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Morphology and Compatibility in Blends of Poly(vinyl methyl ether) and Poly(ε-caprolactone-block-butadiene) Copolymer

HUANG YIPING, LIU XIAORONG, CAO YANG, HU YUAN and CHEN GUANGMEI*
Department of Chemical Engineering, Anhui University, Hefei-230 039, China
E-mail: chen_gm168@yahoo.com.cn

The morphology and compatibility of the poly(vinyl methyl ether) (PVME) with poly(ε-carpolactone-block-butadiene) copolymer (PCL-b-PB) have been studied by polarized light microscope (PLM), differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR). In the PVME/PCL-b-PB blends, ring-banded spherulites have been observed at various compositions and crystallization temperatures from 33 to 42ºC. The FTIR studies revealed that some weak interaction existed between PVME and the PCL-b-PB. The thermal analysis displayed the blends presented a single glass transition temperature (T_g) at each composition. The fraction of PCL that crystallized in the blends increased with increasing the PVME content up to about 40 wt% of PVME. The crystallization ability of PCL block in the blends was affected by PVME content. The dSC results indicated that PVME was partially compatible with the PCL-b-PB. The existence of some weak interaction and partial compatibility in the PVME/PCL-b-PB blends had influence on the formation of PCL ring-banded spherulites. Moreover, the existence of PB block affected the crystallization behaviour of PCL.

Key Words: Poly(vinyl methyl ether), Poly(ε-caprolactone-block-butadiene) copolymer, Compatibility, Ring-banded spherulite.

INTRODUCTION

Polymer blends and block copolymers, comprising as one constituent poly(ε-caprolactone) (PCL), have been studied extensively due to their remarkable crystallization morphology[1-4]. It turned out that the crystallization temperature at which the PCL spherulites demonstrated the ringed extinction patterns became much lower in some blends, such as the blends of PCL with poly(vinyl chloride) (PVC) or nitrocellulose (NC)[5,6]. In these blends, the ringed extinction patterns became clearer and more regular. In the mixtures of PCL with PVC, PCL had been proved to be miscible with PVC in the whole composition range in the amorphous state. The hydrogen bond interaction existed between the carbonyl group in PCL and the α-hydrogen in PVC[5]. Another system[6] of PCL/NC was also miscible and exhibited a strong hydrogen bond interaction between the PCL carbonyl group and NC hydroxyl group and a dipole-dipole interaction between the carbonyl group of PCL and the nitrate-ester groups of NC.

Extensive discussions about ring-banded spherulite formation can be found in the literature, but the exact mechanism for the appearance of these bands is still not known. Keith and Padden[7] proposed that the ring-banded structure was formed by axial twisting of lamellae under the influence of surface stress and cooperative arrangement of twisted crystallities. They also advanced that thermodynamically compatibility and the existence of specific interaction between the two components were due to the formation of the ring-banded spherulites between host and diluent polymers. The formation of the ring-banded spherulites in two blends of PCL/PVC and PCL/NC sustained their deduction. On the other hand, Nojima and co-workers[8] could not find the growth of the ringed spherulites in the blend of PCL and polybutadiene (PB), because PCL and PB did not show the compatibility.

However, the beautiful ringed extinction patterns had been observed in the blends of PCL with PCL-b-PB, in which PCL was partially compatible with the PCL-b-PB, but there was not any specific molecular interaction between components in the blends[8]. Similarly, in the blends of PCL with TCL and BCL, it had been proved that PCL was partially compatible with TCL and BCL and the clear ringed extinction patterns in PCL/TCL and PCL/BCL blends had been observed[9,10]. It was also obviously there was no specific molecular interaction between the specific groups in these blends. The above-mentioned examples imply that it is difficult to say that specific molecular interaction and miscibility are important for the formation of ring-banded spherulites.

Furthermore, there is evidence from above-mentioned examples that the block copolymer plays an important role in the area of compatibilization of the polymer blends. Hence, it is challenging to study the phase behaviour and crystallization of blends containing the PCL as block. In the blends of PVME with a diblock copolymer poly(ε-caprolactone-trimethyl carbonate) (PCL-b-PTMC), PVME was miscible with the PCL block, but a microphase-separated morphology in the molten state was found, PVME residing inside PCL domains[11]. It is well established that the homopolymer blends of PVME and polystyrene (PS) or PCL were miscible[12], but for the blends of PVME and poly(styrene-block-ε-caprolactone) block copolymer (PS-b-PCL), PVME was only dissolved in the PCL block[13]. The clear ringed extinction patterns can be observed in the PVME/PCL-b-PTMC blends, but not in the blends of PVME with PS-b-PCL. In order to discuss further the effect of the block copolymer containing the PCL on the morphology and compatibility in the blends, we focus on the blends of PVME with semicrystalline copolymer PCL-b-PB. Samples are studied by optical microscopy (PLM), differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR). The results suggest that the PB block and PVME affect the morphology and compatibility of the blends.

EXPERIMENTAL

Polymers: PVME used in this study was commercial product provided by Polysciences INC, supplied as a 50 wt% water solution. The water was completely removed, by air drying at room temperature for 3 d and then by vacuum dyring at 60ºC for at least 72 h. The intrinsic viscosity of PVME in butanone gave M_v = 32500 g.mol^{-1}. The glass transition temperature of PVME is -25ºC. The number-average molecular weight (M_n) of PCL evaluated by vapour pressure osmometry was 10000 g mol^{-1}. The PCL-b-PB block copolymer used in this study was synthesized by anionic polymerization under in our laboratory and then was subjected to further purification procedures. The ^{1}H NMR confirmed that the expected PCL-b-PB block polymer was formed and that the PB content was about 6.9 wt%.

Blend preparation: PVME and the PCL-b-PB block copolymer were mixed and dissolved in tetrahydrofuran, yielding about 3 wt% solution. In this way, blends of different compositions were prepared. The blend compositions are listed in Table-1. The solvent was cast on the glass plate and evaporated at room temperature during several days and then under vacuum drying at 60ºC for several days.

TABLE-1
DSC RESULTS FOR PVME/PCL-b-PB BLENDS
AT DIFFERENT COMPOSITIONS

Samples	Content of PVME (wt %)	T_g (ºC)	T_m (ºC)	ΔH_f (J/g)	Cr (%)	T_m^0 (ºC)
PCL100	0	-65	56	69.3	50.9	62.6
PCL95	5	-57	55	67.7	52.3	61.2
PCL80	20	-58	55	52.7	48.4	63.4
PCL60	40	-54	54	50.8	62.2	61.6
PCL40	60	-50	55	26.0	47.8	61.0
PCL20	80	-35	53	3.3	12.1	–
PVME	100	-25	–	–	–	–

Optical microscopy: The crystallization of the PCL block in the blends was investigated by a polarized light microscope with a hot stage. The blends were heated for 5 min at 100ºC and isothermally crystallized at the crystallization temperature T_c = 33, 36, 39 and 42ºC, respectively. Photographs of the samples were taken. The resulting morphologies were studied as a function of blend composition.

DSC measurements: Melting and crystallization behaviour as well as glass transition temperature of the PCL-b-PB block copolymer and the PVME/PCL-b-PB blends were studied by DSC using a Perkin-Elmer Pyris-1 apparatus.

Ordinary scanning: The PCL-b-PB block copolymer and the PVME/PCL-b-PB blends were heated from 20 to 80ºC for the first scan at 20ºC/min and maintained at 80ºC for 5 min. Then the blends were cooled down to -100ºC at a rate of 160ºC/min and kept at this temperature for 1 min. Subsequently, the samples were heated again from -100 to 80ºC for the second scan. A heating rate of 20ºC/min was used. The midpoint of the slope change of the heated capacity was taken as glass transition temperature (T_g). The melting point (T_m) of each sample was located in the maximum of their respective endothermal peaks.

Isothermal crystallization experiments: Samples were heated from 20 to 80ºC at 20ºC/min and maintained for 5 min at 80ºC, followed by rapid cooling at a rate of 160ºC/min to the respective crystallization temperatures: 30, 33, 36, 39 and 42ºC. Afterwards, the corresponding melting temperature were determined by heating the blends with a rate of 20ºC/min to 80ºC.

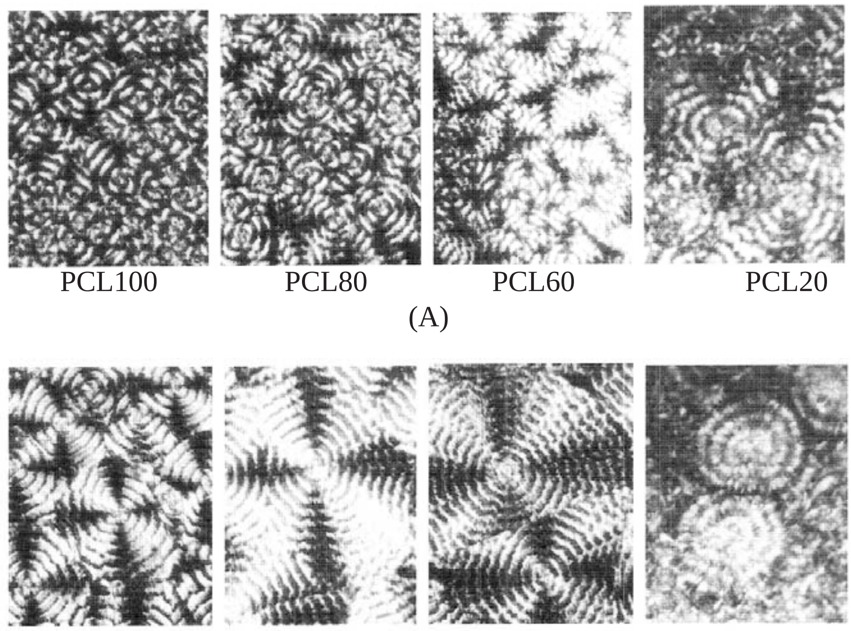
Fourier transform infrared measurements: FTIR spectra were obtained using a NEXUS 870 FT-IR instrument. Thin films of all samples were cast on KBr windows from 0.5% (w/v) tetrahydrofuran solution. After most of the solvent was evaporated at room temperature, the films were transferred to a vaccum oven and kept at 60ºC for 1 week to remove residual solvent. All spectra were recorded at room temperature and at a resolution of 2 cm^{-1} after 32 scans, singal averaged. The films used in this study were sufficiently thin to obey the Beer-Lambert law.

RESULTS AND DISCUSSION

Morphology of the PVME/PCL-b-PB blends

Some selected examples of the spherulite morphologies of the PVME/PCL-b-PB blends with different PVME content and at different temperatures, obtained using the polarizing microscope, are shown in Fig. 1. The PCL-b-PB block copolymer can form the ringed spherulites at 33ºC and clear and regular rings at 39ºC. It was reported[14] that the pure PCL never has an extinction ring at below 40ºC and has a crude banding with large radial separations in the range of 50-100 μm at above T_c = 45ºC. Such result indicates that the PB block has an important influence on the formation of the ringed spherulites of the PCL block, even though the content of PB in the copolymer is very low-only 6.9 wt%.

Fig. 1 also shows the polarizing micrographs of the PCL block in the PVME/PCL-b-PB blends at 33 and 39ºC. It can be seen that all the pictures shows distinct ring-banded spherulites. The PCL block in the PVME/PCL-b-PB blends can grow ringed spherulites with regular Maltese cross when the PVME content is from 5 to 40%.



PCL100 PCL80 PCL60 PCL20

(A)

PCL100 PCL80 PCL60 PCL20

(B)

Fig. 1. Spherulite morphology of PVME/PCL-b-PB blends, crystallized from the melt at (A) 33ºC and (B) 39ºC, obtained by optical microscopy with crossed polar

These phenomena indicate that the addition of PVME can decrease the crystallization temperatures at which the PCL grow ringed spherulites and improve the formation of ringed spherulites of the PCL block. However, it should be noted that the PCL block ringed spherulites are less regular when the PVME/PCL-b-PB blends, it is known that the PCL crystallization ability decreases dramatically when PVME content is over 40 %. Such a phenomenon can be understood that the presence of a large amount of the amorphous may lead to decreasing the PCL crystallization ability to grow regular ring-banded spherulites.

Interaction between PVME and PCL-b-PB

Fig. 2 shows the FTIR spectra of the PVME/PCL-b-PB blends in the hydroxyl groups stretching region from 3200 to 4000 cm^{-1} and in the carbonyl groups stretching region from 1600 to 1900 cm^{-1} at room temperature. As shown in Fig. 2a we can find that the absorption bands of hydroxyl groups in the blends are composed of two vibrations regions:

3750-3500 and 3500-3200 cm^{-1}, related to free and hydrogen-bonded, respectively. With an increasing of the PVME content in the blends, the maximum absorption peak position of hydrogen-bonded groups shifts obviously to lower frequencies and it shifts to 3310 cm^{-1} when the PVME content is *ca.* 40 %. These observations indicated that in all systems, there is hydrogen bond interaction in the blends. Because the content of hydroxyl as the end groups of PCL is very low, the hydrogen bond interaction is weak.

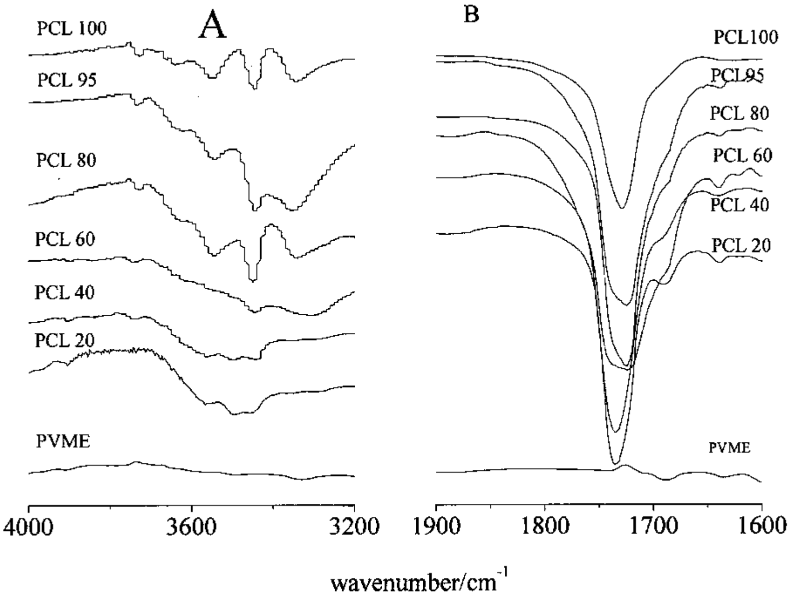


Fig. 2. FTIR spectra of the PVME/PCL-b-PB blends. (A) is the hydroxyl region (B) the carbonyl region

In Fig. 2(b), it can be seen that the maximum carbonyl absorbance peak for the PCL-b-PB block copolymer is at 1730 cm^{-1}. When PVME content increases, the maximum carbonyl absorbance peak for the PVME/PCL-b-PB blends shifts to lower frequency slightly and shifted to 1723 cm^{-1} with increasing PVME content up to *ca.* 40 %. However, the maximum carbonyl absorbance peak shifts to higher frequency and finally shifts up to 1736 cm^{-1} with increasing PVME content when PVME content. Coleman *et al.*[15] suggested that the bands at 1724 and 1734 cm^{-1} for pure PCL represent the crystalline and amorphous phase, respectively. The carbonyl absorbance peak for the PCL-b-PB block copolymer at 1730 cm^{-1} indicates that the PB blocks play a negative effect to the crystallinity of the PCL block. The degree of crystallinity of PCL in the blends increases with the increasing of the PVME content. Although PCL block has the largest crystallinity (62 %, shown by DSC measurements) when PVME content is 40 % in the blend, the carbonyl groups peak at 1723 cm^{-1} and a shoulder exists at lower frequency imply that some weak interaction between the (C=O) groups of PCL and some groups exists in PVME/PCL-b-PB blends. However, when the PVME content is above 40 %, the enhancement of shoulder at higher frequency and the transition of the maximum carbonyl absorbance peak indicate the increase of the amorphous phase in the blends and the weaking of the PCL crystallization ability.

On the basis of the corresponding shifts of the (O–H) groups bands and the (C=O) group bands, it is evident that the PVME/PCL-b-PB blends exist hydrogen-bonded interactions and some weak interaction between the compositions. The above discussions about the spherulite morpholigies and the FTIR spectra of the blends indicate that the existence of the weak interaction between PVME and the PCL-b-PB block copolymer has some improvement to the formation of regular ringed spherulities of the PCL block.

Compatibility of PVME with PCL-b-PB

The glass transition temperatures (T_g), the melting temperatures (T_m) and fusion enthalpy (ΔH_f) of the PVME/PCL-b-PB blends, measured in the second heating cycle, are summarized in the Table-1 as a function of the weight fraction of PVME content in the blends.

Table-1 shows that a single T_g is observed at each composition and the T_g changes with the PVME content. The existence of a single and compositional dependent T_g implies that PVME and PCl-b-PB block copolymer are compatible. However, the T_g value of the PVME/PCL-b-PB blends increases regularly but not linearly with composition. These results mean that the PVME/PCL-b-PB blends may be partially compatible.

Furthermore, the depression of the melting point of a crystalline polymer in polymer blends is frequently used to estimate the magnitude of the polymer-polymer interaction. Fig. 3 clearly shows the melting endotherms for the PVME/PCL-b-PB blends for the second heating scan. It can be seen that the melting peak are almost unchanged with PVME contents in the blends, so it suggest the interaction between PVME and the PCL-b-PB block copolymer is very weak. The FTIR experimental results also demonstrate that the interaction in the blends is weak. But a shoulder peak can be observed at a lower temperature for each curve in Fig. 3 and its area becomes smaller with increasing PVME content when the PVME weight fraction is below 40 %. The above results indicate that the PVME content perfects the crystallization of the PCL block in the blends. It is suggested that PVME content has some influence to the crystallization behaviour of the PCL block.

The crystallinity (Cr) of the PCL block was calculated from the enthalpy of melting (ΔH_f) by equation (1):

$$Cr = \Delta H_f/(W_{PCL} \times (\Delta H_f^0) \quad (1)$$

where W_{PCL} is the weight fraction of PCL in the blends and ΔH_f^0 = 135.5 J/g is the reference melting enthalpy of 100 % crystalline PCL[16].

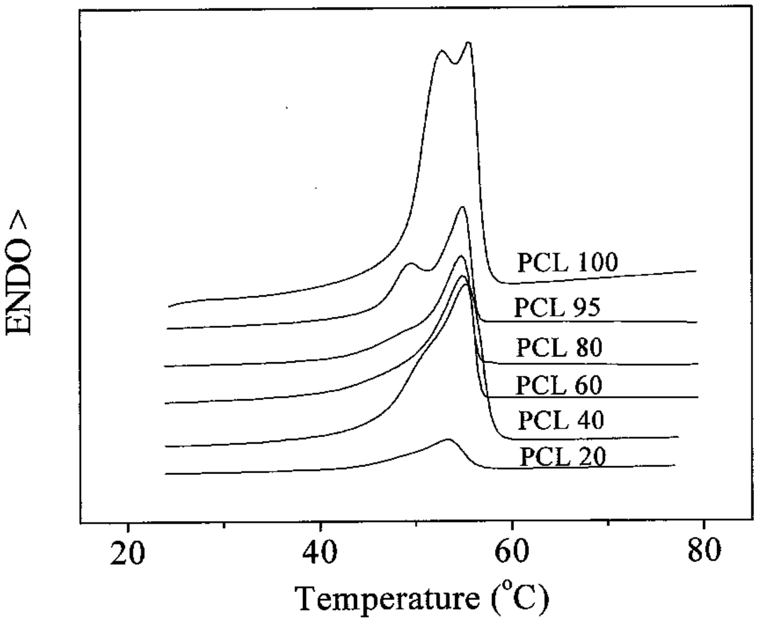


Fig. 3. Second heating scan of DSC thermograms of PVME/PCL-b-PB blends. The heating rate is 20°C/min

The PCL crystallinities (Cr) that developed in the course of the thermal procedures are shown in Table-1 as a function of weight fraction of PVME with respect to the PCL block in the blends. The crystallinity of the pure PCL-b-PB copolymer reaches a value of about 51 % in the second scan. Increasing the PVME content leads to higher the PCL block crystallinity when the PVME weight fraction is below 40 %. Increases of the PCL crystallinity with increasing PVME content is also observed for blends of PCL and PVME[17], in blends of PVME and PCL-b-PTMC block copolymer[11] and in blends of PVME and PCL-g-PS block copolymer[13]. It might be concluded that PVME promotes the crystallization of PCL in the lower PVME content. From Table-1, it also can be seen that the crystallinity decreases dramatically when the PVME weight fraction exceeds about 40%.

A step-wise annealing procedure after Hoffman and Weeks[18] was employed to estimate the equilibrium melting temperatures of the blends under discussion. The Hoffman-Weeks plots of PVME/PCL-b-PB blends give the equilibrium melting points (T_m^0) and the results are summarized in Table-1. Extrapolation results in T_m^0 = 61.2 - 63.4°C show that the equilibrium melting points are almost unchanged with PVME contents, which has similar phenomenon with the melting temperatures. Thus, T_m^0 for the PVME/PCL-b-PB blends are below for the homopolymer PCL in PCL/PVME blends ($T_m^0 = 73ºC$)[17]. It indicates that the PB block plays an important role on the crystallization ability of the PCL block in the blends.

Isothermal crystallization experiments gave another important parameter for the PVME/PCL-b-PB blends the half-time of crystallization, $t_{0.5}$, defined as the time taken for half of the crystallinity to develop. Fig. 4 presents the plots of half-times of crystallization as a faction of crystallization temperature for different blend compositions. One observes that the rate of crystallization ($t_{0.5}^{-1}$) for the blends decreases with increasing of the PVME content. The similar behaviour was observed in PCL/PVME blends[17]. In addition, Fig. 4 also shows that the rate of crystallization for PCL used in PCL/PVME blends[21] is higher than that for PCL block in PCL-b-PB block copolymer.

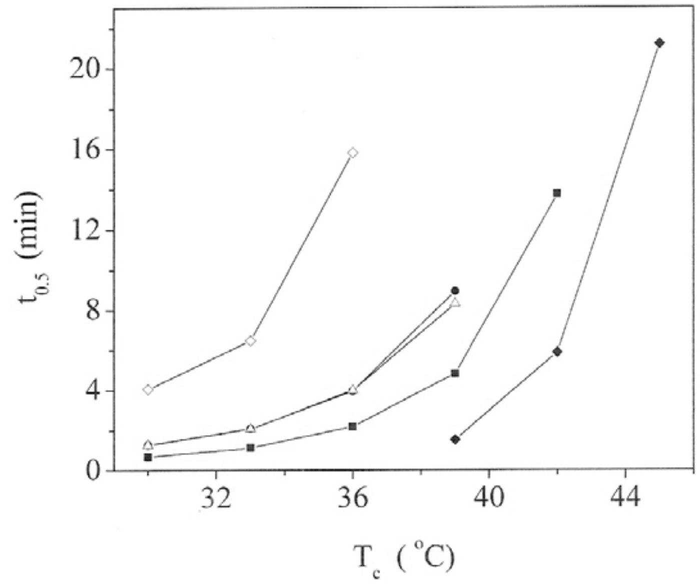


Fig. 4. Half-time of crystallization *vs.* crystallization temperature for PCL and PCL block in PVME/P(CL-b-B) blends. (♦)PCL; (■)PCL100; (●) PCL95; (△) PCL80; (◇)PCL60

The results of the thermal analysis for PVME/PCL-b-PB blends indicate that the addition of PVME can decrease the crystallization ability of PCL block and the low content of PB also decreases the crystallization ability of PCL. The weakening of the crystallization ability in the blends has some correspondence with the change of the compatibility in the blends. The better the compatibility between components in the blends, the greater the weakening of the crystallization ability of crystallizable components in the blends.

Conclusion

The optical inspection reveals that the addition of the PB block in the PCL-b-PB can evidently influence the formation of ringed spherulites of PCL block, although the PB content is only 6.9 wt% in the copolymer. The PVME/PCL-b-PB blends can form ringed spherulites in a large range of composition at temperature range of 33-42ºC. The analysis of the FTIR spectra of the PVME/PCL-b-PB blends shows the presence of some weak interaction in the blends. In addition, the glass transition temperature values indicate that the PVME may be partially compatible with the PCL-b-PB block copolymer in the PVME/PCL-b-PB blends. Investigation of the melting behaviour and crystallization kinetics of the blends shows that the crystallization characteristics of the PCL block are influenced by the PB block and PVME content.

These experimental results mean that the PVME/PCL-b-PB blends are partial compatibility and some weak interaction exists in the blends. Distinct ring-banded spherulites are found in the blends. these facts suggest that high miscibility may be not a necessary condition for improving the formation of PCL ring-banded spherulites in PVME/PCL-b-PB blends. However, the PB block influences evidently the morphology of the blends and the addition of the amorphous component PVME has some influence on the crystalline morphology of the PCL and compatibility of the two components in the blends.

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