Crystallization of Poly(ε-caprolactone)-Polybutadiene Diblock Copolymers in a Spherical Microdomain Structure

Satoshi Tanimoto¹, Shintaro Sasaki¹, and Shuichi Nojima²*

¹School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), Tatsunokuchi, Nomi-gun, Ishikawa 923-1292, Japan
²Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Introduction

There are several studies on the morphology formed in crystalline-amorphous diblock copolymers. From these studies, the morphology formation of such block copolymers is closely affected by the stability of the microdomain structure in the molten state. When the stability of microdomain structures is low, the morphological reconstruction occurs from a microdomain structure into lamellar morphology due to a large driving force of crystallization. On the other hand, when the stability of microdomain structure is high enough, the crystallization will proceed without any morphology reorganization.

The spherical microdomain structures have disadvantages during crystallization in comparison with the cylindrical or lamellar microdomain structure, since the rearrangement of crystalline chains at the vicinity of the interface between spherical domain and matrix is extremely restricted. In this study, we observed the details of the crystallized spherical microdomain structure as a function of the curvature of spherical interface.

Experimental Section

The poly(ε-caprolactone)-block-polybutadiene diblock copolymers (PCL-b-PB) used in this study were synthesized by a successive anionic polymerization under vacuum in toluene with n-butyllithium as an initiator. The characterizations of the copolymers are shown in Table 1.

<table>
<thead>
<tr>
<th>notation</th>
<th>Mₜotal</th>
<th>MₚCL</th>
<th>Mₚ/Mₚ</th>
<th>PCL/PB (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M44</td>
<td>44000</td>
<td>5300</td>
<td>1.07</td>
<td>10 : 90</td>
</tr>
<tr>
<td>M62</td>
<td>62000</td>
<td>5000</td>
<td>1.13</td>
<td>6 : 94</td>
</tr>
<tr>
<td>M100-1</td>
<td>100000</td>
<td>4000</td>
<td>1.09</td>
<td>3 : 97</td>
</tr>
<tr>
<td>M100-2</td>
<td>100000</td>
<td>10000</td>
<td>1.13</td>
<td>8 : 92</td>
</tr>
<tr>
<td>M100-3</td>
<td>100000</td>
<td>20000</td>
<td>1.12</td>
<td>17 : 83</td>
</tr>
</tbody>
</table>

a) Determined by Membrane Osmometer.
b) Determined by GPC. c) Determined by ¹H-NMR.

The morphology formed in PCL-b-PB copolymers was investigated by small-angle X-ray scattering (SAXS) method. The SAXS measurements were performed at BL-10C in Photon Factory. The spherical morphology was estimated as a function of molecular weight.

Results

Figure 1 shows the SAXS intensity profiles for M44, M62, M100-1, M100-2, and M100-3 in the molten state. Each scattering profile shows several peaks, which correspond to the ratio of 1:√2:√3. This suggests that these copolymer systems have spherical microdomain structures in the melt. Furthermore, some broad scattering maxima marked with gray arrows in Figure 1 can be observed, which indicate the structure factor arising from the isolated sphere. The radius of the spherical microdomain structure was evaluated from the curve fitting of the structure factor for the isolated sphere. The size of the sphere could be controlled with the properties of copolymers and the temperature of the system.

It was confirmed that the scattering intensity maxima attributable to the structure factor of the isolated sphere became broader after crystallization of PCL chains than those observed from the molten system. It suggests that the distribution of the sphere size becomes larger and/or the sphere is distorted considerably by the crystallization.

Table 1: Characterization of copolymers

Figure 1  SAXS profiles for M44, M62, M100-1, M100-2, and M100-3 in the molten state.

* snojima@polymer.titech.ac.jp