

Nanophase-Separated Supramolecular Assemblies of Functionalized Polymers via Ionic Hydrogen Bonding

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1 Introduction

Nanophase separation is the phase separation phenomenon at the nanoscopic scale for multicomponent soft materials, especially block or graft copolymers. Recently, “block or graft supramacromolecules”, including nanophase-separated supramolecular assemblies of two or more polymers through non-covalent bonding, have attracted more attention because non-covalent bonding provide smart materials with stimuli responsiveness by temperature or shear stress. Block or graft-type supramolecular assemblies, however, usually require precise synthesis of end-modified polymers as building blocks. Here in this study¹, we present simple preparation and morphology observation of graft-type supramolecular assemblies via ionic hydrogen bonding by mixing two commodity polymers.

2 Experiment

ω -Carboxyl-terminated poly(dimethyl siloxane) (PDMS-COOH, $M_n \sim 1450$, $PDI \sim 1.6$, $T_g \sim -125$ °C, purchased from Shin-Etsu Chemical Co. Ltd.) and polyethylenimine (PEI, $M_n \sim 1200$, $M_w \sim 1300$, $T_g \sim -56$ °C, purchased from Aldrich) were blended in a mixed solvent of tetrahydrofuran/methanol (5/5=v/v). Then, the solvent was slowly evaporated for 24h, and the blend sample was further dried *in vacuo* for 48h at 35 °C. The weight ratio of PDMS-COOH:PEI in the blends were varied as 25:X ($X = 1\sim 5$), where five blend samples were prepared. The blends were coded as DE-25:X. To investigate the morphological behavior of the blends at the nanoscopic scale, small angle X-ray scattering (SAXS) were carried out at room temperature at the beamline 15A in the Photon Factory, Tsukuba, Japan.

3 Results and Discussion

SAXS profiles of all DE-25:X samples were shown in Figure 1. The profiles of neat PDMS-COOH (DE-25:0) and neat PEI were also shown at the bottom and the top in the figure, respectively. There are no peaks on the profiles of DE-25:0 and neat PEI, indicating no notable electron density difference at the nanoscopic level in the neat samples. However, once both neat samples are mixed, the shapes of profiles became totally different. The blends even with the small amount of PEI such as DE-25:1 show broad peaks at around 1.0 nm^{-1} on their profiles, representing a correlation hole peak which might be originated from electron density difference between PDMS and PEI with the length scale of several nanometers. On the profile of DE-25:2, there are three sharp peaks at 0.85 , 1.7 , and 2.55 nm^{-1} , relative q values

of 1, 2, and 3, indicating a lamellar nanophase-separated structure with domain spacing of 7.4 nm in the blend. Other profiles of DE-25:X ($X \geq 3$) have also sharp peaks at relative q values of 1, 2, and 3, but the location of peaks shifted to lower q values as the X value increases, representing domain spacing expansion probably due to the increase in the thickness of a COOH/PEI phase in nanophase separated structures.

In conclusion, we have demonstrated facile building-up of nanophase-separated supramolecular assemblies composed of two functionalized polymers such as a pair of PDMS-COOH and PEI via ionic hydrogen bonding. The lamellar nanophase separated structures between a PDMS phase and a PEI/COOH phase were also observed in the blends by SAXS measurements.

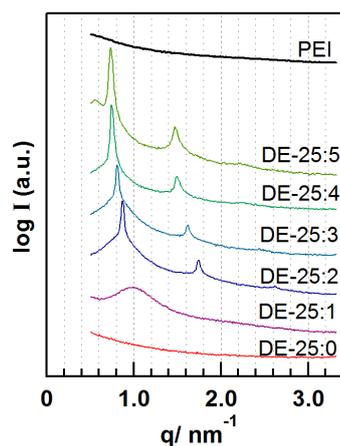


Figure 1. SAXS profiles of DE-25:X ($X = 0\sim 5$) and PEI. SAXS was measured at room temperature.

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References

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