

# Study of Spherulitic Structures by Analyzing the Spherulitic Growth Rate of the Other Component in Binary Crystalline Polymer Blends

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Received April 27, 2007; Revised Manuscript Received September 14, 2007

**ABSTRACT:** The structures in spherulites of poly(butylene succinate) (PBSU) are discussed by analyzing the spherulitic growth rate of poly(ethylene oxide) (PEO) inside PBSU spherulites of PBSU/PEO blends, which are binary blends of crystalline polymers where PBSU spherulites fill the whole volume before PEO spherulites nucleate and grow inside PBSU spherulites. The results indicated that a PBSU spherulite contains wide amorphous regions and that PBSU crystals suppress the molecular mobility of PEO very little. It also implied that PEO crystallizes primarily in interfibrillar regions in PBSU spherulites. The same equation as that for crystalline/amorphous blends was applicable to the dependence of the spherulitic growth rate of PEO,  $G_{\text{PEO}}$ , on the crystallization temperature by using the same activation energy for molecular transport as in a melt. The variation of  $G_{\text{PEO}}$  with the blend composition could be ascribed to the volume fraction of PEO in the amorphous region of PBSU spherulites.

## Introduction

The spherulites of one component in crystalline/crystalline polymer blends are reported to grow inside those of the other component.<sup>1–9</sup> When the difference in the melting temperatures  $T_m$  of the two components is about 50 K, the component with the higher  $T_m$  crystallizes first and fills the whole volume. The other component nucleates and grows inside the spherulites of the higher- $T_m$  component, keeping a spherulitic shape.<sup>7–9</sup> Poly-(butylene succinate)/poly(ethylene oxide) (PBSU/PEO) blends, for instance, show this type of crystallization process.<sup>7</sup> The spherulites of PEO nucleate and grow inside PBSU spherulites.

Two constituents simultaneously develop spherulites in a melt of a blend, such as poly(ethylene succinate)/poly(ethylene oxide) (PES/PEO) and PBSU/poly(vinylidene chloride-co-vinyl chloride), where the  $T_m$  difference is about 30 K.<sup>1–6</sup> In these systems, a spherulite of one component continues to grow inside that of the other component after they contact each other. The penetrating spherulite eventually passes through the penetrated spherulite and grows in the melt again. The difference from the first case, where the  $T_m$  difference is about 50 K, is the sequence and the place of nucleation of the two constituents. The spherulites of one polymer grow inside those of the other component in both cases. The phenomenon is called interpenetrating spherulites.

Although the macroscopic morphology during the crystallization process has been reported, the crystallization dynamics during the formation of interpenetrating spherulites has not sufficiently been investigated. One of the important dynamic properties is the spherulitic growth rate, and another important point is investigating whether or not PEO spherulites show linear growth, as in a melt.

Many systems that exhibit interpenetrating spherulites contain biodegradable polyesters such as PBSU and PES. Blending one polymer with others often improves the mechanical properties of a brittle biodegradable polymer. Studies of the PBSU/PEO system have the possibility of leading to a new biomaterial since PEO has biocompatibility.

This paper reports the analysis of the spherulitic growth rate of PEO,  $G_{\text{PEO}}$ , in PBSU spherulites in the successive spherulitic growth process of two polymers, as described above. The dependence of  $G_{\text{PEO}}$  on the crystallization temperature,  $T_c$ , is examined based on the equation for the spherulitic growth rate in a polymer blend. The amorphous regions inside PBSU spherulites are discussed based on the results. We can expect better accuracy in measuring  $G_{\text{PEO}}$  in PBSU/PEO blends than in blends that show simultaneous crystallization of two components, such as PES/PEO. This is because the size of a penetrated spherulite of PES limits the growth distance of a penetrating spherulite of PEO in the latter case. On the other hand, the size of a PBSU spherulite does not limit it in the former case since a PEO spherulite grows through many PBSU spherulites.

## Experimental Section

PBSU ( $M_w = 140\,000$ ,  $T_m = 114\text{ °C}$ ) is a commercial polymer, Bionolle No. 1001, and was kindly supplied by Showa Highpolymer, Japan. PEO ( $M_w = 100\,000$ ,  $T_m = 67\text{ °C}$ ) was purchased from Sigma-Aldrich Company, USA. Solution-cast blends were prepared with a mutual solvent, chloroform. Blend compositions were PBSU/PEO = 1/9, 2/8, and 4/6 (wt/wt). The cast samples were first dried at room temperature for 2 days before removing the residual solvent in a vacuum at 50 °C for 2–3 days.

A differential scanning calorimeter (DSC6220, Seiko Instruments, Inc., Japan) was used to determine the equilibrium melting point  $T_m^0$  of PEO with the Hoffman–Weeks plot.<sup>10</sup> A blend sample of approximately 5 mg was sealed in an aluminum pan. It was first melted above the melting point of PBSU for at least 5 min on the DSC sample stage, quenched to the desired crystallization temper-

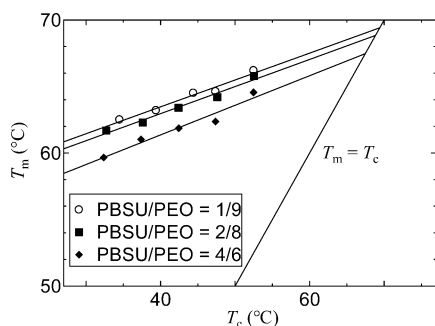
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**Figure 1.** The plot of the melting temperature  $T_m$  of PEO determined by DSC against the crystallization temperature  $T_c$  in PBSU/PEO blends (the Hoffman–Weeks plot).

**Table 1.** Equilibrium Melting Point,  $T_m^\circ$ , Degree of Crystallinity of PBSU,  $f_{\text{PBSU}}$ , Volume Fraction of PEO,  $v_2$ , and Glass Transition Temperature,  $T_g$ , in PBSU/PEO Blends

| PBSU/PEO | $T_m^\circ$ (°C) | $f_{\text{PBSU}}$ | $v_2^a$ | $T_g$ (°C) <sup>a,b</sup> |
|----------|------------------|-------------------|---------|---------------------------|
| 1/9      | 69.4             | 0.038             | 0.95    | −59.1                     |
| 2/8      | 67.8             | 0.080             | 0.90    | −58.2                     |
| 4/6      | 67.5             | 0.186             | 0.79    | −56.2                     |

<sup>a</sup> Values after the crystallization of PBSU and before the crystallization of PEO. <sup>b</sup> Calculated with the Fox equation.<sup>19</sup>

ature for isothermal crystallization, and then scanned at a rate of 10 K/min to obtain a melting peak temperature.

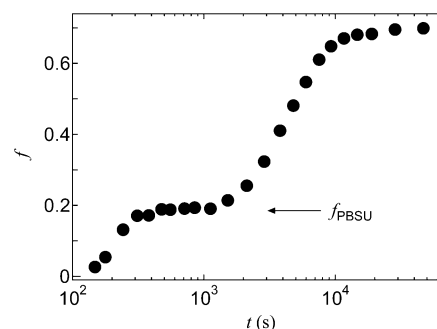
The degree of crystallinity of PBSU was determined by <sup>1</sup>H pulsed NMR (JNM-MU25, Jeol, Japan), whose resonant frequency was 25 MHz. The solid echo pulse sequence<sup>11</sup> was used to acquire spin–spin relaxation behavior. A blend in a sample tube was first melted above the melting point of PBSU before it was transferred into the NMR probe whose temperature was controlled at the desired crystallization temperature. A relaxation function was decomposed into a fast-decaying Gaussian component (crystals) and a slowly decaying exponential component (amorphous chains) after the crystallization of PBSU if the temperature was sufficiently above the glass transition temperature  $T_g$ . The fraction of the intensity of the Gaussian function shows the degree of crystallinity based on the number of protons. The details of this method are found elsewhere.<sup>12</sup>

The spherulitic morphology was observed with a polarizing optical microscope (BH-2, Olympus, Japan) equipped with a temperature controller (Linkam, LK-600PM). A blend film less than 10  $\mu\text{m}$  thick was placed between optical glass plates. It was first melted at about 120 °C and then quenched to the desired crystallization temperature,  $T_c$ . The crystallization process was recorded in a computer with a CCD camera (DP12, Olympus, Japan).

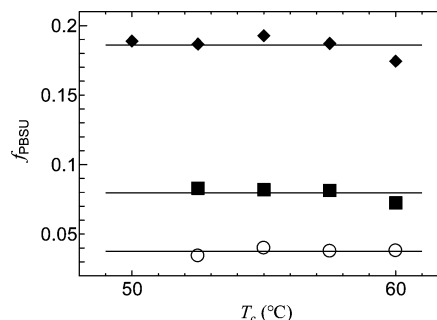
## Results and Discussion

**Melting Point and Crystallinity.** The Hoffman–Weeks plot for PEO is shown in Figure 1. The value of the equilibrium melting point  $T_m^\circ$  decreased with increasing the PEO content,  $\phi_{\text{PEO}}$ . This melting point depression indicates the miscibility in the blends. Table 1 shows the values of  $T_m^\circ$  along with other quantities described below.

Figure 2 shows the change in the fraction of the fast-decaying component of the spin–spin relaxation, namely, the degree of crystallinity, with the crystallization time for PBSU/PEO = 4/6 crystallized at 50 °C. It increased two times: the first increase represents the crystallization of PBSU and the second shows that of PEO. The value between the two increases indicates the degree of crystallinity of PBSU,  $f_{\text{PBSU}}$ . The values of  $f_{\text{PBSU}}$  were regarded as constant in the present temperature range since they showed little  $T_c$  dependence, as shown in Figure 3. The values of  $f_{\text{PBSU}}$  are displayed in Table 1.



**Figure 2.** The change in the fraction  $f$  of the fast-decaying component in the spin–spin relaxation with crystallization time  $t$  for PBSU/PEO = 4/6 crystallized at 50 °C. The arrow indicates the degree of crystallinity of PBSU,  $f_{\text{PBSU}}$ .

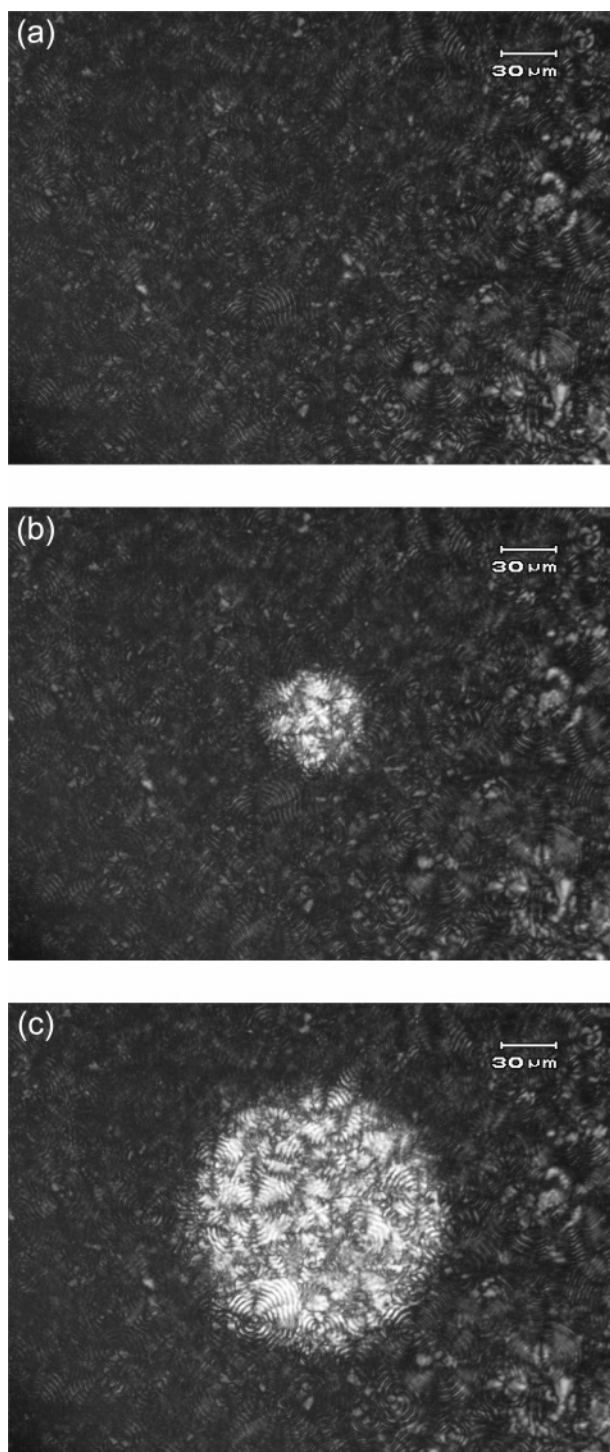


**Figure 3.** The dependence of the degree of crystallinity of PBSU,  $f_{\text{PBSU}}$ , on the crystallization temperature  $T_c$  in PBSU/PEO = 1/9 (○), 2/8 (■), and 4/6 (◆) blends.

**Morphology.** Figure 4 shows polarized optical micrographs of the crystallization process in a PBSU/PEO = 2/8 blend at  $T_c$  = 50 °C. When a molten sample was quenched to  $T_c$ , many small PBSU spherulites of the order of 10  $\mu\text{m}$  in diameter nucleated and filled the whole space (Figure 4a). PEO then nucleated inside the PBSU spherulites (Figure 4b). It continued to grow inside the PBSU spherulites, keeping its spherulitic shape (Figure 4c). The spherulitic growth of PEO continued until it contacted another PEO spherulite. They eventually filled the whole volume, too. Although the PBSU spherulites may be indistinct when they crystallized as in Figure 4a, they became clearer after the growth of the PEO spherulites (Figure 4b,c). The detailed process has been discussed elsewhere.<sup>7</sup>

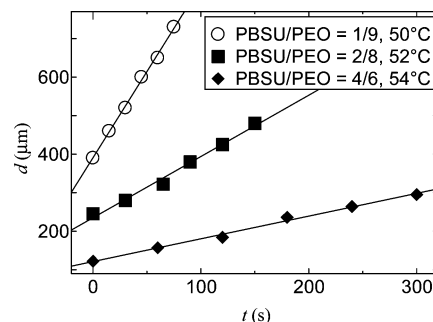
The growth of PEO in PBSU spherulites was proved in our previous works.<sup>3,4,8</sup> First, the increase in brightness, namely, birefringence, shows the crystallization of PEO inside the PBSU spherulites. Second, the change in birefringence inside the PBSU spherulites shows the growth of PEO lamellae alongside the PBSU lamellae instead of forming a layered structure where one spherulite is placed on the other. The polarized micrograph after the crystallization of PEO reflected the original morphology of the PBSU spherulites. This indicates that PEO lamellae grew alongside those of PBSU. If it were a layered structure, PEO lamellae would grow in a radial direction but Figure 4 indicated the existence of no such PEO lamellae. Finally, the characteristic size of the PBSU spherulites (50–100  $\mu\text{m}$ ) is significantly larger than the thickness of the sample (of the order of 1  $\mu\text{m}$ ).

The formation of interpenetrating spherulites has also been investigated by atomic force microscopy.<sup>13,14</sup> It showed continuous growth of penetrating lamellae into a penetrated spherulite alongside the lamellae of the penetrated component<sup>13</sup> and the crystallization of a penetrating component in the interfibrillar regions of a penetrated spherulite.<sup>14</sup>

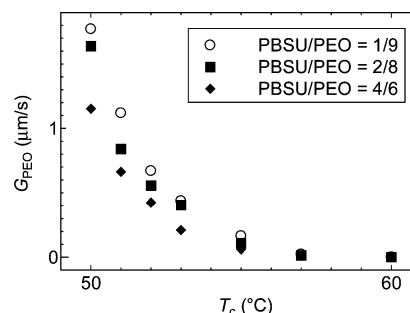


**Figure 4.** Polarizing optical micrographs of the growth process of a PEO spherulite (bright center in parts b and c) inside PBSU spherulites (surroundings) in a blend of PBSU/PEO = 8/2 at 50 °C.

There is a possibility that the lamellae of PEO, which intrinsically do not form banded spherulites, twist in PBSU spherulites. The crystallization of PEO enhanced the brightness more at the bright rings of PBSU than at the dark rings, as shown in Figure 4. If they were untwisted, PEO crystals at the dark rings would be as bright as those at the bright rings since neat PEO shows no extinction rings. This observation may be additional evidence for the formation of interpenetrating spherulites. However, the mechanism of the effect of the crystals of PBSU, the minor component, on the lamellar morphology of PEO should be investigated in more detail.



**Figure 5.** Plots of the diameter of PEO spherulites,  $d$ , against crystallization time,  $t$ .



**Figure 6.** Plots of the spherulitic growth rate of PEO  $G_{\text{PEO}}$  against crystallization temperature  $T_c$ .

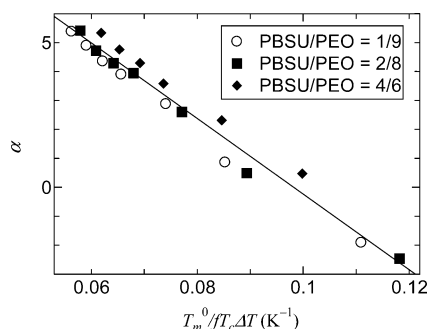
**Spherulitic Growth Rate.** The change in the diameter of a PEO spherulite with crystallization time is shown in Figure 5. Although the growth front of the PEO spherulite may not look sharp enough to measure the diameter with monochrome photographs in Figure 4, it was clear enough with a sensitive tint plate with retardation of 530 nm. The time origin was set at the moment when the diameters were first measured, instead of the time quenched to  $T_c$ . PEO spherulites showed linear growth with time inside PBSU spherulites under all experimental conditions. The half values of the slopes are the spherulitic growth rate of PEO,  $G_{\text{PEO}}$ , since Figure 5 shows the change in diameter of the spherulites. No effects of PBSU spherulitic centers, where PBSU lamellae diverge, on the growth rate of PEO could be confirmed.

Figure 6 shows the  $T_c$  dependence of  $G_{\text{PEO}}$ . The value of  $G_{\text{PEO}}$  decreased with increasing  $T_c$  and with decreasing  $\phi_{\text{PEO}}$  in the blends. This behavior is qualitatively identical to that in a crystalline/amorphous blend. The nucleation frequency of PEO and the recording rate of the instrument limited the experimental range of  $T_c$  to 50–60 °C in this work. Although the  $T_c$  dependence of the spherulitic growth rate is generally bell-shaped between  $T_g$  and  $T_m$ , no such data have been reported for PEO to the authors' knowledge because of a too-fast rate around the maximum. However, the analysis in the present  $T_c$  range was satisfactory, as shown below.

Now we discuss the  $T_c$  dependence of  $G_{\text{PEO}}$  inside PBSU spherulites. The discussion here is based on the spherulitic growth in a melt of a crystalline/amorphous blend. The spherulitic growth rate  $G$  in a polymer blend is expressed by<sup>15,22</sup>

$$G = G_0 v_2 \exp \left[ -\frac{U}{k_B(T_c - T_\infty)} - \frac{K_1 T_m^\circ}{f T_c \Delta T} + \frac{0.2 T_m^\circ \ln v_2}{\Delta T} \right] \quad (1)$$





**Figure 7.** The plot of  $\alpha$  against  $T_m^0/fT_c\Delta T$ . The symbols are identical to those in Figure 6.

where  $G_0$  is a constant,  $v_2$  is the volume fraction of a crystallizing component (PEO in the present analysis),  $U$  is the activation energy for molecular transport,  $k_B$  is the Boltzmann constant,  $T_\infty$  is the temperature below which chain transport is impossible,  $T_m^0$  is the equilibrium melting temperature in a blend,  $\Delta T$  is the degree of supercooling,  $K_1$  is a nucleation constant, and  $f = 2T_c/(T_c + T_m^0)$  is a correlation factor.<sup>16</sup> When  $\alpha$  is defined by

$$\alpha = \ln G - \ln v_2 + \frac{U}{k_B(T_c - T_\infty)} - \frac{0.2T_m^0 \ln v_2}{\Delta T} \quad (2)$$

a plot of  $\alpha$  against  $T_m^0/fT_c\Delta T$  is a straight line independent of  $v_2$  as follows:

$$\alpha = \ln G_0 - \frac{K_1 T_m^0}{f T_c \Delta T} \quad (3)$$

It should be noted that  $v_2$  differs from the original value in analyzing  $G_{\text{PEO}}$  since the crystallization of PBSU expels PEO out of PBSU crystals and increases  $v_2$  of PEO in the residual amorphous regions before the crystallization of PEO. The value of  $v_2$  can be determined by use of the degree of crystallinity obtained by pulsed NMR and the density of the two amorphous constituents, 1.18 g/cm<sup>3</sup> for PBSU<sup>17</sup> and 1.13 g/cm<sup>3</sup> for PEO.<sup>18</sup> Here,  $v_2$  was assumed to be constant throughout the sample since the spherulitic growth of PEO was linear with time and since the samples showed no interspherulitic amorphous regions. The values of  $v_2$  after the crystallization of PBSU are summarized in Table 1.

The change in the blend composition also affects  $T_g$  after the crystallization of PBSU. Since the Fox equation<sup>19</sup> describes the composition dependence of  $T_g$  of the PBSU/PEO blends quenched by liquid nitrogen,<sup>7</sup> where the degree of crystallinity was assumed to be zero,  $T_g$  was calculated with the Fox equation from the weight composition of the blends after the crystallization of PBSU. These results are also indicated in Table 1.

Figure 7 shows the plot of  $\alpha$  against  $T_m^0/fT_c\Delta T$ . Here, a universal value of 6.27 kJ/mol was employed as  $U$ ,<sup>20</sup> and  $T_\infty$  was set at 50 K below  $T_g$  of the blends.<sup>21</sup> It showed that a straight line fitted the data for three different blend compositions. Although one work on  $G$  in a polymer blend used both  $U$  and  $T_\infty$  as the fitting parameters,<sup>22</sup> no such adjustments were made in the present analysis. Note that the value of  $U$  is identical to that in a melt.

The result in Figure 7 and the value of  $U$  therein indicate that the change in  $G_{\text{PEO}}$  with the blend composition in Figure 6 can be ascribed to the change in  $v_2$  induced by the crystallization of PBSU. They also imply that PBSU lamellae do not suppress the molecular mobility of PEO in PBSU spherulites. Hence,

PEO probably crystallizes in wide amorphous regions where the molecular mobility differs little from that in a melt.

After the crystallization of PBSU, PEO can be excluded from PBSU crystals and included in interlamellar, interfibrillar, and interspherulitic regions of PBSU crystals.<sup>23</sup> Interspherulitic regions are precluded here since no such areas were observed by optical microscopy. The discussion about little suppression of molecular mobility described above indicates that the crystallization of PEO in wider interfibrillar regions is more probable than in narrower interlamellar regions. The thickness of a lamella and an amorphous layer is usually of the order of 10 nm, while that of a fibril and an interfibrillar region is of the order of 100 nm–1  $\mu$ m. Rheology and crystallization behavior are reported to be modified from those in the bulk in a film thinner than of the order of 100 nm.<sup>24,25</sup> A small-angle X-ray scattering study also reported the existence of interfibrillar regions in PBSU/PEO blends.<sup>26</sup> The present results therefore imply that PEO crystallizes mainly in the interfibrillar regions of PBSU spherulites.

## Conclusions

The spherulitic growth rate of PEO in PBSU spherulites was investigated. PEO showed linear spherulitic growth inside PBSU spherulites. The value of  $G_{\text{PEO}}$  decreased with  $T_c$  and increased with  $\phi_{\text{PEO}}$  as in the spherulitic growth in a melt of a polymer blend. The equation for the spherulitic growth in crystalline/amorphous blends describes the  $T_c$  dependence of  $G_{\text{PEO}}$  by considering the change in the blend composition in the residual amorphous regions after the crystallization of PBSU. The value of  $U$  was identical to that in a melt here. These results indicated that PEO crystallized in wide amorphous regions where molecular mobility differed little from that in a melt. The present analysis therefore indicated that the crystallization of PEO took place primarily in interfibrillar regions of PBSU spherulites.

**Acknowledgment.** This work was partly supported by the Scientific Frontier Research Project from the Ministry of Education, Science, Sports and Culture, Japan and a Grant-in-Aid for Scientific Research (C) from Japan Society for the Promotion of Science (Grant 90242015). The authors are grateful to Mr. Hideyuki Miyazawa, Mr. Takamune Matsushita, and Mr. Tamotsu Karino for their assistance. Z. Qiu thanks the National Natural Science Foundation, China (Grant No. 20504004) for financial support to contribute to this research.

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MA070973K