detergent treatment, and the hot air (120 °C) treatment. The structures and contact angles did not change throughout the treatments.

In conclusion, we showed that the graft copolymers prepared by the macromonomer method formed large scale supramolecular self-assemblies. The inner structure of self-assembly was estimated and drawn in Figure 3. The key factors for determining the structure of this type of self-assembly are the hydrophobic/hydrophilic balance of graft copolymers, concentration of the solution and evaporation rate of the solvent. Using other graft copolymers,^{14} many kinds of novel, functional and practical self-assemblies can be prepared.

References and Notes

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11 The graft copolymers were prepared by the free radical dispersion copolymerization of PEG macromonomer (Mn=1750 and 4250) and styrene. PEG macromonomer and styrene were dissolved into water-ethanol mixed solvents(7/3 v/v) with N,N'-azobisisobutyronitrile as an initiator. After vigorous degassing, the solution was sealed and kept at 60 °C for 24 h. After the polymerization, the reaction media was dialyzed for 5 days and then lyophilized. The composition of graft copolymers were determined by ^{1}H-NMR using JEOL GSX-400(400MHz) instruments.
12 The coating procedure is as follows; PET film was washed by methanol- and acetone- soxhlet extract, respectively. The dip coating was done under 25% humidity and at 25 °C.
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