

FABRICATION OF NANOSPHERES FROM SUPRAMOLECULAR ASSEMBLY OF END-FUNCTIONALIZED POLYMER MIXTURE

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Introduction

In the polymer blend systems where the constituent polymers are macroscopically phase-separated due to ubiquitous repelling interactions between dissimilar monomer species, the introduction of small functional groups capable of specific interactions (e.g. hydrogen bonding, ionic interaction) can lead to an interesting self-assembly behavior that cannot be observed in the neat polymer blends. One of the simple examples is the binary blend of mono-end-functionalized polymers, viz. A- x /B- y , where the specifically attractive interactions between end-functional pair x and y compete for mixing or demixing with the repulsive nonspecific interactions between A and B polymer.

Self-assembly of polymers within nanospace has attracted growing interest as a means for miniaturization of structural objects or creating novel nanostructures, partly stimulated by the recent development in the production of polymer nanoparticles. As a notable method for manufacturing polymer nanoparticles, the self-organized precipitation (SORP) method provides an easy and robust route that can be applied to various polymers ranging from homopolymers to copolymers [1,2]. This method is based on the polymer precipitation in solvent where the solvent quality for solute polymer is slowly changed from good to poor, achieved by the addition of droplets of nonvolatile poor solvent to the polymer priori dissolved in volatile good solvent.

Here, on the basis of the SORP and the supramolecular assembly of mono-end-functionalized polymer mixture, A- x /B- y , we report the fabrication of nanospheres which themselves have intriguing internal nanodomains of multilevel perforated spheres that have high specific interfacial area. The surface functionality of fabricated nanospheres can also be controlled by varying the mixing ratio of two types of end-functionalized polymers, which therefore enables us to tailor the surface activity of the nanospheres.

Experimental

Our method for preparing nanospheres is based on the SORP of mono-end-sulfonated polystyrene (SPS) and mono-end-aminated poly(1,2-butadiene) (APB) at room temperature. A mixed solute consisting of SPS ($M_n=10.5$ kg/mole, polydispersity index =1.05) and

APB ($M_n=15.0$ kg/mole, polydispersity index =1.05) with a weight fraction of SPS (Φ) is first dissolved in tetrahydrofuran (THF) chosen as a good solvent for both polymers. Subsequently, water drops are slowly added to the end-functionalized polymer solution, which provides a driving force for the polymers to form temporal aggregates nearby each of water droplets. The formation of these fluctuating, temporal aggregates become stabilized more and more by the steady addition of water droplets and the simultaneous evaporation of volatile THF. While the added water gradually becomes a majority solvent, the minority THF solvent, miscible both with polymers and water, plays a role similar to colloidal stabilizer preventing polymer aggregates from excessive growth. During this gradual change of solvent quality leading to the polymer assembly into nanospheres, the 1:1 end-associations between SPS and APB chains occur due to strong ionic interaction between a proton-donating sulfonic acid group of SPS and a proton-accepting amino group of APB ($\text{SO}_3^- \cdots \text{NH}_3^+$), which determines the morphological structure within the nanoparticle in combination with other interactions including the nonspecific repulsion between styrene and butadiene segments.

Results and Discussions

The SPS weight fraction in the mixed solute Φ is the primary variable for controlling the structure of nanospheres in this study. We begin with the case of stoichiometric mixture ($\Phi = \Phi_{ST}$) where the number of sulfonic acid groups of SPS chains is equal to the number of amino groups of APB chains. The transmission electron microscopy (TEM) images of the nanoparticles prepared from mixed solute of SPS and APB with $\Phi = 0.40$ ($\cong \Phi_{ST}$) are shown in Fig. 1a and 1b, where spherical nanoparticles with the diameter of about 270 nm are well-produced by the SORP method. The magnified TEM images in Fig. 1b, where the darker phase corresponds to the APB domains stained by osmium tetroxide (OsO_4) and the lighter phase to SPS domains, shows a very interesting internal morphology that appears at first glance to be concentric dashed circles of SPS domains embedded in the majority APB phase.

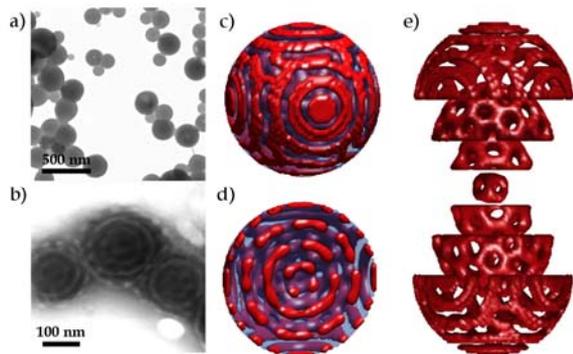


Fig. 1 Nanoparticles prepared from mixed solute of SPS and APB with $\Phi = \Phi_{ST}$. a) TEM image of the produced nanoparticles and b) their internal morphologies. c) The simulated nanosphere and d) its internal structure represented by a radial cross section. Regions of high density of SPS and APB are colored opaque red and transparent blue, respectively. e) The decomposed representation of hierarchical perforated spheres.

To figure out the 3-dimensional geometry of this exotic internal morphology, we simulated a model system using a density functional theory under an assumption that all the SPS and APB chains are end-linked to form styrene-butadiene (SB) diblock-like supramolecules. For the simulation, we numerically integrate Cahn-Hilliard-Cook (CHC) diffusion equation with Landau-Ginzburg (LG) free energy[3] and a surface field in a spherical volume, where both the conformational contributions^[11] of SB diblock and the pairwise interactions between the components (i.e., styrene (S), butadiene (B), and water (W)) are taken into account. Fig. 1c-1e represents the simulated morphologies of the model nanosphere, visualizing its surface and internal morphologies. The simulated morphologies reveal that the dashed circle-like SPS domains shown in Fig. 1b are actually spherical layers perforated by several APB struts connecting concentric APB layers at different level. The structural hierarchy of the perforated spheres in a fashion of spheres-in-sphere is visualized in more detail in Fig. 1e, which clearly shows the mesh-like SPS spherical layers at each of levels.

It is interesting to examine how the surface and internal morphology of nanoparticles are altered when the SPS/APB mixture becomes non-stoichiometric with an excess of SPS chains that may form hydrogen bondings with water molecules. Fig. 2 compares the morphologies of nanoparticle samples prepared from SPS/APB mixtures with $\Phi = 0.40$, $\Phi = 0.45$, $\Phi = 0.50$, and $\Phi = 0.70$. It is observed that the perforated spheres, similar to the structure of the stoichiometric case, are formed inside a uniform outermost SPS layer for $\Phi = 0.45$ (Fig. 2b) and $\Phi = 0.50$ (Fig. 2c). As the SPS fraction is increased further to $\Phi = 0.70$, the inner morphology becomes a uniformly layered structure where SPS and APB form concentric domains (Fig. 2d).

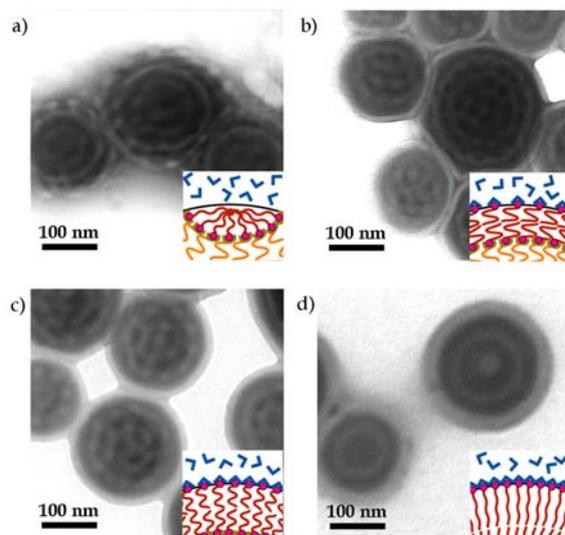


Fig. 2 TEM images of internal morphologies of nanoparticles from mixed solute of SPS and APB with a) $\Phi = 0.4$, b) $\Phi = 0.45$, c) $\Phi = 0.5$, and d) $\Phi = 0.7$. The schematics in the insets represent the molecular arrangements near the surface of nanoparticles.

Conclusions

Nanospheres comprised of complementarily end-interacting two species of polymers have been fabricated by the SORP method. An exotic internal morphology, hierarchically organized perforated spheres, was formed inside the nanosphere prepared from the stoichiometric mixture, resulting from the formation of diblock-like supramolecules and their packing frustration in the spherically confined nanospace. The thickening of the outermost brush layer, accompanied by the enrichment of functionalized groups on the nanoparticle surface, was observed by changing the mixing ratio of the two end-functionalized polymers, which allows us to precisely control the surface functionality of the nanoparticle that can be an essential kernel for further physical or chemical decoration needed in various applications.

References

1. Yabu, H., Higuchi, T., Shimomura, M., *Adv. Mater.*, **17**, (2005), 2062.
2. Higuchi, T., Tajima, A., Motoyoshi, K., Yabu, H., Shimomura, M., *Angew. Chem.*, **120**, (2008), 8164.
3. Gunton, J. D., Miguel, M. S., Sahni, P. S., "Phase Transition and Critical Phenomena", Edited by Domb, C., Lebowitz, J. L. Academic Press, New York, (1983).