

Syndiotactic polystyrene-based blends: crystallization and phase structure

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The crystallization from the melt, the morphology and the miscibility of syndiotactic polystyrene/poly(vinyl methyl ether) (SPS/PVME) blends and syndiotactic polystyrene/poly(2,6-dimethyl-1,4-diphenylene oxide) (SPS/PPO) blends have been analysed by differential scanning calorimetry and optical microscopy. It was found that the kinetic parameters are strongly altered by the blending and by the crystallization conditions. In particular, the spherulite growth rate of SPS decreases if PPO is added, whereas it increases in the case of SPS/PVME blends. The half-time of crystallization is drastically increased by the presence of both PPO and PVME. The PVME segregated into spherical domains in the SPS intraspherulitic region, whereas there is no microscopic evidence that the PPO forms segregated domains. These results were correlated to the viscosity of the melt and the degree of miscibility of the blends. It was concluded that the SPS/PPO system is completely miscible in the amorphous phase, whereas PVME forms with SPS a two-phase separated system. This conclusion results in agreement with the presence of one T_g , composition-dependent, for the SPS/PPO blend, and of two T_g for the SPS/PVME blends.

(Keywords: syndiotactic polystyrene; crystallization; morphology; blends; poly(vinyl methyl ether); poly(2,6-dimethyl-1,4-diphenylene oxide))

INTRODUCTION

For some years in our Institute syndiotactic polystyrene (SPS) has received great attention. The crystallization behaviour and the morphology of this material, reported in previous papers, were compared with those of isotactic polystyrene¹. In the present paper we will report the study of the influence of composition and crystallization temperature on the crystallization process (spherulite growth rate and overall crystallization rate), morphology, phase structure and miscibility of blends of SPS with poly(vinyl methyl ether) and poly(2,6-dimethyl-1,4-diphenylene oxide) (SPS/PVME and SPS/PPO blends). Few data on these blends have been reported in the literature²⁻⁴.

In the case of SPS/PVME blends, preliminary data on the influence of PVME on some morphological and kinetic properties of SPS were reported recently by us². It was found that, whereas for pure SPS only spherulites having positive birefringence were observed, in the case of blends, negative birefringence spherulites are also present. It was noted that for the same crystallization temperature, T_c , and composition, the positive spherulites grow faster than the negative ones. Moreover, on comparing the values of spherulite growth rate of positive SPS spherulites, grown from SPS/PVME blends, with that of plain SPS, at the same crystallization temperature, it was found that values of G were higher for blends than for pure SPS. The temperature dependence of

¹³C cross-polarization/magic-angle spinning (c.p./m.a.s.) intensities for the resonance of SPS/PVME systems indicates that these blends are phase-separated³.

For the SPS/PPO blend, the only paper to our knowledge available in the literature concerns the influence of PPO on the complex polymorphic behaviour of SPS⁴.

Through this study we aim to obtain information also on: (1) the influence of tacticity of the crystallizable component on the miscibility and crystallization behaviour; and (2) the influence of the T_g of the blend on the energy related to the transport of the macromolecules in the melt and hence on the crystallization rate.

Atactic polystyrene (APS) and PVME or PPO have been shown to be miscible at room temperature⁵⁻⁷. Both blends present lower critical solution temperature behaviour. Isotactic polystyrene (IPS), on the other hand, is miscible with PPO⁸, but undergoes phase separation if blended with PVME⁹. With the study of the miscibility of SPS/PVME and SPS/PPO we will complete the analysis of the influence of tacticity on the miscibility of SPS-based blends.

It is well known that the T_g is one of the factors that mainly influence the crystallization rate^{10,11}. The SPS/PVME and SPS/PPO blends can be considered a unique example where it is possible to study and compare directly the influence of the variation of T_g on the crystallization process of miscible blends. In fact, it is possible to note that the T_g of SPS is between the T_g values of PVME and PPO. So if the blends are miscible, $T_g(\text{SPS/PVME}) < T_g(\text{SPS}) < T_g(\text{SPS/PPO})$.

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EXPERIMENTAL

Material and blend preparation

The molecular characteristics of the polymers used in the present work are reported in Table 1. Binary blends of SPS/PVME and SPS/PPO were prepared by casting from *o*-dichlorobenzene at about 130°C.

Optical microscopy

The morphology, the phase structure and the isothermal spherulite growth rate were studied by using an optical polarizing microscope fitted with an automatic hot-stage control. For the measurement of the spherulite growth rate the following procedure was used: Blend films were sandwiched between two microscope slides, heated at $T_c = 340^\circ\text{C}$ and kept at this temperature for 15 min. Then the temperature was rapidly lowered to the pre-fixed T_c and the sample allowed to crystallize. The radial growth rate of an SPS spherulite was monitored during crystallization, taking photomicrographs at appropriate time intervals. From the slope of the radius of the growing spherulite, r , against t lines, G was derived for all the range of T_c explored.

Calorimetric measurements

The overall kinetics of crystallization and the thermal properties of the homopolymers and blends were analysed by differential scanning calorimetry (Mettler TA 3000). The isothermal crystallization process was studied using the following procedure: The sample sealed in a d.s.c. pan was melted at 340°C and kept at this temperature for 15 min. The temperature was rapidly lowered to T_c and the sample allowed to crystallize. The heat evolved during the isothermal crystallization was recorded as a function of the crystallization time.

The glass transition temperatures of the materials were obtained by heating the samples (about 10 mg) from -170 to 350°C at a rate of $10^\circ\text{C min}^{-1}$ and by recording the heat evolved during the scanning process as a function of temperature. The T_g of the sample was taken as the temperature corresponding to 50% of the transition.

RESULTS AND DISCUSSION

Glass transition temperature

Figure 1 reports the d.s.c. thermograms relative to the homopolymers and the two blends. The SPS/PPO blends present a single glass transition temperature, whose values are composition-dependent. The presence of one T_g for this system indicates that the SPS/PPO blend is miscible in the amorphous state.

In the case of the SPS/PVME blends, one or two T_g are detected depending on the composition. For a sample containing less than 20 wt% of PVME, a single T_g is observed. For higher PVME content, two T_g are

Table 1 Number- and weight-average molecular weights M_n and M_w , melting temperature T_m , and glass transition temperature T_g

Sample	M_n	M_w	T_g (°C)	T_m (°C)
SPS		129 000	93	270
PPO	32 000	244 000	200	^a
PVME	34 000	65 000	-28	

^aIn the condition used for the crystallization processes the PPO was not able to crystallize

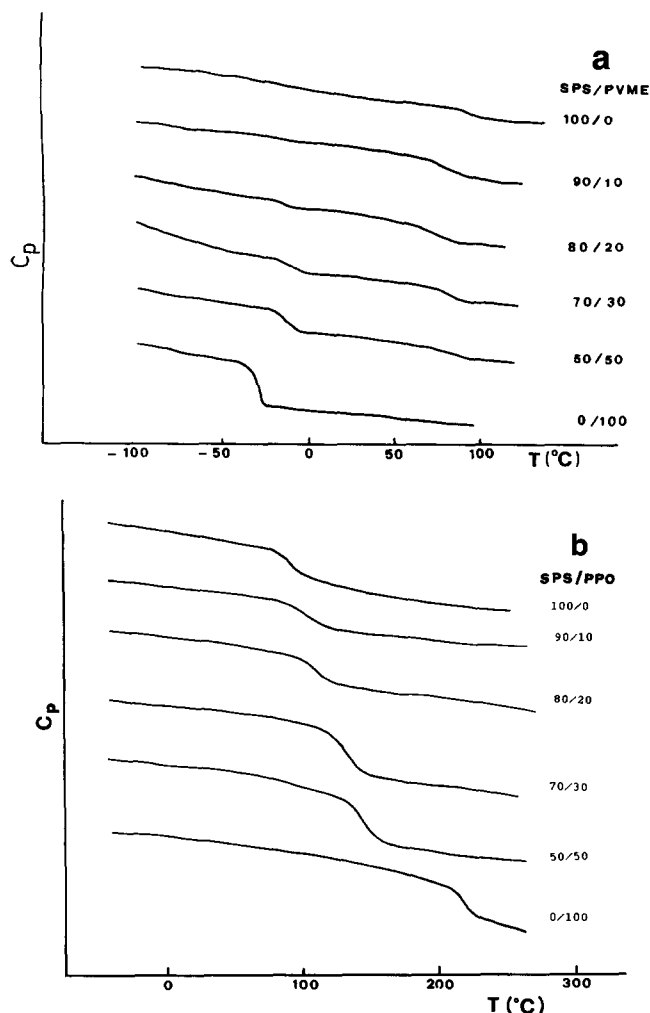


Figure 1 D.s.c. thermograms for the SPS/PVME (a) and SPS/PPO (b) blends

present, whose values are different from those of the homopolymers, and remain constant with composition. These results could indicate that one homogeneous amorphous phase is present when the PVME content in the blend is not higher than 20%; on increasing the PVME content, the resulting blend separated into two phases, one rich in SPS and the other rich in PVME. The composition of these two phases is independent of the nominal blend composition, whereas it depends on the phase diagram of the system and could be approximately found by applying the Fox equation¹²:

$$1/T_g(\text{blend}) = (W/T_g)(\text{PVME}) + (W/T_g)(\text{SPS})$$

In this way, for blends containing more than 20 wt% of PVME, the compositions of the two phases turn out to be 83/17 SPS/PVME for the SPS-rich phase and 13/87 SPS/PVME for the PVME-rich phase respectively.

Morphology

Optical micrographs of films of SPS and SPS blends are reported in Figures 2–4. For the SPS/PVME blends the melt is not homogeneous (see Figure 3). At 340°C, for all blend compositions, small spherical domains dispersed in a melt matrix are visible. The particles are spherical with dimensions ranging between 5 and 20 μm . This result indicates that liquid–liquid separation occurred during the preparation and/or the melting of the samples. During the crystallization, the SPS

spherulites occluded the PVME particles mainly in the intraspherulitic regions.

In the case of SPS/PPO the melt is homogeneous (see *Figure 4*). After crystallization there is no evidence that the PPO forms segregated domains in inter- and/or intraspherulitic contact regions. This indicates that for

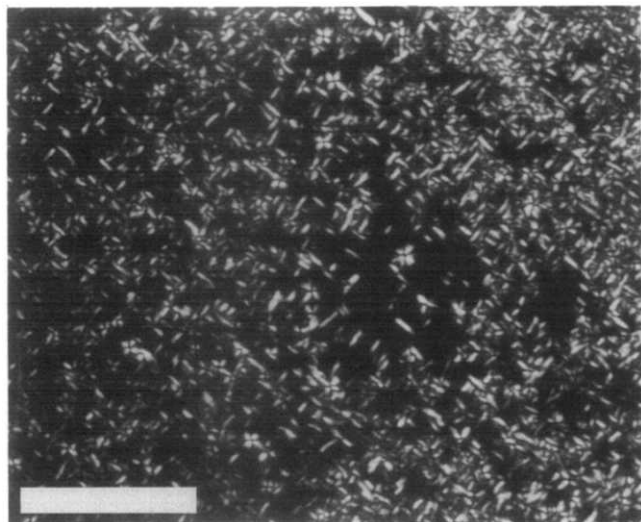


Figure 2 Optical micrographs of a film of SPS crystallized at $T_c = 251^\circ\text{C}$ (scale bar $200\ \mu\text{m}$)

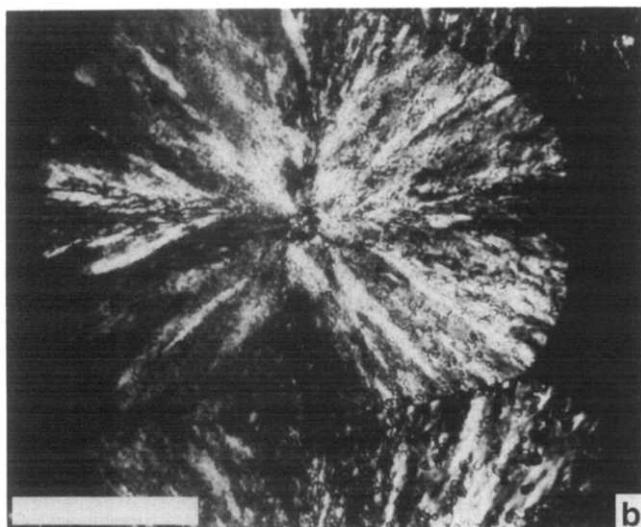
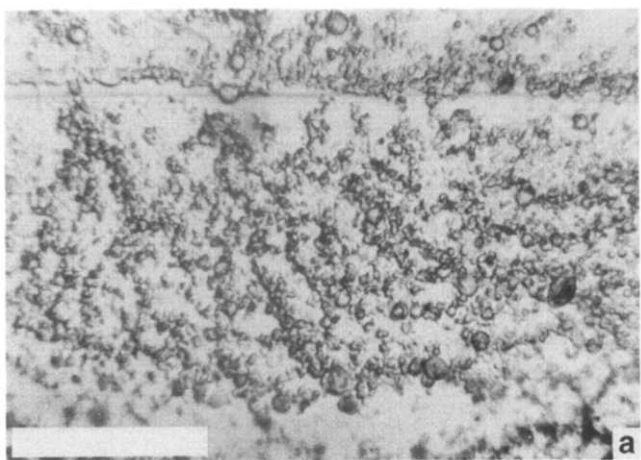


Figure 3 Optical micrographs of a film of SPS/PVME 80/20 blends: (a) in the melt at $T = 340^\circ\text{C}$; (b) after crystallization at $T_c = 235^\circ\text{C}$ (scale bar $200\ \mu\text{m}$)

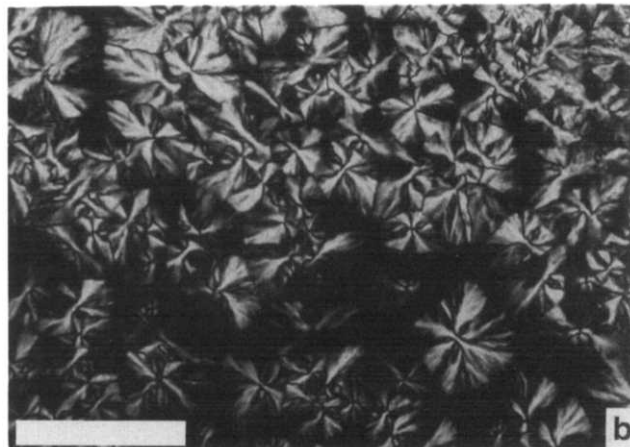
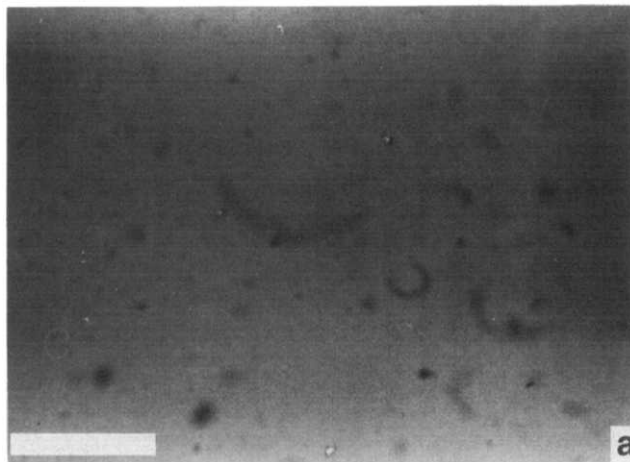


Figure 4 Optical micrographs of a film of SPS/PPO 80/20 blends: (a) in the melt at $T = 340^\circ\text{C}$; (b) after crystallization at $T_c = 240^\circ\text{C}$ (scale bar $100\ \mu\text{m}$)

these blends the PPO is present in interlamellar zones and therefore suggests miscibility at the molecular level of the two components, at $T > T_c$ in the amorphous state, in agreement with the d.s.c. data.

The addition of PVME or PPO strongly influences the apparent nucleation density of the SPS (*Figures 2–4*). In both cases the dimension of the spherulites at the end of the crystallization process is larger than that of pure SPS, indicating that both the polymers reduce the nucleation ability of the SPS.

It seems that this effect is more marked in the case of PVME. In the case of SPS/PVME blends, some of the heterogeneous SPS nuclei can diffuse in the PVME-rich phase during the mixing and the pre-melting process, as reported also in the case of IPS/PVME blends⁹.

In the case of SPS/PPO blends the decrease in the apparent nucleation density can be accounted for by considering the effect of dilution of the SPS nuclei in the melt blend. Work is in progress on this hypothesis.

Crystallization process

Spherulite growth rate. The values of the spherulite growth rate, G , of the SPS/PPO and SPS/PVME blends together with that of undiluted SPS are plotted in *Figure 5* as a function of T_c . It is interesting to note the different effects that the PPO and the PVME have on the spherulite growth rate of SPS. For the same T_c the addition of PVME causes an increase of the spherulite growth rate, whereas the presence of PPO produces a decrease in G . Moreover, in the case of SPS/PVME blends the increase in G is composition-independent; for the

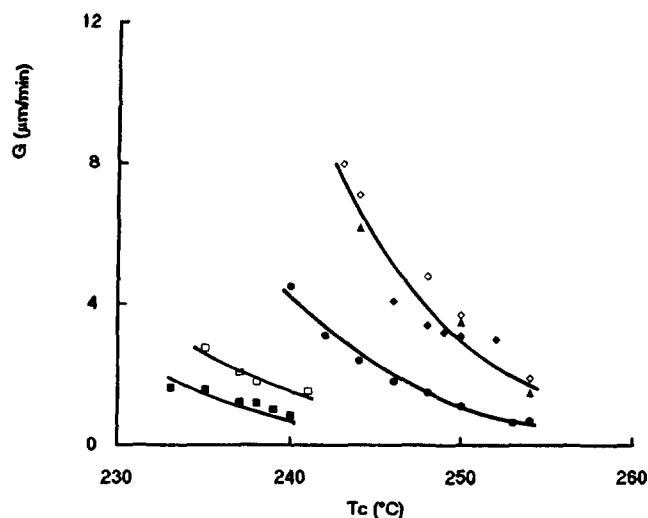


Figure 5 Spherulite growth rate, G , for SPS/PVME and SPS/PPO blends as a function of T_c , for different blend compositions: (●) SPS; (□) SPS/PPO 90/10; (■) SPS/PPO 80/20; (▲) SPS/PVME 80/20; (◇) SPS/PVME 70/30; (◆) SPS/PVME 50/50

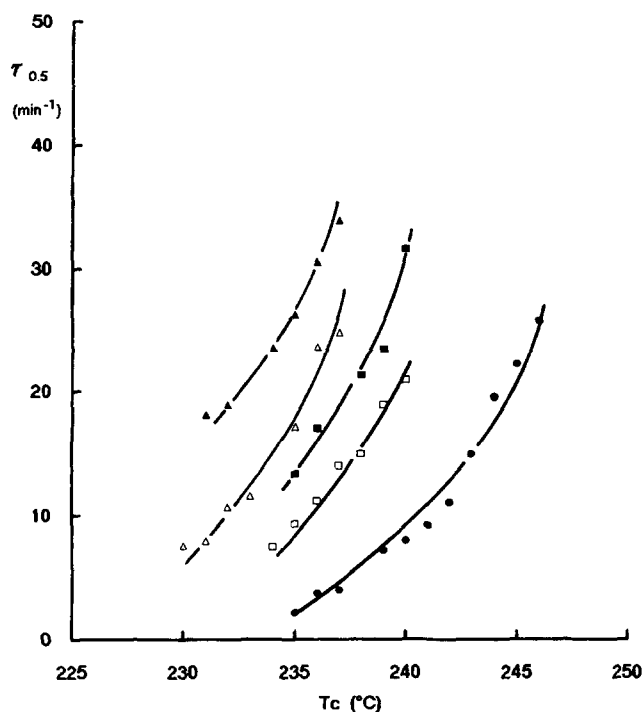


Figure 6 Half-time of crystallization, $\tau_{1/2}$, as a function of T_c for SPS/PVME and SPS/PPO blends for different blend compositions: (●) SPS; (□) SPS/PPO 90/10; (■) SPS/PPO 80/20; (△) SPS/PVME 90/10; (▲) SPS/PVME 80/20

SPS/PPO blends the size of the decrease is function of composition.

The different crystallization behaviours of the two blends may be explained by taking into consideration the different degrees of miscibility of the SPS/PPO and SPS/PVME blends and the effect that the PVME or the PPO has on the T_g of the blends and hence on the mobility of the crystallizable molecules in the melt at the crystallization temperature.

In fact, following the kinetic theory of crystallization^{10,11} of polymers, for a given T_c , the spherulite growth rate is dependent on two energetic terms: the energy required for the formation of a nucleus of critical size, $\Delta\phi^*$; and the energy required for the transport of the crystalline segments in the melt, U^* . In general, for a polymer blend

the presence of a diluent always causes an increase in the energy of formation of a critical size nucleus, $\Delta\phi^*$ (refs. 13 and 14). As regards the energy required for the transport of the macromolecules in the melt, ΔU^* , the glass transition temperatures of the blend and of the crystallizable component must also be taken into account: in fact when $T_g(\text{blend}) > T_g(\text{crystallizable component})$, $\Delta U^*(\text{blend})$ is predicted to be higher than $\Delta U^*(\text{crystallizable component})$; when, instead, $T_g(\text{crystallizable component}) > T_g(\text{blend})$, $\Delta U^*(\text{blend})$ is lower than $\Delta U^*(\text{crystallizable component})$ ^{9,14}.

In the case of SPS/PPO blends, owing to the higher T_g of the blend with respect to the pure SPS, the energy required for the transport of the crystalline segments in the melt, ΔU^* , is also increased. So for this blend, both ΔU^* and $\Delta\phi^*$ negatively influence G .

For the SPS/PVME blends instead, the addition of PVME causes a decrease of the T_g of the SPS-rich phase blend and hence of ΔU^* . This decrease probably overcomes the increase of $\Delta\phi^*$ and gives rise to the enhancement in G . For the SPS/PVME blends the constancy of G with composition can be explained taking into account the fact that, for this blend, phase separation is found. Therefore the composition of the SPS-rich phase, involved in the crystallization process, is constant and independent of nominal composition.

Overall crystallization rate. The half-time of crystallization plotted as a function of T_c for the two blends under investigation is reported in Figure 6. The addition of both PPO and PVME to SPS causes an increase in $\tau_{1/2}$. This effect increases with composition and for the same composition is dependent on the component added to SPS. In fact it can be noted that the addition of PVME causes a larger increase in the half-time of crystallization than that of PPO. This is probably due to the fact that addition of PVME influences more negatively the nucleation process of SPS, as reported in the 'morphology' section.

The Avrami equation¹⁵ was used to analyse the data of the bulk kinetics of crystallization:

$$\ln[-\ln(1-X_t)] = \ln K_n + n \ln t$$

where X_t is the weight fraction of crystallinity at time t , n is the Avrami index and K_n is the overall kinetic rate constant. The experimental data fit the Avrami equation well. The values of the Avrami index, contrary to the theoretical prediction, are non-integral for both samples and range between 2 and 3, indicating mixed crystallization and nucleation mechanisms, in analogy to what happened for isotactic PS⁹.

CONCLUSIONS

The crystallization, the morphology and the phase structure of two syndiotactic polystyrene-based blends were studied and determined. The blends analysed were SPS/PVME and SPS/PPO.

The two blends behaved very differently. For any T_c and composition the SPS/PPO blends are miscible, whereas the SPS/PVME was phase-separated. For the melt miscible SPS/PPO blends at a given T_c the overall crystallization rate and the spherulite radial growth rate were strongly depressed with respect to pure SPS. For the SPS/PVME blends, instead, the addition of PVME caused an increase in the spherulite growth rate, whereas a decrease in the overall crystallization rate

was observed. For both blends the morphology after crystallization was spherulitic, but in the case of SPS/PVME spherical domains of the PVME-rich phase were observed in intraspherulitic regions, whereas there was no microscopic evidence of segregated domains for the SPS/PPO blends.

The different degrees of miscibility and viscosity of the melt were considered to be responsible for the differences in morphology, phase structure and crystallization behaviour of the two blends.

The influence of the PS tacticity on the miscibility of PS/PVME blends was also determined by comparison of the miscibility of the SPS/PVME blend with blends containing isotactic and atactic polystyrene. The analysis led to the hypothesis that PS with regular molecular configuration (IPS, SPS) is less miscible with PVME than the APS.

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