

# Microphase Separation and Crystallization of Crystalline–Amorphous Type Block Copolymer. VI. Crystalline Part in Crystalline Domain

SATOSHI ISHIKAWA

Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16, Jōnan, Yonezawa 992, Japan

## SYNOPSIS

The crystalline and amorphous areas in poly(tetrahydrofuran) (PTHF) domains in a poly(tetrahydrofuran-*b*-isoprene) (crystalline–amorphous, PTHF = 52 wt %) film were distinguished by transmission electron microscopy and the relation between the crystallization and domain shape was clarified. The ratio of PTHF domain containing amorphous area was low in the case of the fewer interfaces of the small curvature formed by poly(isoprene) domain. The PTHF crystallization was closely related to the interface shape.

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## INTRODUCTION

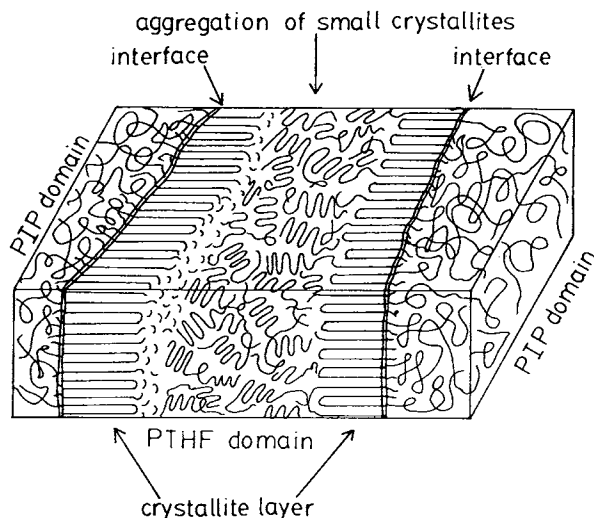
It is well known that diblock copolymers with two amorphous sequences generally form micelles in solutions above the critical micelle concentration. As the solvent is evaporated, the micelles are deformed, and finally various types of microdomains are retained in the film. They have been classified into five types of morphologies.<sup>1</sup> The domain formation has been treated theoretically by thermodynamics.<sup>2,3</sup>

On the other hand, crystalline–amorphous type block copolymers show more complicated morphologies<sup>4–7</sup> than those of the amorphous–amorphous type because the crystallization and micelle formation occur simultaneously. Recently, crystalline (hydrophobic)–amorphous (hydrophobic) type block copolymers, namely, poly[tetrahydrofuran (THF)-*b*-styrene (ST)],<sup>8</sup> poly(2-methyl-2-oxazoline-*b*-ST),<sup>9</sup> and poly( $\epsilon$ -caprolactone-*b*-ST),<sup>10</sup> were synthesized. In these copolymers, crystallization occurred after micelle formation during evaporation of solvent. The resulting domain surface was disturbed by the crystallization.

In our preceding papers, poly[THF-*b*-isoprene (IP)]s (crystalline–amorphous) were synthesized.<sup>11</sup> The process of microdomain formation and crys-

tallization with various solvents were studied using benzene (good for both sequences) and two kinds of selective solvents (good for one sequence and poor for another sequence).<sup>12–14</sup> Then the microstructure of the poly(tetrahydrofuran) (PTHF) domain with lamellar structure was examined with transmission electron microscopy (TEM), gel-permeation chromatography, small-angle X-ray scattering, and differential scanning calorimetry. For the structure with lamellar domains (prepared from benzene solution), the crystallization of PTHF occurred after the micelle formation and the crystallization began in the vicinity of the interface.<sup>12</sup> Then the higher order structure of the poly(THF-*b*-IP) with lamellar domains was elucidated (Fig. 1).<sup>13,14</sup> The PTHF domain consists of three layers and crystallite shape and size of the outer part of the PTHF domain were different from those of the inner part. The PTHF chains run perpendicular to the interface.

In the perfectly straight lamellar domain [Fig. 2(a)], the crystallization occurs uniformly. But it is difficult in an experiment to keep the domains' shape completely straight. In the usual casting condition, the domains bend at random [Fig. 2(b)] and there are some domain ends [Fig. 2(b), arrow]. In this shape it is expected that the crystallization cannot occur uniformly in comparison with the case of the perfectly straight lamellar domain and there are some parts that cannot crystallize because one end



**Figure 1** Model of the poly(THF-*b*-IP) film with lamellar structure.<sup>13-14</sup>

of the crystalline chain is connected with the amorphous chain on the interface. The arrangement of the crystalline chain is affected by the domain shape.

In this work, the crystalline and amorphous parts in the crystalline domain (block copolymer = poly(THF-*b*-IP)) were distinguished by TEM and the relation between the crystallization and domain shape was clarified by analyzing the photograph.

## EXPERIMENTAL

### Synthesis of Block Copolymer

The preparation of poly(THF-*b*-IP) has been reported.<sup>11</sup>  $\bar{M}_w$ s of PTHF and PIP were 118000 and 110000 (PTHF 52 wt %).

### Electron Microscopy

The method to distinguish the crystalline and amorphous parts of the PTHF domain by TEM has been established.<sup>13,15</sup> A drop of 0.05 wt % benzene solution of the block copolymer was deposited on copper mesh covered with a thin carbon film. The specimen was dried well at atmospheric pressure and room temperature for 5 days. Subsequently, one drop of 0.005 wt % *n*-hexane solution of a sustaining agent [*N*-vinylcarbazole (Vcz)] was deposited. The agent diffused into the amorphous part of PTHF. After *n*-hexane evaporated, the specimen was exposed to the vapor of osmium tetroxide (OsO<sub>4</sub>) and the amorphous part of PTHF (containing Vcz) and PIP domain were stained.

TEM observation was carried out using a Hitachi

H-500 transmission electron microscope. The accelerating voltage was 100 kV.

### Analysis Method

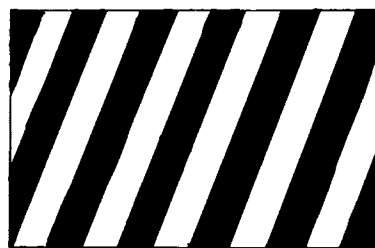
The relation between the domain shape and the amorphous part in the PTHF domain was analyzed by the following method. The shape of PTHF domains obtained in TEM photographs were classified into five types (Fig. 3).

*Type A:* The PTHF domain surrounds a spherical PIP domain and the PTHF domain was surrounded by an outer PIP domain [Fig. 3(a)].

1. The PTHF domain was completely surrounded by PIP domain [(a)-1].
- 2.-5. The PTHF domain was connected to the outer PTHF domain at one, two, three, or four parts [(a)-2, 3, 4, or 5, respectively].

*Type B:* One end of the PTHF domain was the "dead end" [Fig. 3(b)].

*Type C:* The PTHF domain was the bent lamellar domain with a sandwiched PIP domain [Fig. 3(c)].



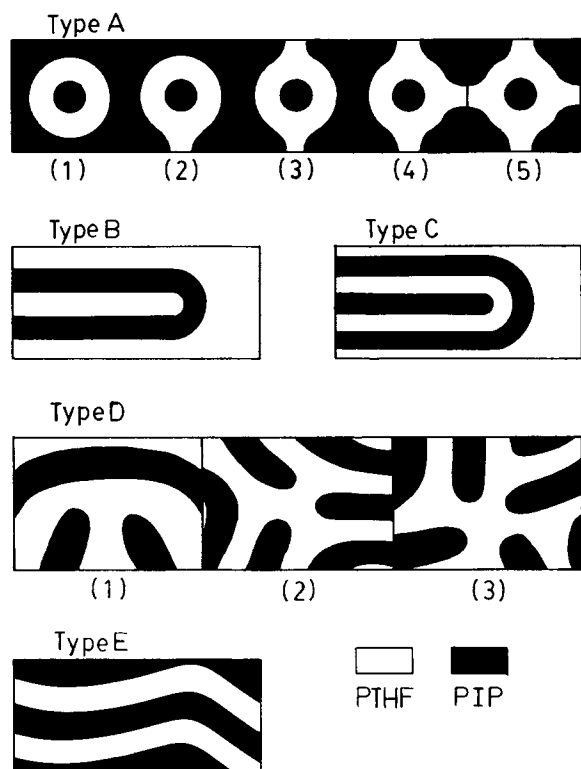
(a)



(b)

□ PTHF    ■ PIP

**Figure 2** Model of the lamellar structure of the block copolymer film: (a) perfect straight lamellar domain and (b) lamellar domain with some domain ends. Arrow: the end of the PIP domain.



**Figure 3** Model of the classified domain shape.

*Type D:* The ends of the PIP domain (two, three, or four) were gathered. The PTHF domain branched at this point [Fig. 3(d)].

*Type E:* PTHF and PIP domains are alternating lamellar structure.

Next, it was ascertained whether the following parts were stained or nonstained about the above-classified PTHF domain:

*Type A1:* PTHF domain; 2-5: the same area as that shown in 1. (circled area);

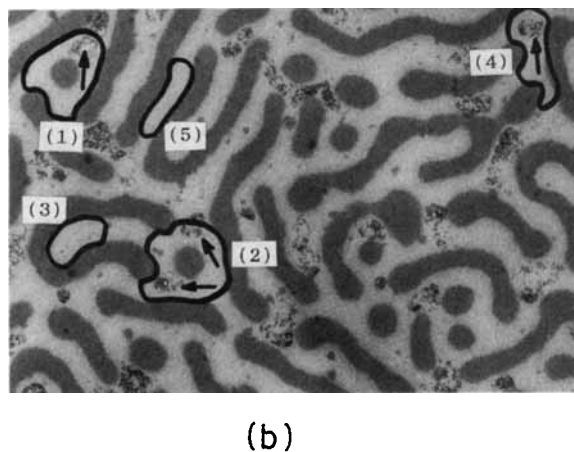
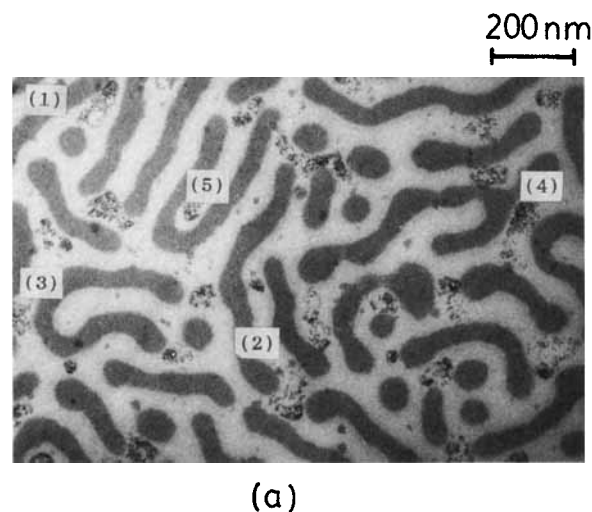
*Type B:* the part of the end of PTHF domain (about 100 nm);

*Type C:* the bent lamellar domain and straight domain (about 100 nm) connected to the end of the bent domain;

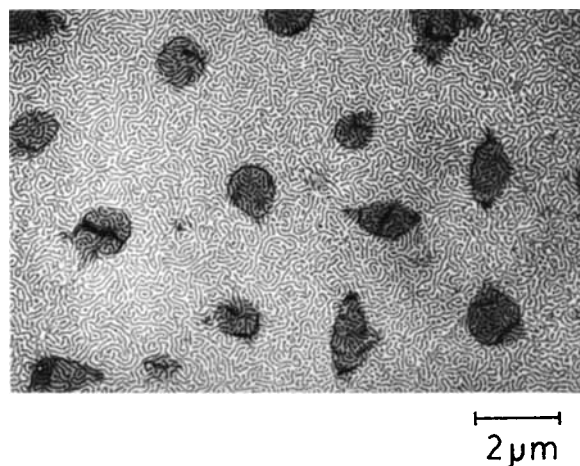
*Type D:* PTHF domain within the distance of 100 nm from each end of the PIP domain;

*Type E:* the straight lamellar PTHF domain.

For example, representative stained and nonstained parts of PTHF domain were shown in Figure 4(a). Dark domains (domain size = about 70 nm) were PIP domains. White domains were PTHF domains and 1-5 corresponded to Type A4, A5, B, D1, and E, respectively [see Fig. 4(b)]. The areas sur-



**Figure 4** Representative TEM photograph of poly-(THF-*b*-IP) film: (a) classified and investigated PTHF domain: (1) type A4, (2) type A5, (3) type B, (4) type D1, (5) type E; (b) investigated areas (black line) about stained or nonstained part, arrows indicate stained parts.



**Figure 5** TEM photograph of the poly(THF-*b*-IP) stained with substaining agent (Vcz) and OsO<sub>4</sub>.

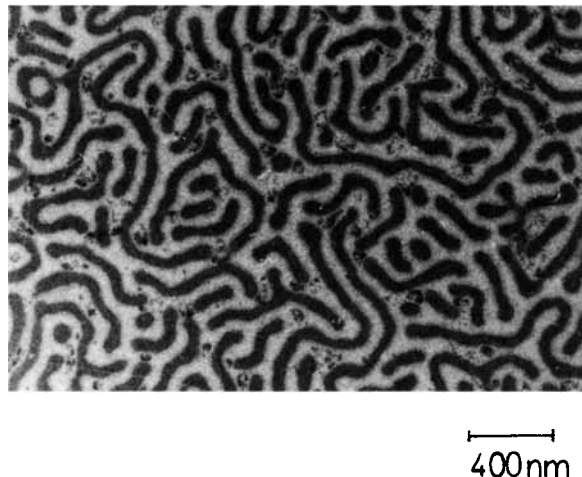


Figure 6 TEM photograph, magnification of Figure 5.

rounded by a black line were investigated about stained or nonstained. If the part stained with Vcz and OsO<sub>4</sub> existed at the inside of the line, the PTHF domain was regarded stained. The arrows in 1, 2, and 4 indicated the stained parts. Then 1, 2, and 4 were regarded stained. The stained part was regarded as the PTHF domains containing amorphous area. By analyzing the wide area of the photograph (about 10 × 10 μm), the number of stained parts and ratio of PTHF domain containing amorphous area were calculated.

## RESULTS AND DISCUSSION

Figure 5 is the TEM photograph of the specimen stained with sustaining agent (Vcz) and OsO<sub>4</sub>. Dark parts are PIP domains. There are some wide areas stained slightly. These are excess Vcz that reacted with OsO<sub>4</sub>. Lamellar domain was observed in a wide area (more than 10 μm).

Figure 6 is the TEM photograph of Figure 5 magnified. There are some dark parts in the PTHF domains (white parts). These are the stained parts

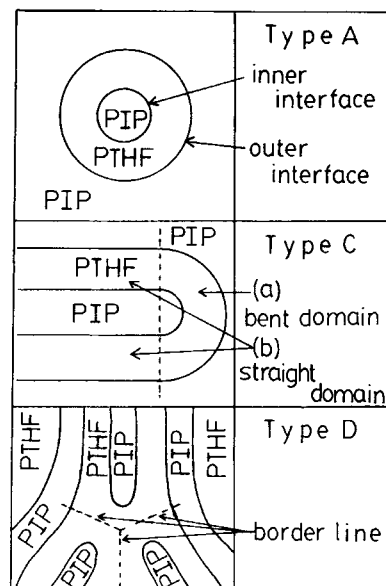


Figure 7 Model of the domain structure: (a) type A, (b) type C, (c) type D.

with Vcz and OsO<sub>4</sub> and correspond to amorphous parts in the PTHF domain.

Table I is the ratio of PTHF domain containing amorphous area in the case of type A investigated with Figure 5. In the TEM photograph the numbers of PTHF domain corresponding to types 1 and 2 were very few (3 or 15). In type A the PTHF domain surrounding the spherical domain of PIP branched and connected with outer PTHF domains. The ratio was very high in each type. The total ratio was 86% and both crystalline and amorphous areas existed in type A. In most cases, the stained parts (amorphous areas) were only one part in one PTHF domain of type A. The strain of PTHF chain by the crystallization concentrated on the stained part. The cause of the strain is explained with Figure 7(a). The domain structure should be lamellar considering the PTHF fraction (52 wt %). However, the condition of domain formation was partially nonequilibrium during the solvent evaporation. Then the curvature of the outer interface of the PTHF domain

Table I Ratio of PTHF Domain Containing Amorphous Area (Type A)

Type	Number of PTHF Domain	Number of Stained PTHF Domain	Ratio of PTHF Domain Containing Amorphous Area (%)
1	3	3	100
2	15	10	67
3	80	70	88
4	100	82	82
5	105	95	90
Total	303	260	86

**Table II Ratio of PTHF Domain Containing Amorphous Area (Types B and C)**

Type	Number of PTHF Domain	Number of Stained PTHF Domain	Ratio of PTHF Domain Containing Amorphous Area (%)
Type B	96	28	29
Type C	40	18	45

was different from that of the inner interface. When the curvature of the inner interface was very small (spherical PIP domain = about 30 nm), the crystallization was limited because the PTHF chains run perpendicular to the interface.<sup>13</sup> In comparison to the unit cell data of PTHF crystallite ( $a = 5.48 \text{ \AA}$ ,  $b = 8.73 \text{ \AA}$ ,  $c = 12.07 \text{ \AA}$ , and  $\beta = 134.2^\circ$ )<sup>16</sup> and the curvature of the interface (30 nm), the strain occurring by the crystallization cannot be neglected. The strain concentrated on one part and that became amorphous and the other part crystallized. In the branched PTHF domain-like types 3–5, the outer interface was a more complicated shape and the strain more concentrated.

Table II shows the ratio of PTHF domain containing amorphous area in the cases of types B and C. In type B, the ratio was low (29%). In this case, the curvature was small like type A. However, the curvature of the outer interface was small but not that of the inner interface because PIP domain did not exist in the PTHF domain. The PTHF chain was dense in the end of the PTHF domain. The crystallization then occurs easily and the amorphous areas were few.

In type C, the ratio was higher than the case of type B but lower than the case of type A. The half of the shape of PTHF domain [see arrow (a) of Fig. 7(b)] is the same as type A. But the remaining PTHF domain [arrow (b)] is a straight domain. Therefore, the ratio of amorphous PTHF domain in type C was about half of that in type A.

Table III is the ratio of PTHF domain containing amorphous area in the case of type D. In type D, few domains like type C are collected to one part [Fig. 7(c)]. But the PTHF domains straightly contact each PTHF domain not the PIP domain on the border lines (see arrow). The interface with the

small curvature formed by the end of the PIP domain was more than that in type A. Therefore, the ratio was less than that of type A.

Table IV is the ratio of PTHF domain containing amorphous area in the case of type E. Semistained is the case of staining at the end of straight domain. The ratio without semistained was 11%. Therefore, the crystallization occurred easily and densely in the straight domain. The end of the straight domain was apt to be amorphous because the part contacted to the other type (A or D).

From these results, the ratio of PTHF domain containing amorphous area was low in the case of the few interfaces of the small curvature formed by the PIP domain. Figure 8 shows the simplified models of PTHF chains for types A–D. One PTHF chain occupies the half of PTHF domain from the junction of the PIP chain. In type A1, there are four areas without PTHF chain and four areas with double PTHF chain. In type B, there are two areas without PTHF chain and two areas with double PTHF chain. The sparse and dense areas are fewer than that of type A. Therefore, the ratio of amorphous area was lower than that of type A. In type C, there is one area with double PTHF chain. Because the density of PTHF chain was high, the crystallization occurs densely. Therefore, the ratio of amorphous area was low. In type D, there are few areas without and with double PTHF chains. In types A and D, the sparse and dense areas are many and both ratios of amorphous areas were high. These phenomenon were caused by the formation of the nonlamellar structure with the block copolymer (1 : 1 volume fraction). The sparse and dense areas of PTHF chain affected the crystallization. The crystallization under a nonequilibrium state differs by the shape of the crystalline domain shape.

**Table III Ratio of PTHF Domain Containing Amorphous Area (Type D)**

Type	Number of PTHF Domain	Number of Stained PTHF Domain	Ratio of PTHF Domain Containing Amorphous Area (%)
1	101	64	63
2	96	60	63
3	69	47	68

**Table IV** Ratio of PTHF Domain Containing Amorphous Area (Type E)

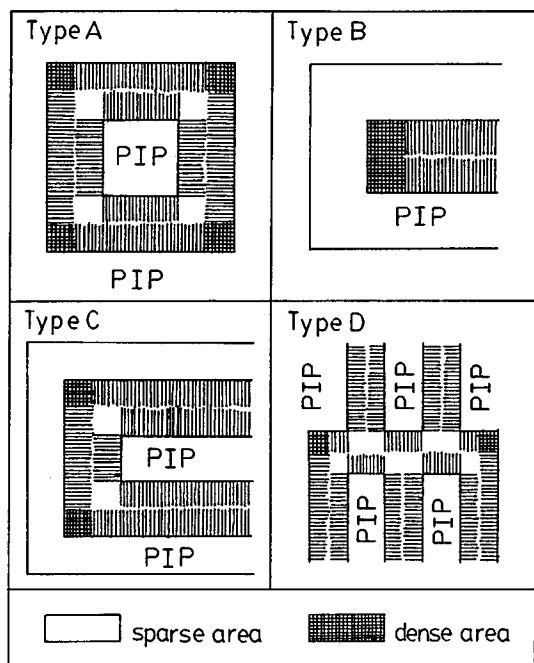
Number of PTHF Domain	Number of Stained PTHF Domain <sup>a</sup>		Ratio of PTHF Domain Containing Amorphous Area (%) <sup>b</sup>	
	Stained	Semistained	Stained	Total
109	12	18	11	28

<sup>a</sup> Stained: stained at the central part of PTHF domain; semistained: stained at the end of straight domain.

<sup>b</sup> Stained: (number of stained/number of PTHF domain) × 100. Total: [(number of stained + number of semistained)/number of PTHF domain] × 100.

## CONCLUSIONS

In this study the crystalline and amorphous parts in the PTHF domain in the poly(THF-*b*-IP) (PTHF = 52 wt %) were distinguished by TEM and the relation between the crystallization and domain shape was clarified by analyzing the photograph. The ratio of PTHF domain containing amorphous area was low in the case of the fewer interfaces of the small curvature formed by PIP domain. The sparse and dense areas of PTHF chain by the interface shape affect the crystallization.



**Figure 8** Simplified model of PTHF chains for types A-D.

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