

# Replicated Banded Spherulite: Microscopic Lamellar-assembly of Poly(L-lactic acid) Crystals in the Poly(oxymethylene) Crystal Framework

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 Electronic Supplementary Information

**Abstract** The morphologies of poly(L-lactic acid) (PLLA) spherulites, when crystallized within the pre-existed poly(oxymethylene) (POM) crystal frameworks, have been investigated. PLLA/POM blend is a melt-miscible crystalline/crystalline blend system. Owing to the lower melting point but much faster crystallization rate than PLLA, POM crystallized first upon cooling from the melt state and then melted first during the subsequent heating process in this blend system. Lamellar assembly of PLLA crystals within the pre-existed POM spherulitic frameworks was directly observed with the polarized light microscopy by selectively melting the POM frameworks. The investigation indicated that PLLA crystals fully replicated the spherulitic morphology and optical birefringence of the POM crystal frameworks, which was independent of  $T_c$ . On the other hand, POM could also duplicate the pre-existed PLLA morphologies. The result obtained provides us a possibility to design the lamellar assembly and crystal structures of polymer crystals in miscible crystalline/crystalline polymer blends.

**Keywords** Banded spherulite; Lamellar assembly; Confinement; Poly(L-lactic acid); Poly(oxymethylene)

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## INTRODUCTION

Banded spherulites periodically exhibiting concentric-rings or extinction-bands are widely observed in many semicrystalline homopolymers and polymer blends (even in double-layered films)<sup>[1–7]</sup>. Miscible blends of two crystalline polymers are themselves interesting and there are a good deal of recent works<sup>[4, 8–35]</sup>. Basically, the components in binary crystalline/crystalline blends simultaneously or separately crystallize depending on the difference between the melting points ( $\Delta T_m$ ) of the two components. The two components with small  $\Delta T_m$  usually exhibit simultaneous crystal growth<sup>[9–17]</sup>, whereas stepwise crystallization is commonly observed for blends with large  $\Delta T_m$ <sup>[18–23]</sup>. Stepwise crystallization, moreover, can also be observed in these blends where the two components have similar melting points but quite different crystallization kinetics<sup>[24–28]</sup>. The second-crystallized polymers are located in the interspherulitic, interfibrillar or interlamellar regimes of the first-crystallized polymers and subsequent crystallization is observed in the remaining melts, inside or even at the boundary of the pre-existing spherulitic frameworks<sup>[18–30]</sup>. It is mainly controlled by the diffusion length  $\delta = D/V$ , where  $D$  is the diffusion ability of second-crystallized polymers and  $V$  is the

velocity of the crystallization front<sup>[8, 36]</sup>. The typical crystallization kinetics and morphology of miscible blends of two crystalline polymers have been commendably reviewed by Jungnickel<sup>[24]</sup>, and Schultz<sup>[4]</sup>.

The interplay between two crystalline polymers in their miscible blends is quite complicated, especially for the influence of pre-existence of the first-crystallized spherulitic crystal frameworks on crystallization of the second-crystallized polymers. Confined and fractional crystallization of poly(ethylene oxide) (PEO) is reported in its miscible blends with poly(butylene succinate) (PBS)<sup>[32–34]</sup>, as well as poly(ethylene sebacate)<sup>[25]</sup>. Similar confined crystallization behaviour is also observed in poly(vinylidene fluoride) (PVDF)/PBS blends, when PBS is subjected to crystallization within the pre-formed PVDF frameworks<sup>[22, 23]</sup>. Pan *et al.* argued that nano-scaled interlamellar confinement of PEO resulted in the confined and fractional crystallization<sup>[32–34]</sup>. Yan *et al.* suggested that the interconnectedness of the molten pockets in the pre-existed crystal frameworks is a significant factor in determining the crystal growth kinetics of the second-crystallized polymers<sup>[23]</sup>. Moreover, Qiu *et al.* reported that nucleation of poly(butylene succinate-co-butylene adipate) is enhanced but crystal growth is restrained within PVDF spherulites<sup>[20]</sup>. Ikehara *et al.* reported that the spherulitic growth rate of PEO within the pre-formed matrix of melt-miscible PBS/PEO blends was greatly dependent on the  $T_c$  of PBS, and the lamellar growth of PEO was templated by the twisted PBS lamellae<sup>[18]</sup>. Solvent etching is a useful

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method for investigation on the lamellar assembly of polymer crystals in binary blends<sup>[37]</sup>. However, microscopic lamellar assembly of PEO crystals within the pre-existed PBS crystal frameworks has not been revealed, because no selective solvent for PBS was found.

Poly(L-lactic acid) (PLLA)/poly(oxymethylene) (POM) blends are crystalline/crystalline polymer systems, exhibiting typically lower critical solution temperature phase behaviors (Fig. S1, in electronic supplementary information, ESI)<sup>[38]</sup>. Over a wide composition range, POM crystallized first into banded spherulites with the incorporation of PLLA and subsequent crystallization of PLLA inside POM spherulitic frameworks resulted in formation of interpenetrated spherulites (IPS), owing to distinct difference in crystallization kinetics<sup>[28]</sup>. During the formation of IPS, the crystallization of PLLA was confined within the pre-existed POM crystal frameworks. As a significant characteristic, IPSs are commonly observed in miscible blends of two crystalline polymers, but the microscopic lamellar assembly of polymer crystals confined within the pre-existed crystal frameworks has not been clearly revealed so far. POM has a much faster crystallization rate than PLLA from the melt, but a lower melting point than PLLA, so POM crystallized first serving as the template for PLLA crystallization and then melted first leaving only templated PLLA crystals during heating process. In this work, we have made an investigation on the microscopic lamellar assembly of PLLA within the pre-existed POM crystal frameworks. Replicated banded spherulites are directly observed in polarized light microscopy by simply melting the POM frameworks. It was found that PLLA replicated the banded-spherulitic morphology and optical birefringence of the POM frameworks, which is independent of  $T_c$  of PLLA but only dependent upon the variation of the POM frameworks. This work provides new insights into microscopic lamellar assembly of banded spherulites under spatial confinement.

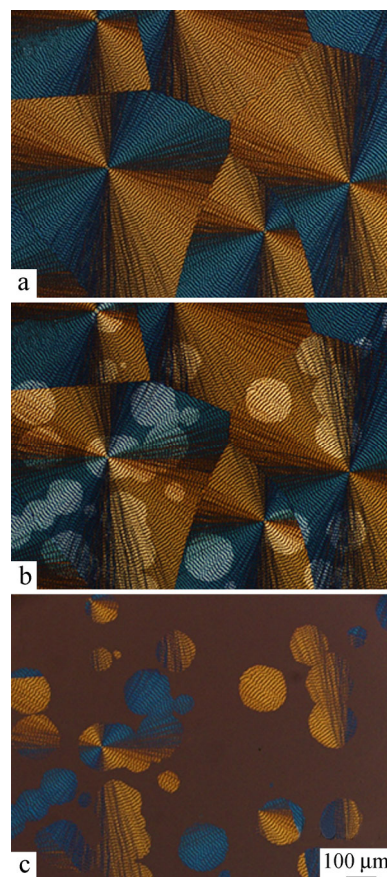
## EXPERIMENTAL

PLLA (3001D,  $M_n = 8.93 \times 10^4$  g/mol,  $M_w/M_n = 1.77$ ) was purchased from Nature Works Co., LLC (USA), including 1.6% D-lactide content. POM (MC 90,  $M_w = 1.743 \times 10^5$  g/mol,  $M_w/M_n = 2.19$ ) was provided by Shenhua Co., Ltd. (China). All the materials were dried in a vacuum oven at 80 °C for at least 12 h in advance. PLLA/POM blends were prepared by melt-blending at 190 °C using a batch mixer (Haake PolyLab QC) with a twin screw (at an initial rotation speed of 20 r/min for 1 min and subsequently raised to 50 r/min for 5 min). The samples for polarized light microscopic observation were prepared by spin-coating using hexafluoroisopropanol as a mutual solvent. The solution (10 wt%) was spin-coated onto unfiled glasses. Crystal morphology of PLLA/POM blends was imaged by a polarizing light microscope (Olympus BX51) equipped with a digital camera and a hot stage (Linkam LTS 350).

## RESULTS AND DISCUSSION

Melt-miscible PLLA/POM blends with more than 20 wt% POM exhibited stepwise crystallization behavior<sup>[28]</sup>. Figure 1 shows the morphology of a 70/30 PLLA/POM blend at

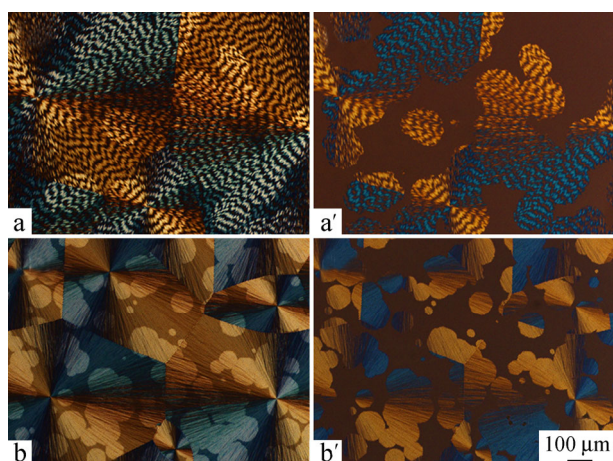
different crystallization and melting stages. It is clear from Fig. 1(a) that POM crystallized first into regular banded spherulites at 145 °C and occupied the whole melt volume before PLLA could nucleate. The formation of banded spherulites has commonly been ascribed to the cooperative lamellar twisting along the growth direction<sup>[39–43]</sup>, and lamellar twisting of POM in PLLA/POM blends was observed<sup>[26, 27]</sup>. It is very interesting that POM with trigonal unit cell formed banded spherulites in the presence of PLLA, as lamellar twisting was usually found in chiral polymers or polymers with asymmetric unit cell/lamellar structures. Crist *et al.* suggested that polymers with high symmetric unit cell, *e.g.* POM, may also form spherulites but with very large band spacing that is difficult to detect<sup>[3]</sup>. A decreased band spacing of POM spherulites was considered as a response to enhanced asymmetric surface stresses from PLLA molecules absorbed on lamellar surfaces<sup>[44]</sup>. The symmetric surface stresses should be originated from the different folding conformations between the opposite lamellar surfaces, as proposed by Lotz and Cheng<sup>[45]</sup>. Upon lowering  $T_c$  to 130 °C, PLLA started to crystallize within the pre-existed POM frameworks with formation of IPS. The formation of IPS was revealed by the



**Fig. 1** Polarized light microscopic images of PLLA crystallization within the POM spherulitic frameworks: (a) the POM crystal frameworks obtained by subjecting to crystallization at 145 °C for 25 min; (b) the PLLA crystallization performed at 130 °C for 50 min; (c) the sample heated to 165 °C before the PLLA crystallization was completed (A 70/30 PLLA/POM blend sample was used). All the images share the same scale.)

enhanced birefringence of areas where PLLA crystals appeared, as shown in Fig. 1(b). It can also be confirmed by a subsequent heating of the sample to a temperature between melting points of the two polymers. In this case, the POM crystals has a  $T_m$  of 163 °C and the PLLA crystals has a much higher  $T_m$  of 172 °C under slow heating conditions. At  $T = 165$  °C, the POM crystals were melted and the PLLA crystals still remained, as shown in Fig. 1(c). Note that the PLLA crystallization process was controlled to be not completed before heating, so that we can well distinguish the pre-existed POM crystals from the subsequent PLLA crystals (similar hereafter, if no particular statements). It was clearly from Fig. 1(c) that PLLA crystals replicated banded-spherulitic morphology and optical birefringence of the POM frameworks. In fact, no banded spherulites were observed in neat PLLA under the same crystallization conditions (Fig. S2, in ESI). In other words, the pre-existed POM crystals acted as a template on lamellar assembly of PLLA crystals. It is an unusual case that the “host” spherulitic frameworks (the first crystallized POM crystals) of IPS melted first leaving only the “guest” PLLA crystals during the heating process. It, therefore, provides a microscopic view of lamellar assembly of polymer crystals under the pre-existed solid crystal frameworks.

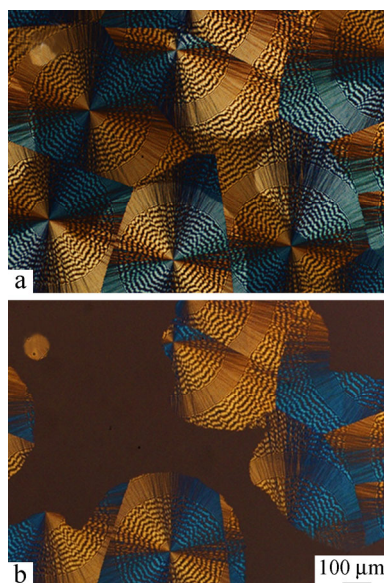
The band spacing of the host POM spherulites increased with the increase of  $T_c$ , because of the depressed degree of supercooling. Generally, the lower degree of supercooling, the larger thickness of the lamellae, and the increased thickness of lamellae would make it much more difficult to twist<sup>[46]</sup>. The band spacings of POM spherulites are 20 and 5  $\mu\text{m}$ , respectively, when isothermally crystallized at 150 and 140 °C. We investigated the PLLA morphologies under the different banded spherulites at the same  $T_c$ . Figure 2 shows the PLLA crystal morphologies crystallized at the same  $T_c$  (130 °C) under the different POM banded-spherulitic frameworks. The POM crystal frameworks were formed at



**Fig. 2** Polarized light microscopic images of PLLA crystallized at 130 °C within two POM spherulitic frameworks with different band spacing when the POM crystal frameworks were obtained at (a) 150 °C and (b) 140 °C, respectively, and (a', b') the samples heated to 165 °C before the PLLA crystallization was completed (A 70/30 PLLA/POM blend sample was used. All the images share the same scale.)

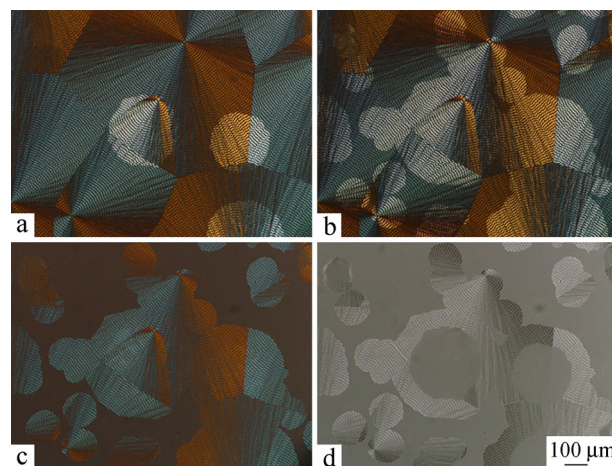
150 and 140 °C, respectively, with prolonged crystallization time (POM was fully crystallized). It is clear that the PLLA spherulites fully duplicated the morphologies of POM crystal frameworks and different PLLA band structures were achieved at the same  $T_c$ . On the other hand, it is found that the templated PLLA crystals exhibited an elliptical outline within the high-temperature-obtained POM frameworks (Figs. 2a and 2a'), whereas those exhibited nearly-circular shapes within the low-temperature-obtained POM frameworks (Figs. 2b and 2b'). For the crystallization of PLLA, it might be regarded as the case of confined crystallization within multiple nanostructured layers, the twisted layers, due to the interlamellar/interfibrillar inclusion of PLLA chains within the POM spherulites<sup>[26, 27]</sup>. In this case, lamellar aggregates mostly orientated along the layer plane<sup>[47]</sup>. In other words, most of PLLA lamellae were in a growth along the same direction of POM crystals. It can be convinced by the enhanced birefringence of POM frameworks where the PLLA crystals appeared. In fact, it is a widely accepted viewpoint<sup>[4, 17, 23]</sup>. But for the development of a spherulite, it is a three-dimensional assembly process of lamellae/crystal fibrils, as convinced by the ellipsoidal/nearly-circular growth of PLLA crystals. It means that some lamellae should cross the adjacent nanostructured twisting layers. The ellipsoidal growth of PLLA crystals illustrated that the interconnectivity of the adjacent interlamellar/interfibrillar regions of POM decreased at a high  $T_c$ . Compared to the high-temperature-obtained POM frameworks, those obtained at a low temperature possessed a relatively high interconnectivity of the adjacent interlamellar/interfibrillar regions. It is very clear from the nearly-circular growth of PLLA crystals. To further illustrate the lamellar assembly duplication phenomena of PLLA within the POM banded-spherulitic frameworks, an alternatively patterned POM banded spherulitic framework was carefully designed. The POM crystal frameworks were prepared by subjecting to crystallization at 147 and 137 °C alternatively, so that the patterned POM banded framework was achieved with the periodic band spacings. PLLA was then isothermally crystallized at 130 °C under the patterned POM banded framework. Figure 3 shows the polarized light microscopic images of PLLA crystallized at 130 °C within the alternatively patterned POM spherulitic frameworks and the morphologies of PLLA after the melting of POM crystals at 165 °C. By removal of the POM frameworks, as shown in Fig. 3(b), alternatively patterned banded PLLA spherulites were achieved, indicating again the excellent templating effect of POM frameworks on lamellar assembly of PLLA.

It is further found that the microscopic lamellar assembly of PLLA was only determined by the pre-existed POM crystal frameworks, independent of the  $T_c$  of PLLA. The 145 °C-crystallized POM crystal frameworks were prepared and used as the template, and PLLA was subjected to crystallization at various  $T_c$ , as shown in Fig. S3 (in ESI). It was very clear that a different time period was required for complete crystallization at each  $T_c$ , but the spherulitic morphology of PLLA was just a simple replication of that of the host POM spherulites. To make a more visual illustration, PLLA was subjected to crystallization at  $T_c = 140$  and 130 °C



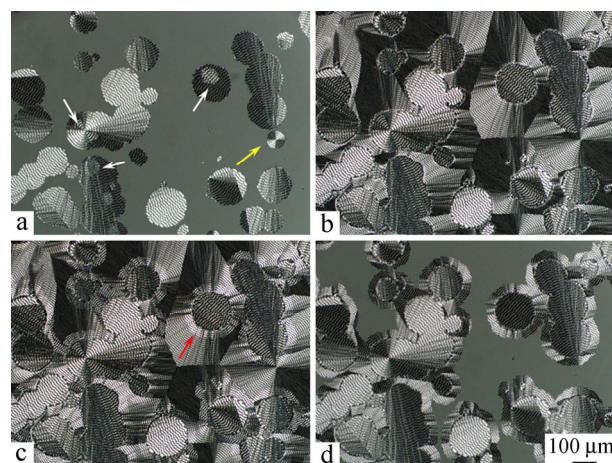
**Fig. 3** Polarized light microscopic images of PLLA crystallized at 130 °C within the alternatively patterned POM spherulitic frameworks prepared by subjecting to crystallization at (a) 147 °C and (b) 137 °C alternatively (A 70/30 PLLA/POM blend sample was used, and the sample was heated to 165 °C before the PLLA crystallization was completed. All the images share the same scale.)

in sequence within the same POM frameworks, as shown in Fig. 4. It is clearly seen from Fig. 4(b) that PLLA crystals either randomly developed within the POM crystal frameworks, or continuously propagated from the original growth fronts formed at  $T_c = 140$  °C, when  $T_c$  was decreased to 130 °C. No detectable spherulitic morphology differences were observed for the areas of PLLA crystals that crystallized at 140 and 130 °C, as shown in Fig. 4(c). However, the subsequent melting behaviours are different for the PLLA crystals crystallized at 140 and 130 °C, as shown in Fig. 4(d). It is interesting that the PLLA crystals obtained at  $T_c = 140$  °C had an unexpectedly lower melting point than those crystallized at 130 °C, during the very slow heating process of *in situ* observation. A similar thermal process was also performed by differential scanning calorimetry, as shown in Fig. S4 (in ESI). During the slow heating process, one can clearly see from Fig. S4(a) (in ESI) that the 130 °C-crystallized PLLA crystals show double melting points while the 140 °C-crystallized PLLA crystals show single melting point. Double melting points should be originated from melting-recrystallization of the 130 °C-crystallized PLLA crystals under very slow heating conditions (1 K/min). The only one melting point of the 140 °C-crystallized PLLA is a bit lower than the higher melting point of PLLA crystallized at 130 °C. It is consistent with the optical observations, as shown in Fig. 4(d). Similar melting phenomena have been observed in neat PLLA, as shown in Fig. S4(b) (in ESI). We can therefore conclude that the PLLA fully duplicated the spherulitic morphologies of POM, independent of  $T_c$ . However, the lamellar thickness of the PLLA was dependent on  $T_c$ . The lower  $T_c$  induced the thinner crystal lamellae with lower  $T_m$ .



**Fig. 4** Polarized light microscopic images of PLLA within the POM spherulitic frameworks: PLLA first subjected to crystallize at (a) 140 °C for 2 h, and (b) 130 °C for 45 min, and (c) first heated to 165 °C and (d) then 170 °C (The POM crystal frameworks were obtained at 145 °C. A 70/30 PLLA/POM blend sample was used and the PLLA crystallization was still uncompleted when heated. All the images share the same scale.)

The fact that PLLA fully duplicates the spherulitic morphologies of POM framework provides a facile route to “design” the lamellar assembly and crystal structures of PLLA in the blends. Figure 5 illustrates the construction of a “combined” banded spherulite of PLLA. The 70/30 PLLA/POM blend sample illustrated in Fig. 1 was used for further investigations. In this case, the 70/30 sample was rapidly cooled to 145 °C again, after isothermally heated at 170 °C for 5 min. At  $T = 170$  °C, the pre-existed POM crystals were fully melted while the PLLA crystals still remained (as confirmed by Fig. S5, in ESI). A reverse templating effect of PLLA frameworks on POM crystals was clearly observed in



**Fig. 5** Design of combined PLLA spherulites with “core-shell” crystal structures and optical birefringence

The 70/30 PLLA/POM blend sample illustrated in Fig. 1 was used for further investigations. After isothermally heated at 170 °C for 5 min, the sample was cooled to 145 °C for (a) 1 min, (b) 15 min, (c) 45 min. Then, (d) the sample was heated to 165 °C, revealing the novel combined structures and optical birefringence of PLLA spherulites. All the images share the same scale.

Fig. S5 (in ESI). Figure 5(a) shows that POM started to crystallize either within the templated PLLA banded spherulites (white arrows) or in the residual melt (yellow arrow). At  $T_c = 145\text{ }^\circ\text{C}$ , the crystallization rate of POM is much faster than that of PLLA. Therefore, the “new” POM banded spherulites occupied the whole melt space after isothermal at  $145\text{ }^\circ\text{C}$  for 15 min, while the PLLA spherulites survived from the last heating with hardly any change (no growth due to the very slow crystal growth rate at  $145\text{ }^\circ\text{C}$ ), as shown in Fig. 5(b). The prolonged isothermal time at  $145\text{ }^\circ\text{C}$  induced the gradual growth of PLLA spherulites. As shown in Fig. 5(c), PLLA spherulites continued their growth within the “new” POM banded-spherulitic frameworks (red arrow) after being kept isothermally for another 30 min. The subsequently crystallized PLLA crystals duplicated the morphology of the narrow POM banded spherulites. Therefore, novel jointed PLLA banded crystals were achieved. This was clearly observed and confirmed by the melting of the POM crystals (Fig. 5d). PLLA forms “combined” banded spherulites of PLLA with novel “core-shell” structure and optical birefringence.

## CONCLUSIONS

Replicated banded spherulites—microscopic lamellar assembly of polymer crystals within pre-existed banded spherulites—have been demonstrated in melt-miscible crystalline/crystalline PLLA/POM blends. POM crystallized first serving as the template for PLLA crystallization, and then melted first leaving on the templated PLLA crystals during the heating process. The unique properties of PLLA/POM blends make them an ideal model for investigation on lamellar assembly of semicrystalline polymer crystals confined within the pre-existed solid crystal frameworks. The microscopic lamellar assembly of PLLA was templated (confined) within the POM banded spherulites and replicated the spherulitic morphology and optical birefringence of the POM spherulites, which was independent of  $T_c$ . The confinement of lamellar assembly and easily programmable and removable properties of POM crystals frameworks make it possible for us to design the crystal structures of PLLA. This work provides a new insight into microscopic lamellar assembly of banded spherulites under spatial confinement.

## Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at: <https://doi.org/10.1007/s10118-018-2085-z>.

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