Polymer Vol. 39 No. 23, pp. 5871–5876, 1998
0032-3861/98/$ – see front matter
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PII: S0032-3861(97)10247-6

Miscibility of polypropylenes of different stereoregularity†

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(Revised 31 October 1997)

The melt miscibility of high molecular-weight atactic polypropylene with both isotactic and syndiotactic polypropylene was examined. High molecular-weight atactic polypropylene was found partially miscible with syndiotactic polypropylene and immiscible with isotactic polypropylene. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: atactic polypropylene; isotactic polypropylene; syndiotactic polypropylene)

Introduction

Recently, polyolefins endowed with new properties have been obtained by using metallocene catalysts. Among other polymers, high molecular-weight atactic polypropylene (HMWaPP) has been obtained by using these catalysts[1,2].

From the practical point of view, the availability of HMWaPP is important because it allows to obtain a new type of flexible and elastic polypropylene (PP) by mixing it with crystalline PP.

From the theoretical point of view, the availability of HMWaPP allows the study of the dependence of miscibility on tacticity in blends of PPs of different tacticity.

This topic has already received attention in the literature[3]. In Ref. 3 the melt miscibility of atactic PP (aPP) with isotactic PP (iPP) and syndiotactic PP (sPP) was studied: aPP was reported to be miscible with iPP and immiscible with sPP. However, only one sample of aPP was examined and this sample was endowed with a low M_w (50 000 g mol^{-1}). Also in Ref. 3, the results of an equation of state theory were given according to which aPP was predicted to be miscible with iPP over the whole composition range for molecular weights up to a few millions and sPP was predicted to be immiscible with aPP even for very low M_w of aPP.

Here we report an experimental miscibility study performed on the same type of blends studied in Ref. 3 where, however, the atactic component is HMWaPP. HMWaPP is synthesised from metallocene catalysts and, as typical of these catalyst products, it has a narrow molecular weight distribution (MWD)[1,2].

The miscibility of aPP with tactic PP in the molten state is difficult to study because these materials possess similar physical properties, i.e. refractive indexes. Moreover, the T_g values are almost the same for both components. It is typical to resort, in these cases, to the study of blends frozen from the liquid state relying on the fact that the system did not have time enough to evolve to a more stable thermodynamic state (see, for example, Ref. 4). For the blends here reported, the study was performed only on the solid state, inferring from this the properties of the molten state. The morphology was studied by transmission electron microscopy (TEM). The staining technique used was found to be able to highlight the phases well enough to allow an in-depth morphological analysis.

Experimental

The molecular properties of the samples used in this work are shown in *Table 1*.

Intrinsic viscosity (IV) was measured in tetrahydronaphtalene at 135°C.

Gel permeation chromatography was performed with a Waters 150 instrument at 135°C using orthodichlorobenzene and monodisperse polystyrene standards.

^{13}C n.m.r. analysis was performed in a Bruker AC200 instrument at 120°C in $C_2D_2Cl_4$.

The samples were prepared by mixing the components in a Bambury at 200°C for 10 min at 50 rpm. The blends obtained in this way were compression moulded at 200°C into plaques 1 mm thick and subsequently cooled in a water-cooled press.

Transmission electron microscopy (TEM) was carried out to examine the micro-morphology of the samples. The specimens were stained with RuO_4. Ultra-thin sections were cut from the compression-moulded plaques using a Reichert Ultracut-S ultramicrotome equipped with a FCS cryo-device. The specimens were at −130°C and the knife was at −60°C to avoid plastic deformation. The thin slices were put on copper grids and examined with a Philips 301 TEM operating at 80 kV[5]. In a system consisting of two phases, RuO_4 preferentially stains the more amorphous phase mainly because of the different density of the two phases.

T_m and T_c data were obtained from d.s.c. from the first heating and cooling scans (heating and cooling rate, 20°C min^{-1}) performed on the compression moulded plaques using a Perkin-Elmer DSC-7 instrument.

T_g was measured by dynamic mechanical thermal analysis at a frequency of 1 Hz and a scan rate of 2°C min^{-1} using a tensile Rheometrics DMTA instrument.

Results

aPP/iPP. Blends of aPP with both polydisperse iPP from Ziegler-Natta (ZN) catalysis and with narrow MWD iPP of different degrees of tacticity from metallocene catalysts were studied.

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† Presented at 'XIII Convegno Italiano di Scienza e Tecnologia delle Macromolecole', Genova, 21–25 September 1997

Table 1 Molecular characteristics of the PPs used for the blends

	IV (dl g^{-1})	M_w (g mol^{-1})	M_w/M_n	mmmm (%)[a]	mm (%)[a]	rr (%)[a]	mr (%)[a]	rrrr (%)[a]
Moplen Q30P	2.65	640 000	7.5	91.5	93.8			
LMWaPP	0.45	29 000	6.8		33	39	29	
HMWaPP-I [7]	2.57	472 000	2.3					
HMWaPP-II [7]	1.77	280 000	2.5		17	35	48	
HMWaPP-III [7]	2.01							
iPPMet-I [8]	1.70	293 000	2.3	99.3	99.6	0.13	0.27	
iPPMet-II [9,10]	1.91	382 000	3.5	93.7	96.1	1.30	2.60	
sPP [11]	1.89	250 000	7.2			91.7		84.6

[a] mmmm, isotactic pentads; mm, isotactic triads; rrrr, syndiotactic pentads; rr, syndiotactic triads; mr, aspecific triads

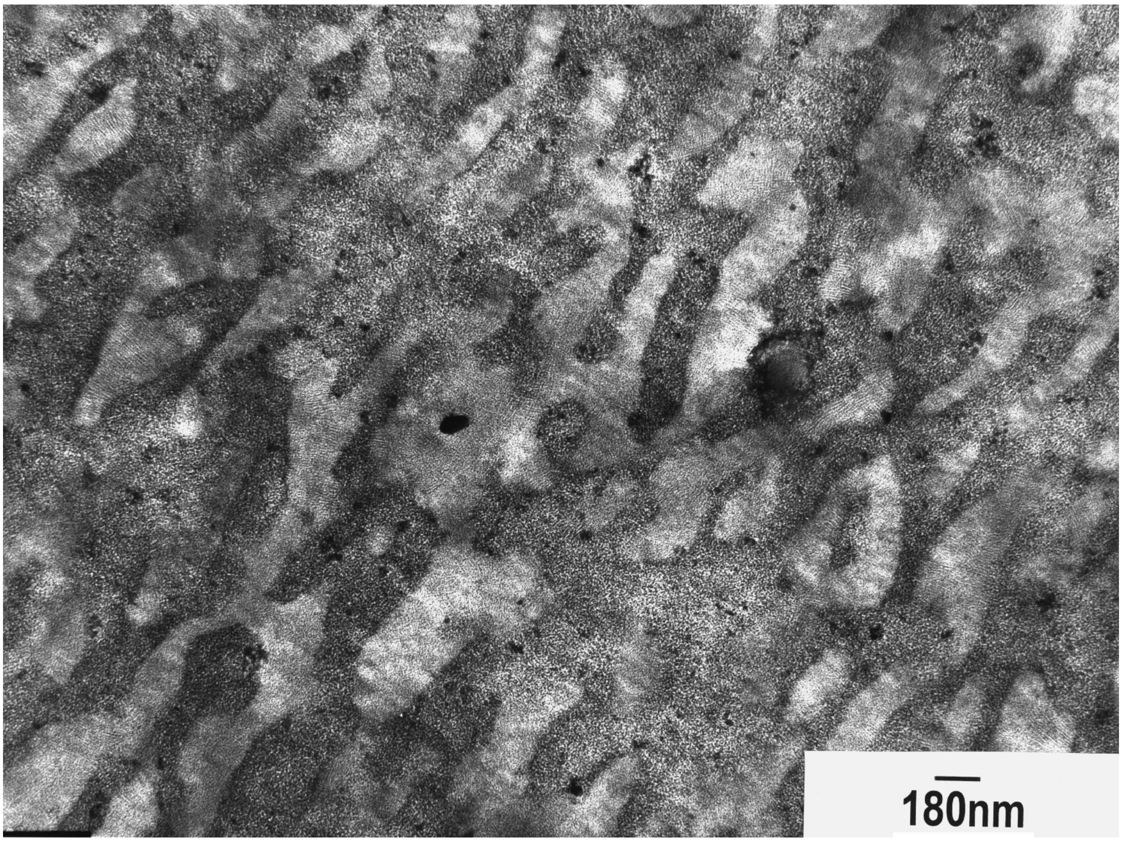

Figure 1 TEM micrograph of the blend Moplen Q30P/HMWaPP-I (50/50, w/w) (×55 000). The darker phase is the amorphous HMWaPP phase and the lighter phase is the crystalline Moplen Q30P phase

ZN catalysts provide iPP of large MWD and large tacticity distribution. The iPP from the ZN catalyst which was used in this work is Moplen Q30P, a commercial Montell sample of IV = 2.65 dl g^{-1}. Moplen Q30P was blended with HMWaPP-I, an aPP sample of IV = 2.57 dl g^{-1}. The molecular characteristics of these samples are reported in *Table 1*. Blends of composition Moplen Q30P/HMWaPP-I (30/70, 50/50 and 70/30, w/w) were prepared. All these blends showed phase separation; none of them was macroscopically transparent. For example, *Figure 1* shows the TEM micrograph of the 50/50 blend.

Preliminary rheological measurements on these blends are in agreement with this result.

In these blends neither T_m nor T_c of iPP are appreciably affected by the mixing, as shown in *Table 2*.

The M_w of the components of the blend was found to play a key role in the thermodynamics of the aPP/iPP system. As a matter of fact, by lowering the M_w of the atactic component the system becomes fully miscible, as already extensively reported for blends of iPP with both narrow MWD aPP[3] and polydisperse aPP[6]. A blend consisting of a sample of aPP of low M_w (LMWaPP: a commercial sample of aPP obtained by extraction with solvents from iPP from ZN catalysis) is homogeneous from the microscopic point of view, and fully transparent from the macroscopic point of view. The TEM micrograph of a blend of Moplen Q30P/LMWaPP (50/50, w/w) is shown in *Figure 2*.

Table 2 D.s.c. data for the blend Moplen Q30P/HMWaPP-I

	Moplen Q30P/HMWaPP-I (w/w)				
	100/0	70/30	50/50	30/70	0/100
T_m (°C)	165	162	160	160	—
T_c (°C)	111	107	107	106	—
T_g (°C)	5	4	6	7	6

In these blends the T_c of iPP is lowered upon mixing and the T_g of the blend depends on composition (*Table 3*).

Metallocene catalysts provide iPP of narrow MWD and

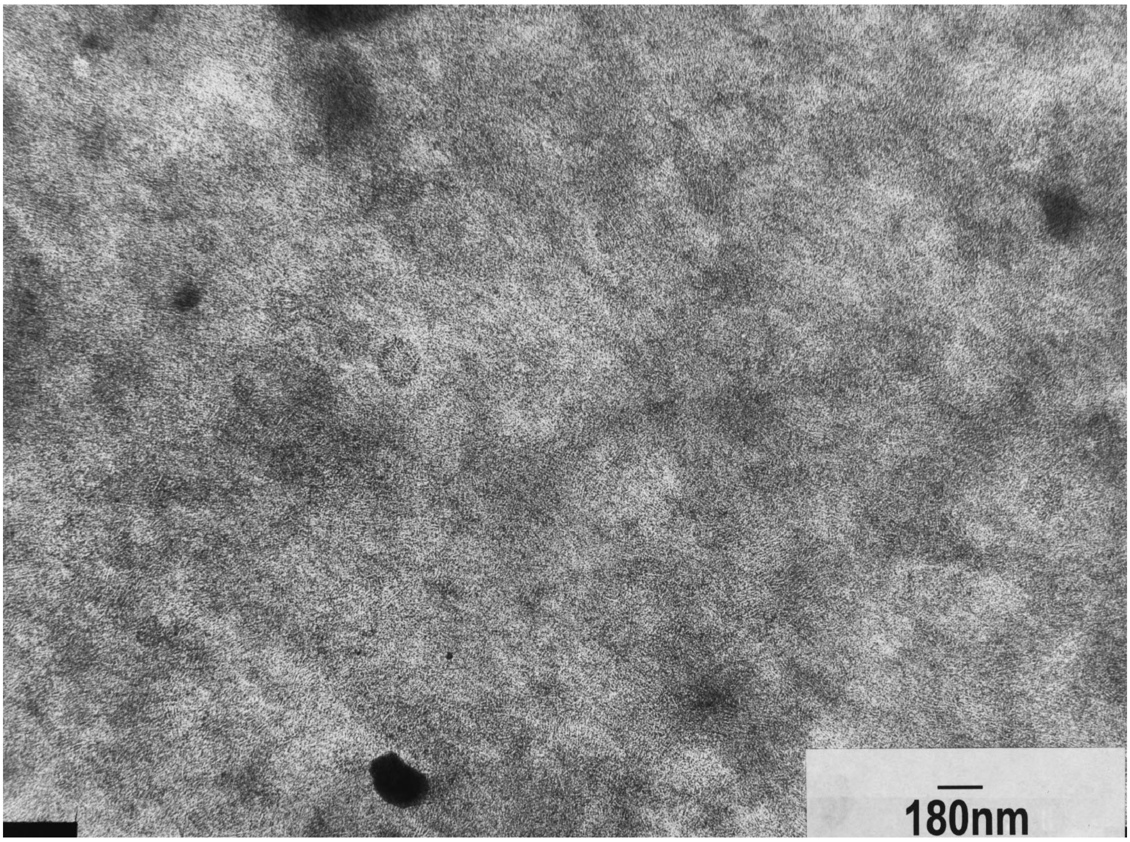

Figure 2 TEM micrograph of the blend Moplen Q30P/LMWaPP (50/50, w/w) (×55 000). This system is homogeneous

Table 3 D.s.c. data for the blend Moplen Q30P/LMWaPP

	Moplen Q30P/LMWaPP (w/w)				
	100/0	70/30	50/50	30/70	0/100
T_m (°C)	165	158	162	159	—
T_c (°C)	111	97	95	93	—
T_g (°C)	5	0	−3	−5	−7

Table 4 D.s.c. data for the blend sPP/HMWaPP-I

	sPP/HMWaPP-I (w/w)				
	100/0	70/30	50/50	30/70	0/100
T_m (°C)	142	141	141	140	—
T_c (°C)	87	80	74	57	—
T_g (°C)	17	12	8	9	6

narrow tacticity distribution (iPPMet). Also, the degree of tacticity depends on the metallocene. To investigate the effect of the narrow MWD and of the degree of tacticity of iPP on the miscibility with HMWaPP, two blends were prepared: iPPMet-I/HMWaPP-II (50/50, w/w) and iPPMet-II/HMWaPP-III (50/50, w/w). In these blends the iPP component has a different degree of isotacticity having been synthesised from two different metallocene catalysts, as reported in *Table 1*.

Figures 3 and *4* show the TEM micrographs of these blends: both systems show phase separation; however, the phase boundary looks qualitatively different. This could mean that the degree of tacticity can affect the miscibility in the molten state. The blend shown in *Figure 3* was quenched in liquid nitrogen immediately after moulding to offset the effect of the different crystallisation rate of iPPMet-I, higher than for iPPMet-II.

aPP/sPP. SPP samples were obtained from metallocene catalysts.

The TEM micrographs of blends of sPP/HMWaPP-I of composition 70/30, 50/50 and 30/70 (w/w) are shown in *Figures 5–7*. The HMWaPP used in these blends has IV = 2.57 dl g^{-1} and sPP has IV = 1.89 dl g^{-1}, as reported in *Table 1*. This system is miscible depending on the composition: *Figure 5* suggests that the blend of composition 70/30 (w/w) sPP/HMWaPP-I is homogeneous, while the blends of composition 50/50 (w/w) (*Figure 6*) and 30/70 w/w (*Figure 7*) sPP/HMWaPP-I are phase separated. In fact, in these blends the T_g is only partially dependent on composition. T_c is heavily lowered upon mixing (*Table 4*).

Conclusions

HMWaPP was found to be partially miscible with sPP and immiscible with iPP. However, the M_w of the components plays a major role in the thermodynamics of these systems. The degree of tacticity of the components and the composition of the blend can also affect miscibility.

Acknowledgements

The authors are indebted to L. Resconi who provided all the samples and to I. Camurati who performed the n.m.r. analysis.

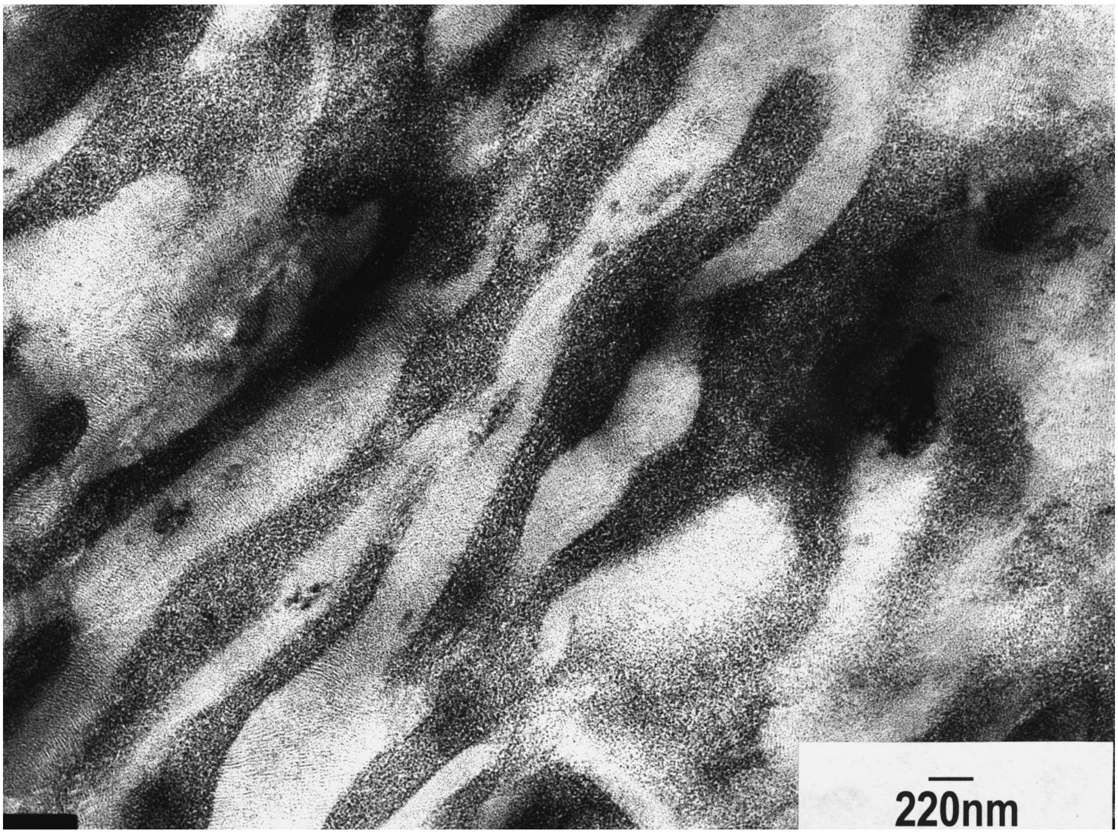

Figure 3 TEM micrograph of the blend iPPMet-I/HMWaPP-II (50/50, w/w) (×45 000). The darker phase is the amorphous HMWaPP-II phase and the lighter phase is the crystalline iPPMet-I phase

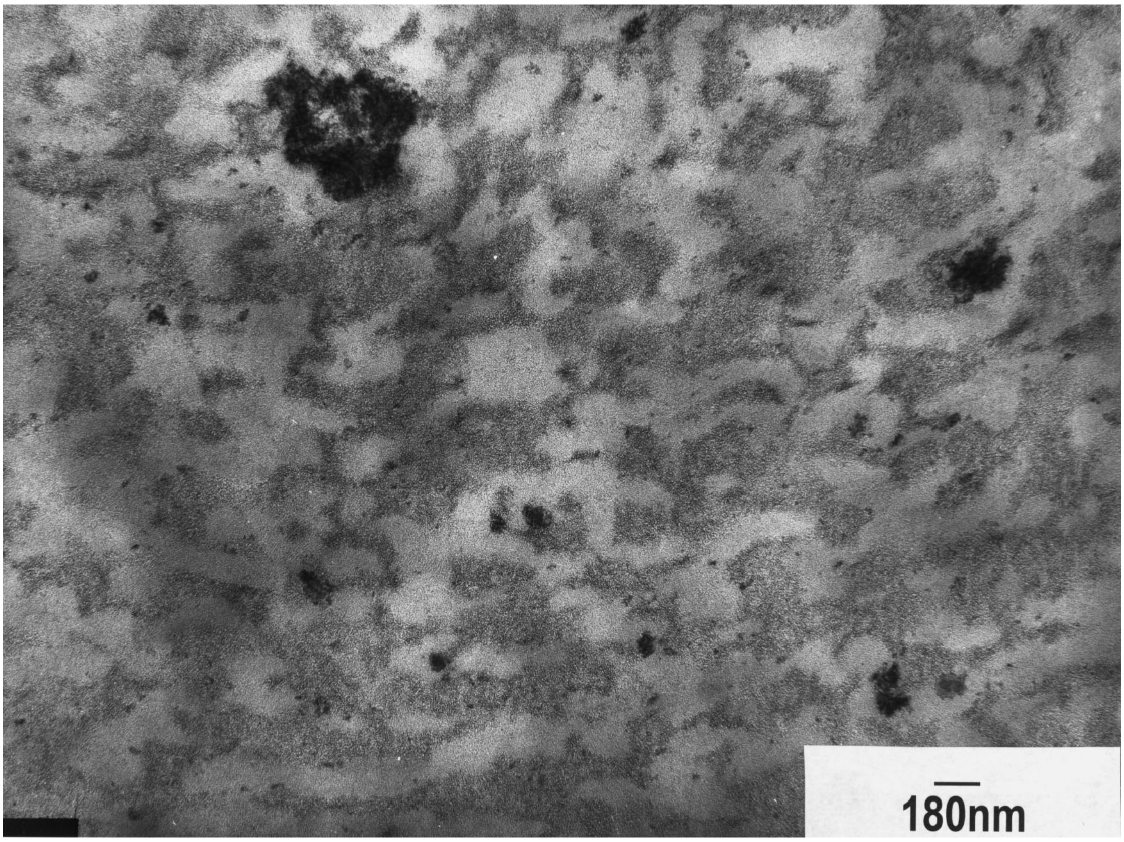

Figure 4 TEM micrograph of the blend iPPMet-II/HMWaPP-III (50/50, w/w) (×45 000). The darker phase is the amorphous HMWaPP-III phase and the lighter phase is the crystalline iPPMet-II phase

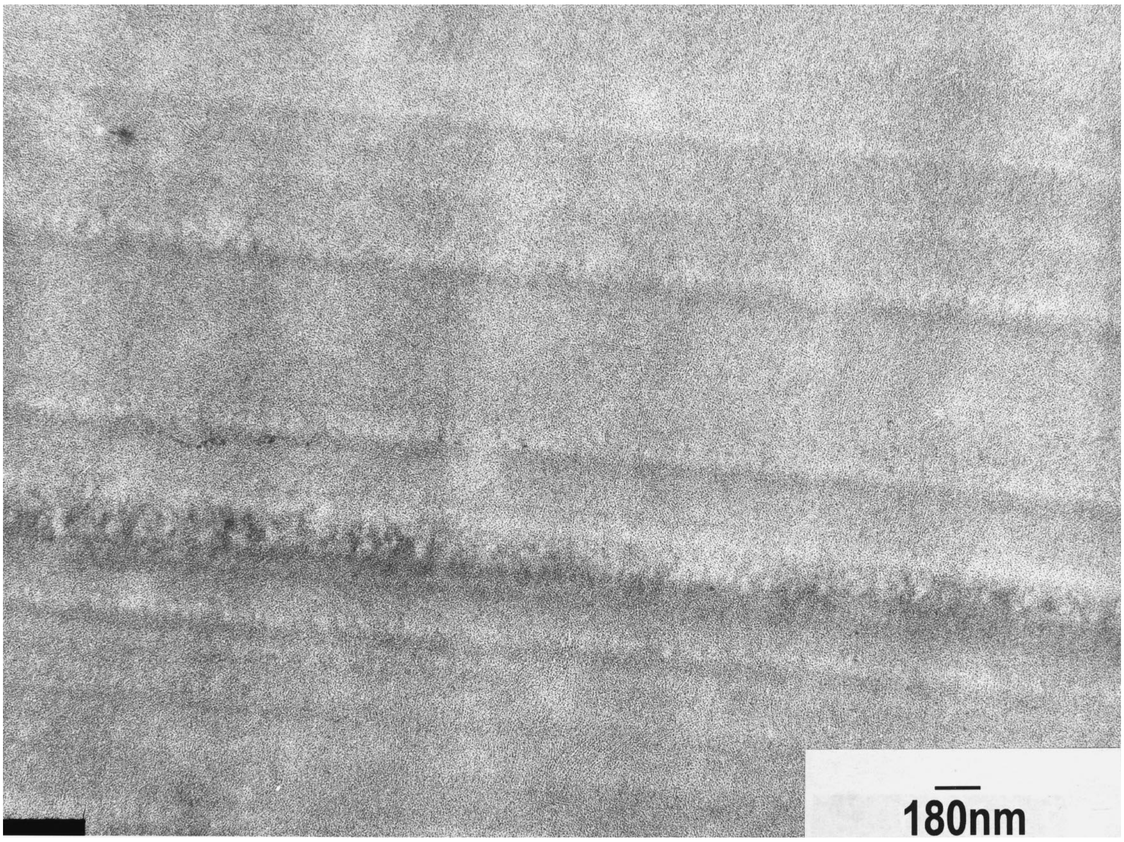

Figure 5 TEM micrograph of the blend sPP/HMWaPP-I (70/30, w/w) (×55 000). This system is homogeneous

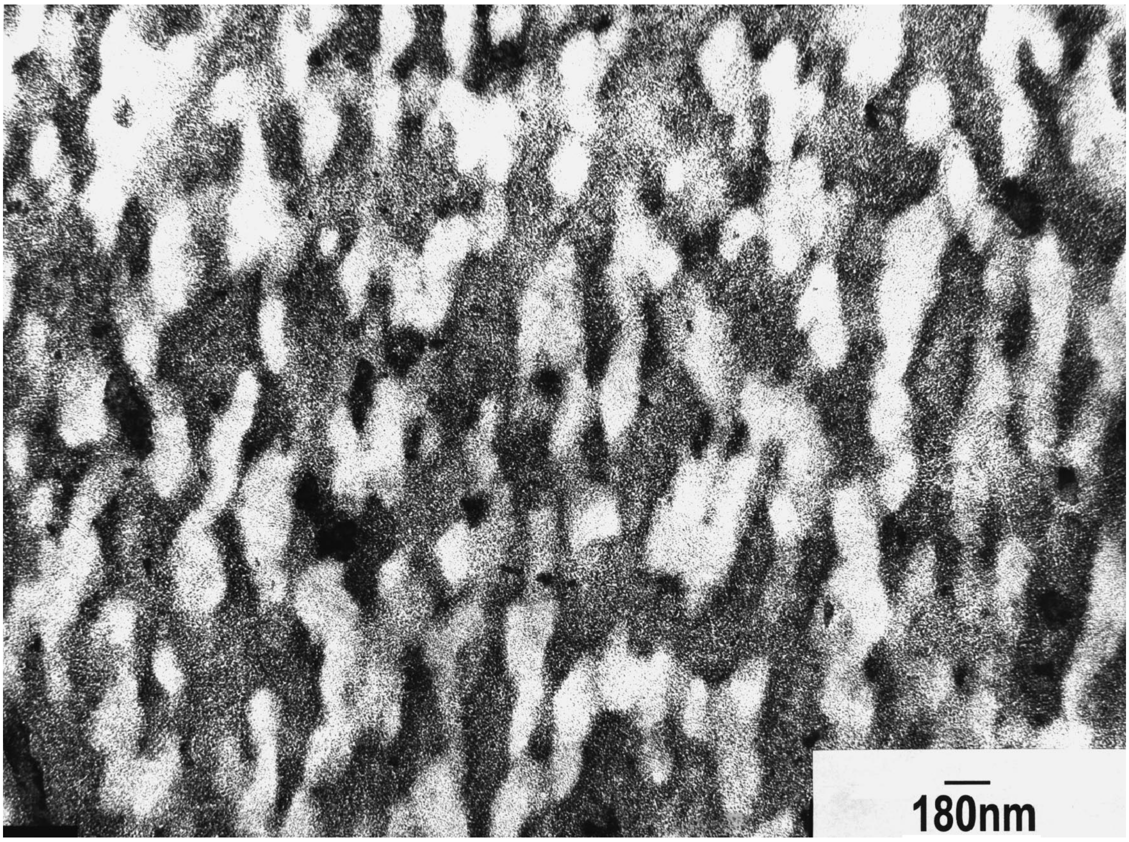

Figure 6 TEM micrograph of the blend sPP/HMWaPP-I (50/50, w/w) (×55 000). The darker phase is the more amorphous phase richer in HMWaPP-I and the lighter phase is the more crystalline phase richer in sPP

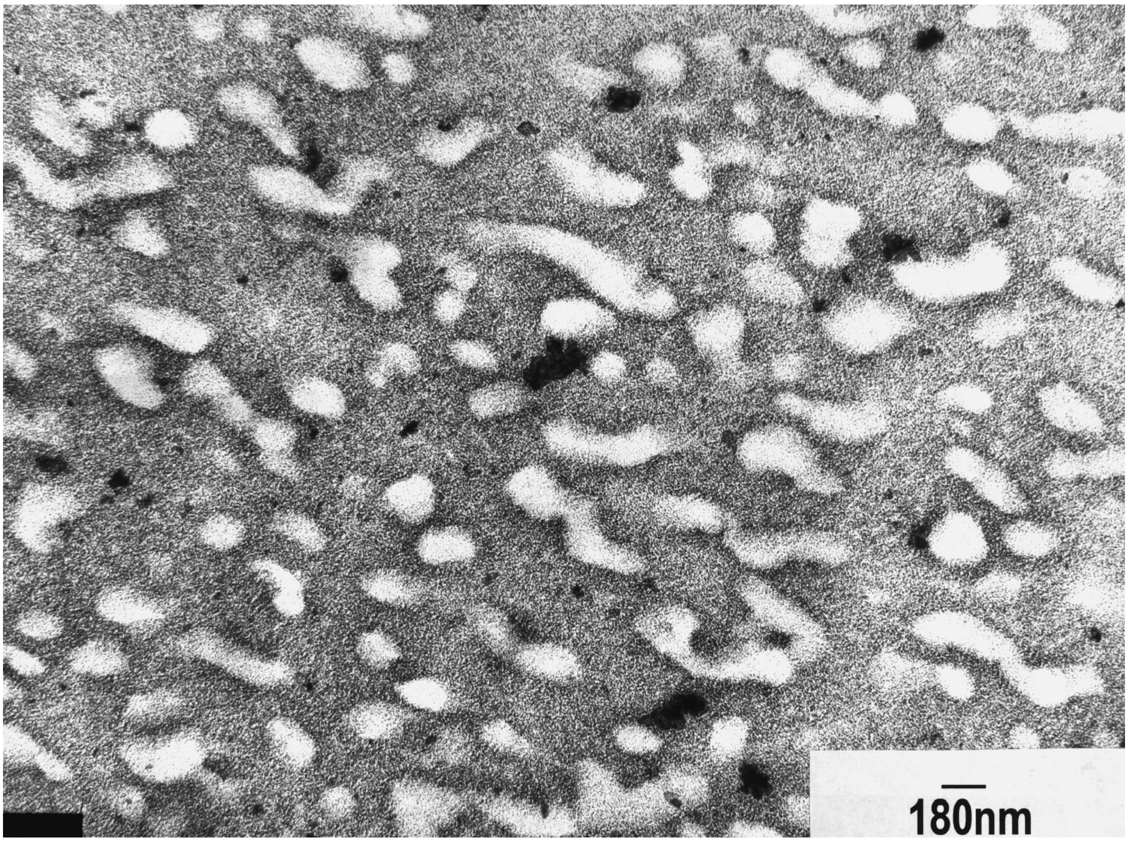

Figure 7 TEM micrograph of the blend sPP/HMWaPP-I (30/70, w/w) (×55 000). Same as in *Figure 6*

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