論文 / 著書情報
Article / Book Information

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Title(English)	Simultaneous Crystallization Behavior of Crystalline－crystalline Diblock Copolymers
著者(和文)	大澤俊
Author(English)	Satoshi Osawa
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種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	有機・高分子物質　専攻	申請学位（専攻分野）： Academic Degree Requested	博士　（　工学　） Doctor of
学生氏名： Student's Name	大澤 俊	指導教員（主）： Academic Supervisor(main)	野島 修一
		指導教員（副）： Academic Supervisor(sub)	

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this study, various polyethylene-*block*-poly(*β*-propiolactone) (PE-*b*-PPL) diblock copolymers are synthesized and the mechanism of simultaneous crystallization in crystalline-crystalline diblock copolymers is investigated. The PE-*b*-PPL has unique and appropriate characteristics for this purpose, that is, both blocks have close crystallizable temperatures T_c and show a strong segregation behavior, where the microdomain structure is preserved after the crystallization of both blocks. Furthermore, the electron densities of PE and PPL are quite different, so that it is possible to examine a detailed morphology after crystallization using small-angle X-ray scattering (SAXS) techniques.

In **Chapter 1,** the introduction and the purpose of this study were described.

In **Chapter 2**, the synthesis method employed in this study and the molecular characteristics of PE-*b*-PPL used in Chapters 3-5 were described in detail.

In **Chapter 3**, the crystallization behavior of PE-*b*-PPL copolymers was systematically examined with a wide range of crystallinity of PE blocks X_{PE} ($0 \leq X_{PE} \leq 0.33$) to clarify the simultaneous crystallization of PE-*b*-PPL. X_{PE} was controlled by changing the proportion of ethyl branches in PE blocks ($\psi_{1\text{-}2}$). The morphology formation observed in PE-*b*-PPL copolymers is classified into following three types by the value of X_{PE}.

1. X_{PE} (> 0.3) (PE-PL5 and PE-PL6)

The lamellar microdomain structure formed in the melt is completely destroyed by the advance crystallization of PE blocks and the crystalline lamellar morphology is formed instead. PPL blocks subsequently crystallize within the PE crystalline lamellar morphology to yield crystalline lamellar morphology.

2. $0.12 < X_{PE} < 0.26$ (PE-PL10, PE-PL15, and PE-PL20)

The crystallizability of PE blocks is not large enough not to destroy the lamellar microdomain structure, and PE blocks crystallize within it. The crystallization of PE blocks reinforces and stabilizes the existing lamellar microdomain structure against the subsequent crystallization of PPL blocks. The PPL blocks also do not destroy the lamellar microdomain structure and crystallize within it.

3. $X_{PE} = 0$ (PE-PL31)

Only PPL blocks crystallize to form crystalline lamellar morphology. This morphological transition

occurs when the PE blocks do not crystallize and the lamellar microdomain structure is not reinforced.

In **Chapter 4**, we crystallized PPL blocks separately into the β-form (βPPL) or δ-form (δPPL), and investigated the effects of crystal structures of PPL blocks on the crystallization behavior of PE-*b*-PPL. This is the first study to achieve different crystalline morphologies by using the polymorphism of constituent blocks in crystalline-crystalline diblock copolymers. To make T_c of PE and PPL blocks closer, PE blocks with $\psi_{1\text{-}2}$ = 18% were used. In summary, we propose the crystallization mechanism of EPLδ and EPLβ based on the results obtained in this chapter.

EPLδ

The δPPL blocks crystallized simultaneously with PE blocks, which led to the combined crystallization and the large crystallinity, yielding the largely distorted lamellar microdomain structure.

EPLβ

The sequential crystallization of PE and βPPL blocks in EPLβ did not destroy the lamellar microdomain structure, because the crystallizability of PE blocks was sufficiently small. The PE blocks crystallized within the lamellar microdomain structure and stabilized it against the subsequent crystallization of βPPL blocks. As a result, the advance crystallization of PE blocks slightly deformed the lamellar microdomain structure, and the sequential crystallization of βPPL blocks occurred within the crystallized lamellar microdomain structure.

In **Chapter 5**, we examined the simultaneous crystallization of PE-*b*-PPL when the PE blocks were confined in a cylindrical microdomain structure to decrease T_c of PE blocks to the extent comparable to that of PPL blocks. This method has an advantage for using chemically “pure” PE blocks without decreasing the crystallizability due to high $\psi_{1\text{-}2}$. The value of $\psi_{1\text{-}2}$ = 10% was used in this study, which was the same as that obtained by usual anionic polymerization. Furthermore, in this chapter, PE-*b*-PPL copolymers with PPL blocks crystallized into β-form (EPLβ) or δ-form (EPLδ) were separately prepared by controlling the thermal history. The cylindrical microdomain structures of EPLβ and EPLδ in the melt were confirmed by SR-SAXS results. It was also revealed that the morphologies of EPLβ and EPLδ were practically preserved through the crystallization (i.e. break-out crystallization did not occur), however, the regularity was decreased after crystallization. The long period of microdomain structures L and full width at half maximum (FWHM) of the first peak in the SR-SAXS curves were examined by time-resolved SR-SAXS experiments. The L and FWHM values of EPLδ during crystallization were monotonically increased, as the crystallinities of PE and δPPL blocks. The discontinuous change in L and FWHM was not observed during the crystallization of EPLδ. Therefore, simultaneous crystallization with PE blocks confined in cylindrical nanodomains successfully achieved during the isothermal crystallization of EPLδ without using PE blocks having higher $\psi_{1\text{-}2}$ values.

Finally, the general conclusion of the simultaneous crystallization of crystalline -crystalline diblock copolymers is described in **Chapter 6.**