Swelling Kinetics of PEO/PCL Multiblock Copolymer Swelling

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Introduction

Hydrogels have received significant attention because of their biocompatibility which makes them applicable to medical implants, biosensors, and matrices of drug delivery. This properties come from their low interfacial tensions with surrounding biological fluids and tissues. Therefore, hydrogels have been studied by many ways. However, the microscopic view of the kinetics of hydrogels which is related to the intermolecular interactions was not disclosed.

Methods and Materials

Sample is the amphiphilic multiblock copolymer composed of hydrophilic biocompatible poly(ethylene oxide) (PEO) and hydrophobic boidegradable poly(ε-caprolactone) (PCL). The PEO/PCL multiblock copolymer was synthesized by dissolving dicarboxy-terminated PEO (M_w=2000g/mol) and PCL (M_w=2000g/mol) purchased from Aldrich Chemical Co. in a dry methylene chloride.

We investigated the swelling kinetics of PEO/PCL multi-block copolymer in water, which has high solubility for PEO at room temperature, by in-situ small-angle x-ray scattering (SAXS) at 8-ID-I APS. A charge coupled device(CCD) x-ray camera is used for collecting the small-angle x-ray scattering data. We used data reduction software called “coherent” to analyze the acquired data.

Results and Discussion

To investigate the swelling kinetics of PEO/PCL, purified water was injected into dried multiblock copolymer samples, which were crystallized at at 10 □, at room temperature. The full frame images of the acquired data are shown in Fig. 1.

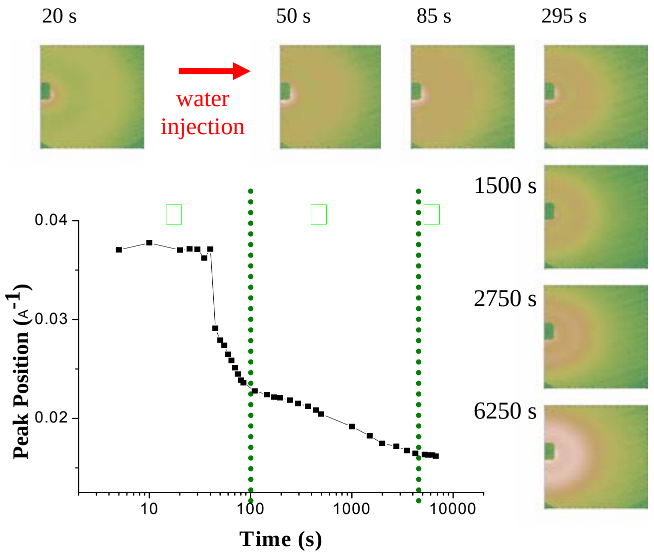

Fig. 1. Evolution of peak positions of PEO/PCL SAXS patterns

From the CCD image, the peak positions of the SAXS pattern was obtained.

The graph in Fig. 1. shows the evolution of the peak positions during swelling which represents the characteristic length scale of the density modulation, the distance between each PEO/PCL block. In region I, which is ~ 100 second after injecting water, the peak position shifts to low-q side rapidly. The peak shifts gradually in region □, and finally saturates (region □)

In region I, the swelling of the PEO/PCL multiblock proceeds mainly by the association of water molecules with the hydrophilic PEO. The water molecules form hydrogen bonding with the oxygen atom in the PEO (-CH2-O-CH2-). The formation of the hydrogen bonding disrupts the monoclinic crystalline structure weakly connected by the Vander Walls interaction. The semicrystalline PEO, therefore, melts during the swelling, and the polymer chains relax. Macroscopically, during the swelling, the gel volume increases in the initial stage swelling. Therefore, this PEO melting process domonates the rapid peak shifts. The peak shift to the low-q side indicates that the polymer chains are elongated.

After the melting process of PEO is almost finished in region □, the block copolymer consists of the PCL crystalline and the melted amorphous blocks. However, the hydrogen bonding cannot destroy the strong covalent bonds connecting the PEO and the PCL blocks. Therefore, the peak positions move to the low-q side in region □. It means that the distance between the PCL and melted PEO blocks increases. Finally, it saturates even though more water molecules are associated with PEO.

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Reference

REFERENCES IN TEXT: Sequential numbers in brackets beginning with [1] and placed BEFORE final punctuation, i.e., [1] J. Doe, R.P. Brown, B.-P. Smith, Polym. Sci. Pol. Phys. **90**, 4196-4180 (2002).

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