Dependence of Electrical Properties of Polypropylene Isomers on Morphology and Chain Conformation

Liberata Guadagno¹*, Marialuigia Raimondo¹, Vittoria Vittoria¹, Antonio Di Bartolomeo², Vincenzo Tucci³, Biagio De Vivo³, Patrizia Lamberti³

¹Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno, Via Ponte Don Melillo – 84084 Fisciano (SA), Italy

²Dipartimento di Fisica “E. Caianiello”, Via S. Allende – 84081 Baronissi (SA), Italy

³Dipartimento di Ingegneria dell’Informazione e Ingegneria Elettrica Università di Salerno, Via Ponte Don Melillo – 84084 Fisciano (SA), Italy

*corresponding author: lguadagno@unisa.it
Phone number +39 089 964142 – Fax +39 089 964057
Summary

The electrical properties of polypropylene isomers were correlated to the morphology and chain conformation of differently obtained isotactic (iPP) and syndiotactic (sPP) samples. In the case of iPP, a crystallized and a smectic sample were prepared, whereas in the case of sPP two crystalline helical samples and a mesophase with the chains in trans planar conformation were considered. The phase composition was obtained for all samples comparing X-ray diffractograms and transport properties of vapors, that give the crystallinity and the amorphous fraction respectively. The fraction of mesophase was obtained by difference of the previous values. The study of the morphology evidenced similarities and differences among the samples, that were discussed and correlated to the phase composition. The electrical conductivity was measured for all samples, and the syndiotactic isomer showed the lowest value as well as a dependence on the structure. Instead, the isotactic isomer showed the same behavior for either polymorph. Based on the structural and electrical results, a phenomenological explanation of the conduction mechanisms taking place in the different forms has been proposed. In particular, the current in iPP seems to be controlled by Schottky emission, i.e. by field assisted thermo-ionic injection of carriers from the electrode into the polymer, whereas for the sPP more than one mechanism is likely to be effective, although the ionic transport appears as the predominant one. The experimental data confirm a different behaviour of the ionic conduction properties for the different polymorphs, highlighting the greater insulating characteristics of the mesomorphic structure of the syndiotactic isomer.
INTRODUCTION

In recent years thermoplastic polymers are more and more replacing conventional materials, either in structural high performances or in very qualified specialty applications, behaving as multifunctional materials. The lightness, the chemical resistance, the easiness to be thermally processed and oriented, the ability to assume a variety of shapes and sizes, the relatively slow aging and weathering, the possibility to tailor the chemical structure for specific applications, etc. make these materials very advantageous and therefore worth of a thorough study.

Indeed, polymeric materials, more than others, show a complex frame of interwoven relationships among microstructure, processing procedures and physical properties.\textsuperscript{1-2} As an example, the orientation of the crystalline phase and the amount of the amorphous one are highly relevant for the mechanical performance of a polymeric material in structural applications.\textsuperscript{3-4} Furthermore, cold drawing of polymeric films, performed to optimize their orientation, clearly shows that different initial structures can affect the final properties of the fibers\textsuperscript{5-9}.

Attempts to rationalize the response of polymers in terms of their structure and morphology have been performed mainly for mechanical properties. It has been shown that the mechanical properties depend indeed on many factors, often hardly correlated, such as phase composition, features of the amorphous component, crystallite size and perfection, morphology and polymorphism. This is particularly relevant in olefinic polymers, such as iso and syndio polypropylene or polystyrene, that exhibit highly variable mechanical properties, strongly depending on orientation, polymorphism and morphology.

Instead, limited investigation has been barely developed so far for other physical properties, as barrier, electrical or optical properties, in spite of their increasing importance for high-value specialized applications.

Concerning the electrical properties, polymers generally behave as insulating systems, although in the last decades the exciting discover of conductive polymers has opened new theoretical developments as well as important applications. In electrical insulation technology materials with higher reliability are required for severe operating conditions. To display a good performance, an insulating material should have a very low electrical
conductivity, a high dielectric strength, a strong resilience to aging and to degradation due to temperature variations and weathering.

Recent developments in metallocene catalysts have made it possible to tailor the tacticity of polypropylene and to obtain a highly syndiotactic polymer (sPP), showing new and interesting properties with respect to the isotactic one (iPP). It is more ductile at room temperature and possesses greater impact strength, besides showing elastic properties when oriented. Moreover, some studies have suggested that the electrical properties of sPP are superior to those of iPP.\textsuperscript{10-12} This effect translates into higher resistance to pulse breakdown with respect to iPP. This characteristic, combined with a consistently higher resistance to impact than iPP, makes sPP particularly suitable for insulation in electrical machinery. It has been also shown that sPP is particularly appropriate in the manufacturing of insulated cables and therefore could be used to substitute conventional cross-linked polyethylene, which requires complex cross-linking using peroxides for successful welding.\textsuperscript{11} However, the complex polymorphic behavior and the consequent morphology of syndiotactic polypropylene make it difficult to define a complete correlation among the physical properties and an accurate comparison with the isotactic isomer or other polymers. As a matter of fact few studies have been performed to investigate the physical properties of different structures and morphologies.

Four crystalline forms of sPP have been described so far. Form I and II are characterized by chains in the \((T_2G_2)_n\) helical conformation,\textsuperscript{13-14} whereas form III and IV present chains in trans planar and \((T_6G_2T_2G_2)_n\) conformations, respectively.\textsuperscript{15-16} Different kinds and amounts of disorder of the crystalline phase, depending on the degree of stereoregularity and the mechanical and thermal history, were described in rapidly crystallized samples. In specimens quenched from the melt in a bath at 0°C for many days, the presence of a trans-planar mesophase was recognized\textsuperscript{17-19}. Mixtures of different polymorphs are obtained in the usual processing conditions and this makes it difficult to associate the measured physical properties to a well characterized structure and morphology. On the other hand, although the isotactic isomer of polypropylene shows only the helical conformation of the chains, it can crystallize in a monoclinic form or in a liquid-like smectic form, lacking a true order.

In this paper we report investigations regarding the electrical properties of well characterized sPP and iPP polymorphs. The samples were obtained in well defined
conditions of crystallization and the structural organization was investigated with different techniques, such as X-ray diffraction (WAXD) and atomic force microscopy (AFM).

The charge transport properties of iPP and sPP polymorphs have been analyzed and some possible correlations of the electric behavior with the morphological and structural properties of the polypropylene isomers are proposed. We emphasize the pioneering nature of our work, that has to be indentation as first step towards the comprehension of a complex topic, whose study requires extensive experimental efforts on chemical, structural and electrical characterization as well as on theoretical modeling of molecular dynamics and carrier transport mechanisms.

EXPERIMENTAL

Materials. Syndiotactic polypropylene (sPP) was synthesized according to a previous procedure. The polymer was analyzed by $^{13}$C-NMR spectroscopy at 120°C on an AM 250 Bruker spectrometer operating in the FT mode at 62.89 MHz, by dissolving 30 mg of sample in 0.5 mL of C$_2$D$_2$Cl$_4$. Hexamethyl disiloxane was used as internal chemical shift reference. It resulted composed of 91% syndotactic pentads. Isotactic polypropylene (iPP) (trade name iPP T30G) was obtained from Basell. It resulted composed of 88% isotactic pentads.

Samples Preparation. Three different polymorphs of sPP and two polymorphs of iPP were prepared for this work: sPPA, sPPB, sPPC, iPPS, and iPPM.

sPPA: polymer powders were molded in a hot press at 150°C, forming a film 100±10 μm thick, and rapidly quenched in a bath at 0 °C, and left in the cold bath for 3 days.

sPPB: polymer powders were molded in a hot press, at 150°C, forming a film 100±10 μm thick, and rapidly quenched in a bath at 100°C and left for 1 hour at this temperature.

sPPC: polymer powders were dissolved in orthodichlorobenzene at high temperature; afterwards the solvent was evaporated at 70°C, obtaining a 100±10 μm solvent cast film.

iPPS: polymer powders were molded in a hot press at 180°C, forming a film 100±10 μm thick, and rapidly quenched in a bath at – 80 °C and left in the cold bath for 3 hours.

iPPM: polymer powders were molded in a hot press at 180°C, forming a film 100±10 μm thick, and rapidly quenched in a bath at 100 °C and left in the cold bath for 3 hours.

Methods
**Wide-Angle X-ray Scattering.** Wide-angle X-ray patterns (WAXD) were obtained using a Brucker diffractometer (CuKα-Ni filtered radiation) with a scan rate of 1°(9)/min.

**Atomic force microscopy.** All samples investigated by atomic force microscopy were initially etched. The etching reagent was prepared by stirring 1.0 g potassium permanganate in a solution mixture of 95 ml sulfuric acid (95-97%) and 48 ml orthophosphoric acid (85%). The films were immersed into the fresh etching reagent at room temperature and held under agitation for 24 hours. Subsequent washings were done using a cold mixture of 2 parts by volume of concentrated sulfuric acid and 7 parts of water. Furthermore the samples were washed successively with 30% aqueous hydrogen peroxide to remove any manganese dioxide. The samples were washed with distilled water and kept under vacuum for 2 days.

The AFM data were acquired at room temperature in an ambient atmosphere (30%-40% humidity) in tapping-mode (TMAFM) with a NanoScope III multimode AFM (Digital Instruments, Santa Barbara (CA) using microfabricated silicon tips/cantilevers. All the images have been recorded simultaneously in height and in amplitude. The height images show the profile of the sample surface quantitatively (assuming that the oscillation of the cantilever is damped similarly at all locations), the amplitude images provide in some cases much clearer contrast of the surface feature compared to height images.

**Electrical Measurements.** In order to investigate the relations between the structure and the conduction mechanisms on the five different samples, measurements of d.c. conductivity as a function of the applied field have been performed on disc samples (thickness 100±10 μm, diameter 20 mm) equipped with vacuum deposited silver electrodes (diameter 5 mm). The measurement system, depicted in Fig. 1, remotely controlled by the software LABVIEW®, is composed by a high voltage generator FUG HCN 35-6500 (max output voltage 6.5 kV, max output current 5 mA), a pico-ammeter Keithley 6514 (min current 10⁻¹³ A), and a suitable shielded cell with temperature control.
For each step of the applied voltage, the current has been measured for 1200 s, an interval which has been found sufficient in order to achieve a quasi steady state value with variations less than 2%. A discharge time greater to 1800 s has been adopted in order to allow that the current reached the background noise level.

RESULTS AND DISCUSSION

Crystalline structure

In Fig. 2 we show the X-ray diffractograms (A, B, and C) of three sPP samples.
Fig. 2 X-ray diffractograms of sample sPPA, sPPB and sPPC.

For sample sPPA (sample A) the diffracogram shows a broad peak centered at about 2θ=17° with a shoulder around 2θ=24°. It was already shown that a sPP sample, stabilized at low temperature for long time, is characterized by chains in trans-planar conformation, organized in a new phase that was interpreted as a mesophase, or also paracrystalline disordered phase, containing lateral disorder in the packing of the trans-planar chains. A small reflection at 2θ=12.3°, corresponding to the (200) reflection of both the helical form I and form II is present too, indicating that a very small fraction of chains in helical conformation was formed, probably upon removing sample from the cold bath and keeping it at room temperature.

In Fig. 2 we also show the X-ray diffractograms of samples sPPB (sample B) and sPPC (sample C), crystallized at 100 °C and 70 °C in the solvent, respectively. Both samples crystallized in the most stable form I, characterized by the intense peaks at 12.3° of 2θ, corresponding to the (200) reflection, 15.9° of 2θ corresponding to the (010) reflection, and 20.8° of 2θ corresponding to the (210) reflection. In the case of sample C,
obtained by casting from orthodichlorobenzene at 70 °C, we observe an incipient peak, of low intensity, at 18.9° of 2θ. This peak indicates that a small fraction of the crystalline phase crystallized in the ordered modification of form I, in spite of a lower temperature of crystallization with respect to sample B. Although 70 °C is a low temperature to allow the ordered form crystallization, the presence of solvent molecules does have a mobilizing effect similar to an increase of temperature, and indeed the incipient crystallization of the ordered form is visible in the X-ray pattern.

The diffraction patterns for the samples crystallized in the helical form I (B and C samples) indicate that qualitatively the amorphous contribution is different in the two samples. The phase compositions of samples B and C were investigated using the combination of two different techniques: X-ray diffraction and transport properties of vapor at low activity. The calculation of the phase composition using this two combined techniques is particularly useful when in the semi-crystalline samples is present also a mesophase together with the crystalline and amorphous phase. This method was found valid in the case of isotropic samples of isotactic \(^{21}\) and syndiotactic polypropylene.\(^{22}\)

Previous investigations of the samples structure, here analyzed, allowed to determine the phase composition, in terms of fraction of amorphous and crystalline component and mesophase present in each sample. The results are reported in Table 1.

The crystallinity (\(\alpha_c\)) of sample B is about 30 %, higher than that of sample C (\(\alpha_c = 24\%\)). Moreover, the profile sharpness of sample B qualitatively indicates larger crystals than in sample C. For samples B and C, the size of crystallites \(D_{hkl}\) in the direction perpendicular to the reflecting (hkl) planes is calculated using the Sherrer equation: \(^{23}\)

\[
D_{hkl} = \frac{K\lambda}{w\cos\theta}
\]

where \(D\) is the crystallite size, \(\lambda\) is the wavelength of the employed X-rays, \(\theta\) is the diffraction angle, \(w\) is the half-height width, and \(K\) a constant generally assumed as 0.9.

The results are also reported in Table 1 for the values of \(D_{2θθ}\), the coherent crystalline domain size in the direction perpendicular to the (200) planes, and of \(D_{θ1θ}\), perpendicular to the (010) planes. As expected, the values found for the crystallite dimensions are smaller in the case of sample C.
Table 1  Crystallinity, \( \alpha_c \), Crystallite Coherence Lengths Perpendicular to Reflection Planes 200 (\( D_{200} \)) and 010 (\( D_{010} \)), Fraction of Amorphous Phase, \( \alpha_a \), and Mesophase Fraction, \( \alpha_m \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \alpha_c ) (%)</th>
<th>( \alpha_a ) (%)</th>
<th>( \alpha_m ) (%)</th>
<th>( D_{200} ) (Å)</th>
<th>( D_{010} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9 ± 1</td>
<td>79 ± 5</td>
<td>12 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>30 ± 2</td>
<td>59 ± 3</td>
<td>11 ± 2</td>
<td>584 ± 25</td>
<td>433 ± 13</td>
</tr>
<tr>
<td>C</td>
<td>24 ± 1</td>
<td>73 ± 3</td>
<td>3 ± 0.5</td>
<td>448 ± 15</td>
<td>351 ± 11</td>
</tr>
</tbody>
</table>

Estimated errors are supplied.

In Fig. 3 the X-ray diffractogram of iPP, crystallized at 100°C (sample M) or quenched at – 80 °C (sample S), are shown. In diffractogram of sample M, we observe the peaks of the most common crystal form in iPP that is the \( \alpha \)-phase having a monocline crystal structure. In fact, we can note the most intense peaks at \( 2\theta = 14.1^\circ, \ 2\theta = 17.0^\circ, \ 2\theta = 18.6^\circ, \ 2\theta = 21.3^\circ, \ 2\theta = 21.9^\circ \), corresponding to the \((110), (040), (130), (111), (131)/(041)\) reflections respectively. From the diffractogram, we derived the crystallinity of the sample as the ratio of the integral intensity under all crystalline peaks to the sum of integral intensities under the crystalline peaks and amorphous halo. The results are shown in tab. 2, where it is also reported the crystallites size.

In the diffractogram of sample S, the smectic iPP is apparent, showing the main peaks at 14.8° and 21.8° of 20. The fraction of smectic phase was investigated by transport properties of an organic vapor, by comparing the sorption of the sample with the sorption of a completely amorphous sample. Indeed it was found that the smectic phase is impermeable to the vapors at low activity, allowing the determination of the phase composition\(^{21}\). The present sample shows a smectic phase of 0.50, in very well agreement with previous results.
Fig. 3 X-ray diffractogram of iPP, crystallized at 100°C (M) or quenched at 0°C (S).

Table 2  Crystallinity, $\alpha_c$, Crystallite Coherence Lengths Perpendicular to Reflection Planes 110 ($D_{110}$), 040 ($D_{040}$), 130 ($D_{130}$) and Fraction of Amorphous Phase.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\alpha_c$ (%)</th>
<th>$\alpha_a$ (%)</th>
<th>$D_{110}$ (Å)</th>
<th>$D_{040}$ (Å)</th>
<th>$D_{130}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>59 ± 3</td>
<td>41 ± 2</td>
<td>287 ± 10</td>
<td>276 ± 9</td>
<td>170 ± 6</td>
</tr>
</tbody>
</table>

Therefore the two isotactic polymorphs, monoclinic and smectic, have a similar fraction of ordered phase (0.50 and 0.59 respectively).

**Morphology**

In Fig. 4 we show the AFM photos of sample A at two different magnifications, scan size 20 µm (top image) and scan size 1,15 µm (bottom images).
Fig. 4 AFM images of A sample at magnification of 20 μm and 1.15 μm. (left, height images; right, amplitude images).

In this sample, mainly organized in a mesophase with the chains in trans-planar conformation, no spherulitic morphology is evident. A featureless surface is observed in top image, with a slight roughness. In the height images (left) dark regions appear, which indicate less ordered material that has been removed by the etching procedure, corresponding to deeper regions in the AFM images. Such regions could contain amorphous material or entanglements due to chain folding. In the bottom image a higher magnification is shown, where globular structures are observed, with diameter of about 0.06 μm, generated by the coalescence of ordered domains. However, observing the finer details of the globular entities, a lamellar structure can be observed. In particular in the right lower side of the photo at scan size 20 μm, we observe a bundle of parallel lamellae with lozenge shape, characterized by lateral dimensions of about 3 and 6 μm. Globular
structures of small size (about 0.06 μm) are visible, containing smaller lamellae with a random orientation. Such morphology, for the first time observed for the mesophase of sPP in a previous paper, was found in a qualitative agreement with the nearly bidimensionality suggested by the obtained Avrami coefficients and in a quantitative agreement with the fractal dimension D of 1.71 evaluated for the AFM images\(^{24}\). At higher magnification we can observe that the globular structures are very interpenetrated with the amorphous matrix.

In Fig. 5 the AFM photo of sample B at two magnifications is reported.

![AFM images of B sample at magnification of 20 μm and 3.91 μm. (left, height images; right, amplitude images).](image)

**Fig. 5** AFM images of B sample at magnification of 20 μm and 3.91 μm. (left, height images; right, amplitude images).
In this case, spherulites of about 5, 6 μm are clearly evident; they are full up, showing many mutual contacts and a reduced inter-spherulitic amorphous phase. This means that the amorphous fraction of sample B (59% as shown in Table 1) is mainly located in trapped domains among intra-spherulitic regions; in fact the stacks of parallel lamellae of spherulitic structure extend up to the boundaries of the adjacent spherulites (see fig. 5 at magnification 3.91 μm). This observation has also been confirmed by images acquired in contact-mode (not reported here). In higher magnification of fig.5, long lamellar crystals with an average thickness of ca. 30-60 nm can also be observed inside the spherulites.

The AFM photo of sample C reported in fig. 6 shows smaller spherulites with respect to B sample (about 4 μm of diameter). At variance with sample B, in this case the spherulites are immersed into an amorphous matrix completely segregated. The high amorphous fraction of sample C (73%) is located in the inter and intra-spherulitic regions. Also in this case, the average thickness of lamellar crystals is of the same order of magnitude of that found in the B sample. In conclusion, although these two last samples (B and C) have very different amorphous fractions (59 % and 73%) differently distributed, they show lamellar crystals of similar dimension.
Fig. 6 AFM images of C sample at magnification of 20 μm and 10 μm. (left, height images; right, amplitude images).

In fig. 7 the AFM photo of isotactic polypropylene crystallized at 100°C is shown.
Very well developed spherulites are evident, much larger than those of sPP crystallized at the same temperature. They are impinged and clearly show the inside lamellar structure. Instead, the smectic sample of iPP, shown in Fig. 8, at a magnification of 20 and 12.5 μm, does not show an evident structure.
However if we enlarge the photos of both the monoclinic and the smectic sample of iPP (Fig. 9, at a magnification of 990 nm) we observe a fine structure very similar for both samples, constituted by ordered zones that were defined “lump crystals”\textsuperscript{25}. They are hierarchically organized in the monoclinic sample, into lamellae and into spherulites, whereas in the smectic sample they remain without a superior organization. The amplitude image of sample S seems to show areas where there is no structure to be seen, but a more deep investigation through comparison with the height image shows that the flattest areas, in the amplitude image, are simply constituted of ordered “grain” of smaller size, so the more the magnification increases, the more the two polymorphs (M, S) show analogy in the morphology.

\textbf{Fig. 8} AFM images of S sample at magnification of 20 μm and 12.5 μm. (left, height images; right, amplitude images).
Electrical Properties

Polymers can be considered as disordered materials, disorder being attributable to chemical or structural defects, in which the electric transport may take place, due to either electrons or holes, through localized states in the forbidden gap. In particular, amorphous phase in semicrystalline materials constitute disordered regions with respect to the ideal crystalline structure\textsuperscript{26}. Due to the structure complexity it is likely that more than one conduction mechanism is active in the same material. An excellent review concerning the mechanisms of the charge transport in polymers, with particular reference to polyethylene is presented in a recent paper\textsuperscript{27}. As pointed out therein, different experimental techniques, such as space charge detection, electroluminescence experiments, etc., must be combined to map charge distribution at different space and time scales inside a dielectric and develop accurate models of the electrical conduction in polymers. Nevertheless, to identify the prevailing conduction mechanisms in our samples and propose suitable correlations with their morphological and structural properties, we can rely on measurements of
integral averaged quantities, such as current, and fit experimental data into the theoretical laws of the available macroscopic models. Despite of the limitations of such approach, a first insight on the conduction mechanism is achieved.

We have investigated if the underlying conduction processes in our systems can be attributed to mechanisms controlled by electrode-polymer interface, i.e. field-assisted (Schottky) thermo-ionic emission, or those governed by bulk phenomena. For these latter phenomena we have analysed whether the current density $J$ vs. electric field $E$ can be attributed to the Poole-Frenkel mechanism in which the charge motion occurs due to the release of charge carriers from traps via field assisted lowering of the trap depth or to a hopping process in which the carriers may move from site to site by getting over a potential barrier.

In particular, the Schottky field-assisted thermo-ionic emission at the electrode-polymer interface is given by\(^2^8\)

$$J_S = A_C T^2 e^{-\frac{\phi_S - \beta_S \sqrt{E}}{kT}}$$

(1)

where $A_C$ is the emission constant, $\beta_S = \sqrt{\frac{e^3}{4\pi\varepsilon_0\varepsilon_r}}$ is the Schottky coefficient, $k$ is the Boltzmann constant, $\varepsilon_0\varepsilon_r$ is the material permittivity, $e$ is the electron charge, $T$ is the absolute temperature and $\phi_S$ is the height of the potential barrier at the conductor-insulation interface.

In the Poole-Frenkel model the $J$ vs. $E$ relation has the following expression:

$$J_{PF} = B e^{-\frac{\phi_{PF} - \beta_{PF} \sqrt{E}}{kT}}$$

(2)

where $\beta_{PF} = 2\beta_S = 2\sqrt{\frac{e^3}{4\pi\varepsilon_0\varepsilon_r}} = \sqrt{\frac{e^3}{\pi\varepsilon_0\varepsilon_r}}$ is the Poole-Frenkel coefficient which is double that of the Schottky model, $\phi_{PF}$ is the variation of the potential barrier associated to a trap, $B$ is a constant and the other symbols are the same as in the Schottky model\(^2^8\).

Finally, the hopping mechanism is described by:
\[ J = 2ne\lambda\delta e^{-\frac{\phi}{kT}} \sinh \left( \frac{\lambda eE}{2kT} \right) \] (3)

where \( n \) is the ions concentration, \( \lambda \) is the hopping distance, \( \delta \) the attempt-to-escape frequency.

In Fig. 10 the \( J \) vs. \( E \) plots are reported for the different systems. We observe that iPP is more conductive, by about two orders of magnitude, than sPP, in accordance with similar results already reported in literature\(^{10}\). The similar behaviour and values of conductivity for sample with an apparently unlike morphology (large spherulites with a lamellar internal structure in sample M and no spherulites for sample S), may be justified by considering that the structure at the nanoscale is indeed very similar. In fact, as shown in Fig. 9, they are mainly constituted by lump crystals which may (sample M) or may not (sample S) be hierarchically organised in lamellae and spherulites and exhibit the same amount of amorphous phase.

Moreover, smectic and monocline iPP do not exhibit sensible variations in the conductivity, whereas, on the other side, the crystalline samples (B and C) of the syndiotactic isomer, are characterised by an increase of the current density of about one order of magnitude with respect to that of the mesophase sample (A).
Fig. 10  Plots of the log J vs log E for the 5 samples.

The search for the model able to fit the experimental data is accounted for in Figs. 11-13. In particular, in Fig. 11 the Schottky plot, i.e. log(J) vs. sqrt(E), is shown for the different materials. In Fig. 12 the Poole-Frenkel curves, i.e. log(J/E) vs. sqrt(E), are depicted, whereas in Fig. 13 the effectiveness of the hopping behaviour is tested. The inserts in the Figures show the correlation coefficients R^2, indicating the goodness of the fit.

For the iPP, the highest value of the correlation coefficient, (R^2=0.996 for M and R^2=0.998 for S) is found for the Schottky mechanisms, which is therefore as the predominant one. In this case, the current is limited by the injection of carriers from the electrode into the polymer.

The correlation coefficients and the values of the high frequency permittivity obtained from the Poole-Frenkel plots of Fig. 12 indicate that this mechanism may be less effective in explaining charge transport. Indeed, the resulting R^2 are the lowest for all the samples and the values of ε are too high for polypropylene samples (the accepted ε at value in the temperature range 30-120°C is about 2.2). Such a result seems to exclude the charge detrapping mechanism, which may happen at much higher electric fields, as reported by other groups^{11,28}.

For the sPP samples, as shown in Fig.13, the ion hopping mechanism appears as the prevailing one (R^2=0.969 for A, R^2=0.989 for B and R^2=0.981 for C) in accordance with previous results^{11}. Indeed, for sPP samples more than one mechanism could be effective, which explains the lower value of R^2 achieved for these materials. Moreover, it can be observed that the behaviour of the curves in terms of slope conforms to the fraction of ordered phase (α_c + α_m) of the different samples. In fact, as evidenced by the plots of Fig. 11, isotactic samples exhibiting equal ordered phase fraction (~60%) are characterised by log(J) vs. sqrt(E) curves of identical slope; for syndiotactic samples the ordered phase degree, together with the slope of the plots, increases from the mesophase (~21%) to the solvent cast (~27%) to the quenched isomers (~41%).

The hopping distances obtained from the interpolation and reported in Fig. 13 are estimated by considering that \( J = a \cdot \sinh(b \cdot E) \) and \( \lambda = \frac{2kT}{e} b \). It results that the sample B is characterized by a greater \( \lambda \) (9.66 nm), whereas the mesophase exhibits a lower value.
Such distances are almost double than those found in [2] at a higher temperature (70°C), but comparable with the value of 6.1 nm found for bi-axially oriented PP at 50°C. It should be considered that in the B sample, as evidenced by the morphological analysis, the crystals have larger diameter and a compact spherulitic phase, thus leading to the conclusion of a greater hopping distance for the charge carriers with respect to the sample C, characterized by spherulites with smaller dimensions wrapped up into an amorphous matrix completely segregated. This observation can be considered also as a good explanation of the different current densities (about one order of magnitude) between the A and C samples. In fact, although such samples are characterised by a similar fraction of amorphous phase (\(\alpha_a\) in Table 1) and hopping distance, the rigidity of the amorphous phase is lower in sample C with respect to sample A (\(\alpha_m\) in Table 1). Such a parameter may influence the attempt-to-escape frequency \(\delta\) of equation (3) and thus explain the lower current density for samples A. This result would imply better insulating performances for the mesophase form of sPP. However, it should be taken into account that a thermal treatment would lead to the more ordered Form I which is characterised by a higher conductivity. Such a result has been confirmed also by the X-ray diffractogram (see Fig. 14) of sample A after a thermal treatment at 90°C (sample sPPA90°C).
Fig. 11  Schottky plots for the different materials. In the insert the correlation coefficient $R^2$ and the relative permittivity resulting from the interpolation are reported.
Fig. 12 Poole-Frenkel plots for the different materials. In the insert the correlation coefficient $R^2$ and the relative permittivity resulting from the interpolation are reported.

Fig. 13 Ionic plots for the sPP samples. In the insert the hopping distance $\lambda$ resulting from the interpolation and the correlation coefficient $R^2$ are reported.
Concluding Remarks

In this paper we have presented the results of a characterization of different polymorphs of sPP and iPP in order to correlate the electrical transport properties with the structural organization of each sample. A thorough investigation of phase composition and morphology led to the following conclusions:

- The sPP helical samples, crystallized in Form I, show a different amorphous phase although the lamellar crystals were found of similar dimensions.
- The sPP sample with chains in trans-planar conformation, organized into a mesophase, shows the highest amorphous fraction and a globular structure in which the ordered domains are very interpenetrated with the amorphous matrix.
The two isotactic polymorphs, that is monoclinic and smectic, show a comparable fraction of amorphous phase and a morphology similar in the fine details. The conduction mechanisms taking place in the different forms are in agreement with those found in previous studies. In particular, the major conduction mechanism for the iPP seems to be of the Schottky type, whereas the ionic transport appears as the predominant one in the sPP. The experimental data confirm that the lower crystallinity and different structural characteristics of sPP leading to higher electrical resistivity than iPP could favour the use of such a polymer as a very interesting insulating material in cable technology.

References