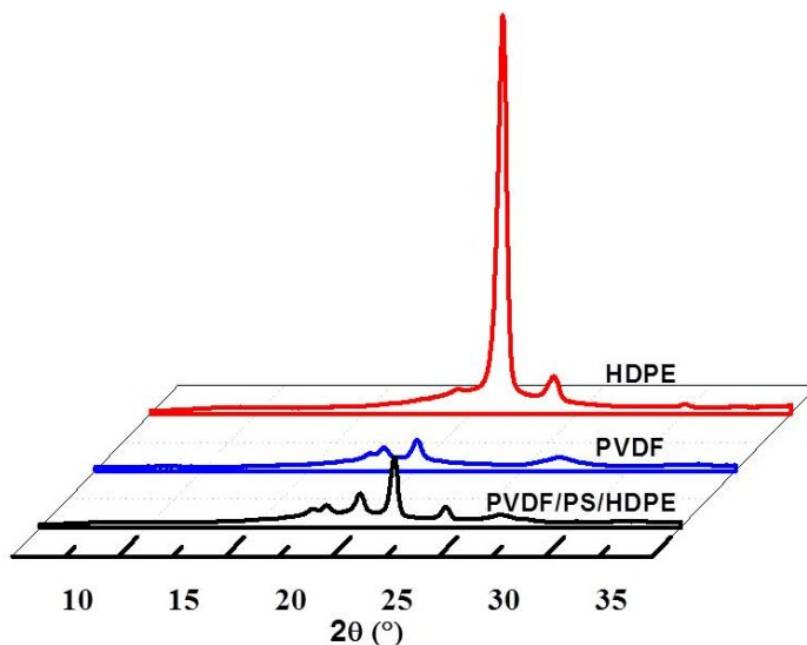


## Electronic Supporting Information

1. Wide-angle X-ray diffraction (WAXS) can provide a convenient way of characterizing the contribution of the individual blend components to the blends. Sukunya Ross<sup>1</sup> et al. successfully mapped out the phase diagrams of PLLA/PCL/CAB ternary blend with WAXS. Rui Dou<sup>2</sup> also studied the crystal structure of PA6 and HDPE in PA6/EPDM-g-MA/HDPE ternary blend with WAXS.

In order to prove that the individual morphologies of the polymers are not affected by the presence of the other polymers in our PVDF/PS/HDPE system, WAXS patterns of pure PVDF, HDPE and PVDF/PS/HDPE ternary blend (Fig. S1) were obtained. The strong peaks appearing at about 18.47, 20.16 and 26.59 were from (0, 2, 0), (1, 1, 0) and (0, 2, 2) lattice plane of PVDF crystals; 21.48, 23.88 were from (0, 0, 1) and (2, 0, 0) lattice plane of HDPE crystals. All of these peaks can be seen in PVDF/PS/HDPE ternary blend (except that the peaks became weaker), which can demonstrate that blending has no significant effect on the type of crystals, in other words, the individual morphologies of the polymers are not affected by the presence of the other polymers in our PVDF/PS/HDPE system, so the phases can be distinguished by polarized optical microscopy.



**Fig.S1** XRD patterns of pure HDPE, PVDF and PVDF/PS/HDPE ternary blend

2. Generally, differential scanning calorimeter (DSC) is widely used to investigate the melting, melt-crystallization behaviors of polymers<sup>3</sup>. The heating curves of pure PVDF, HDPE and ternary

blend were given in Fig.S2, the melting behaviors were summarized in Table S1. The important parameters which can be obtained from the table include:

- a. glass transition temperature ( $T_g$ ),
- b. melting point ( $T_m$ ),
- c. normalized enthalpy of fusion ( $\Delta H_f$ ),
- d. percentage crystallinity ( $X_c$ ).

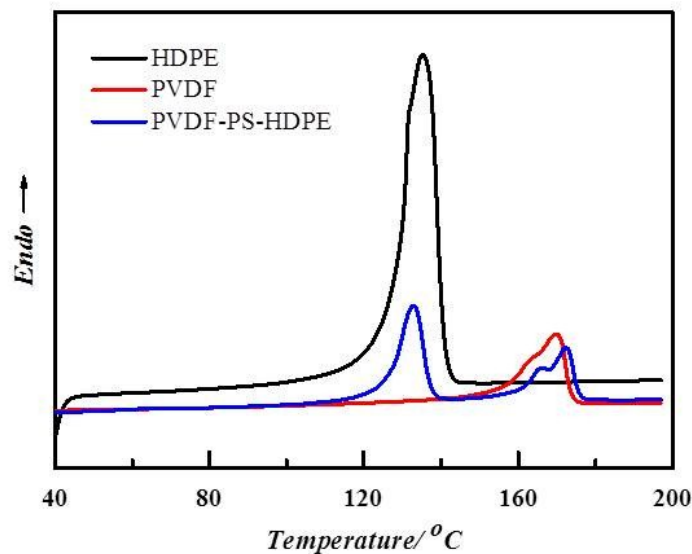
Percentage crystallinity of component polymers in the blend is obtained from the expression:

$$\%crystallinity = (\Delta H_f / \Delta H_f^0) * 100 \quad (1)$$

Where  $\Delta H_f$  is the enthalpy of fusion obtained calorimetrically and  $\Delta H_f^0$  is the enthalpy of fusion of the 100% crystalline.  $\Delta H_f^0$  of PVDF and HDPE was taken as 104.5 J/g, 293.0 J/g respectively.

$T_m$  and percentage crystallinity of pure PVDF were observed as 170°C and 46.7%. It is obvious that the crystallinity and melting point of PVDF remained unchanged after blending (Table S1). However, the melting point of HDPE, especially the crystallinity decreased after blending, which give the further evidence that some PS droplets located in HDPE phase.

Glass transition temperature of pure phase and the blends was obtained by DMA. It indicates that  $T_g$  of PVDF, HDPE and PS are -38.7 °C, -120.5 °C and 116.5 °C respectively. Almost same  $T_g$  can be obtained in the ternary blend which indicated immiscibility of all the phases.



**Fig.S2** DSC heating curves of pure PVDF, HDPE and PVDF/PS/HDPE ternary blends

**Table S1** Effects of blending on the melting and crystallization behaviors

	PVDF	PS	HDPE	PVDF/PS/HDPE ternary blend		
				PVDF	PS	HDPE
$T_g$ (°C)	-38.7	116.5	-120.5	-39.5	118.0	-120.5
$T_m$ (°C)	170	--	135	171	--	132
$\Delta H_f$ (J/g)	48.9	--	190.4	47.3	--	171.1
$X_c$ (%)	46.7	--	65.2	45.6	--	58.5

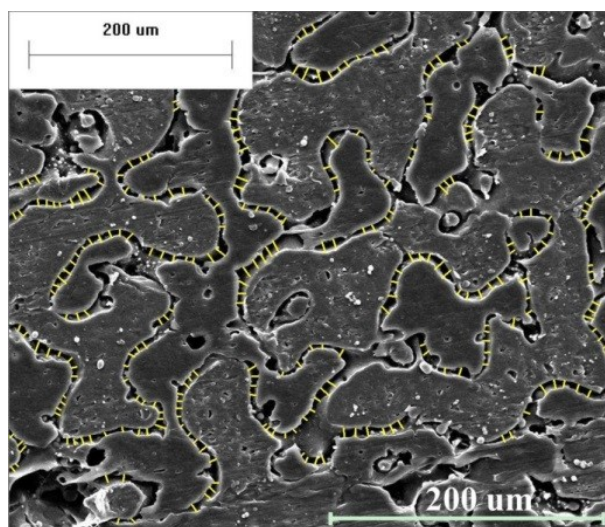
In conclusion, because of the little interaction of the three polymers, the phases can be distinguished by polarized optical microscopy.

[1] S. Ross, P. D. Topham and B. J. Tighe, *Polymer international*, 2014, 63, 44-51.

[2] R. Dou, W. Wang, Y. Zhou, L. p. Li, L. Gong, B. Yin and M. b. Yang, *Journal of Applied Polymer Science*, 2013, 129, 253-262.

[3] T. S. Omonov, C. Harrats and G. Groeninckx, *Polymer*, 2005, 46, 12322-12336.

3. The thickness of PS phase was performed with image analysis of Image-Pro Plus 6. At least 500 PS dispersed domains were measured by manually tracing the phase boundaries and then the average of the results of statistics was calculated. Examples of the measurement are as follows:



**Fig.S3** Example of thickness of PS phase measurements. The segments represent the selected values for quantification at periodic intervals.