Nanoporous Crystalline Phases of Poly(2,6-Dimethyl-1,4-phenylene)oxide
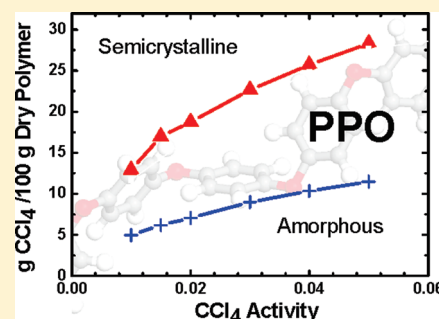
Christophe Daniel,[†] Simona Longo,[†] Gianluca Fasano,[†] Jenny G. Vitillo,[‡] and Gaetano Guerra*,[†]

[†]Dipartimento di Chimica, NANOMATES and INSTM Research Unit, Università di Salerno, Fisciano (SA) 84084, Italy
[‡]Dipartimento di Chimica IFM and NIS Centre of Excellence, Università di Torino, Via Giuria 7, Torino 10125, Italy

ABSTRACT: Crystalline modifications, exhibiting largely different X-ray diffraction patterns, have been obtained for poly(2,6-dimethyl-1,4-phenylene)oxide (PPO), by gel desiccation procedures as well as by solvent-induced crystallization of amorphous films. The choice of the solvent allows controlling the nature of the crystalline phase. Both amorphous and semicrystalline samples of this commercial thermoplastic polymer exhibit a high uptake of large guest molecules (like, e.g., benzene or carbon tetrachloride), both from vapor phases and from diluted aqueous solutions. Surprisingly, the semicrystalline PPO samples present guest solubility much higher than fully amorphous PPO samples. These sorption experiments, as well as density measurements and classical Brunauer–Emmett–Teller (BET) experiments, clearly indicate that the obtained PPO crystalline phases are nanoporous. For these thermally stable PPO-based materials exhibiting nanoporous crystalline and amorphous phases, many applications are predictable.

KEYWORDS: nanoporous crystalline modifications, co-crystalline phases, sorption of organic compounds, nitrogen adsorption isotherms

◼ INTRODUCTION

The improvement of molecular recognition, separation, and storage techniques represents a strategic industrial and environmental objective. This objective is mainly pursued by the design, preparation, and development of nanoporous (microporous by IUPAC definition) materials, that is, by solids containing interconnected pores of less than 2 nm in size. Conventional microporous materials are constituted by amorphous or crystalline inorganic networks (mainly activated carbon, silica, and zeolites). In recent years many nanoporous materials based on organic components have been developed and particularly relevant are those based on polymers because of their typical robustness and durability associated with easy processing to suitable products, like films, membranes, foams, gels, and aerogels.

Commercially relevant nanoporous amorphous polymeric materials were already prepared more than 30 years ago, by formation of hyper-cross-linked polymer networks.[1] Such materials are assembled under kinetic control using irreversible polymerization reactions and are obtained initially as solvent-swollen gels, which on solvent removal display permanent porosity.[1] Highly cross-linked networks have been also prepared around suitable template molecules, so that when the template is removed a receptor site of the correct size and shape is achieved.[2]

Nanoporous amorphous polymeric materials can be also obtained for linear rigid polymers, which do not have sufficient conformational flexibility to pack space efficiently and hence are described as high free volume or ultrapermeable polymers (e.g., polyacetylenes, fluorinated polymers, polyimides, and polyphenyleneoxides).[3] Many amorphous organic nanoporous materials have been prepared by polymers with highly rigid and contorted molecular structures to provide "awkward" macromolecular shapes that cannot pack space efficiently because they do not possess rotational freedom along the polymer.[4]

Recently nanoporous crystalline polymeric materials have been also obtained, for a stereoregular polymer (syndiotactic polystyrene, s-PS).[5] In particular, this commercially available thermoplastic material is able to form co-crystalline phases[6] with several low-molecular-mass guest molecules and, by suitable guest extraction procedures,[7] two nanoporous crystalline forms δ (monoclinic, with empty space organized as cavities)[8] and ε (orthorhombic, with empty space organized as channels)[9] can be obtained. Both crystalline frameworks rapidly absorb volatile organic molecules, even if present in traces in air or water and hence are promising for applications in chemical separations[10] and molecular sensorics[11] and are able to form co-crystalline phases even with very small gas-molecules.[12]

These nanoporous polymeric crystalline phases, because of the presence of all identical crystalline cavities (or channels), present, with respect to the nanoporous polymeric amorphous phases, the advantage of higher guest selectivity.[13] Moreover, by controlling the orientation of the host polymeric crystalline phase it is possible to control, also at macroscopic level, the orientation of the cavities and channels as well as of the possible guest molecules. In this respect, it is worth citing that for s-PS, by suitable processing involving co-crystallization with low-molecular-mass guest molecules, it is possible to achieve the

unprecedented formation of three different kinds of uniplanar orientations,[14] as well as of two different kinds of uniplanar-axial orientations,[15] which allow to reach a three-dimensional orientational order of the all identical cavities. This allows active guest orientation control[16] for co-crystalline films that have been proposed as advanced optical (e.g., fluorescent and photoreactive),[17] electric,[18] and magnetic[19] materials. Moreover, for the nanoporous phases, the different kinds of uniplanar orientation have been shown to be helpful to control guest diffusivity.[20,12b,12c] It is also worth adding that availability of crystalline and co-crystalline s-PS films with different kinds of uniplanar orientation allows the establishing fine structural features, like, for example, experimental evaluation of the orientation of transition moment vectors of host and guest vibrational modes, with respect to the host chain axes.[21]

Polymeric nanoporous crystalline phases have been until now described only for s-PS while new nanoporous crystalline phases are expected for other regular and stereoregular polymers.[6h] In this paper the occurrence of nanoporous crystalline phases exhibiting very high guest solubility, already for low guest activity, is described for poly(2,6-dimethyl-1,4-phenylene)oxide (PPO), that is, a linear regular polymer, which as s-PS has the advantage to be a commercial thermoplastic polymer. This result is particularly relevant because PPO exhibits a high free volume or ultrapermeable amorphous phase and has been recognized as a membrane material with high permeation parameters.[22] Although few papers have recognized that PPO crystalline phases can play a role in gas sorption and transport processes,[4a,23] no correlation between the amount or nature of the crystalline phase and guest sorption properties has been reported. This is mainly due to the scarce information available in the literature relative to the crystalline phases of PPO,[23,24] which is well-defined only for co-crystalline phases with few guest molecules (α-pinene, decalin, tetralin).[25]

■ EXPERIMENTAL SECTION

Materials. The PPO used in this study was purchased by Sigma Aldrich and presents a molecular mass $M_w = 50000$.

PPO gel samples were prepared in hermetically sealed test tubes by heating the mixtures above the boiling point of the solvent until complete dissolution of the polymer and the appearance of a transparent and homogeneous solution had occurred. Then the hot solution was cooled down to room temperature where gelation occurred.

PPO powders were obtained by treating these gels with a SFX 200 supercritical carbon dioxide extractor (ISCO Inc.) using the following conditions: $T = 40\ ^\circ C$, $P = 250$ bar, extraction time $t = 300$ min. PPO amorphous powders have been obtained by treating PPO/decalin gels with the same carbon dioxide extractor, for 16 h.

PPO amorphous films, $50-100\ \mu m$ thick, were obtained by compression molding after melting at $290\ ^\circ C$. The crystallization of these amorphous films has been induced by vapor sorption procedures at different temperatures. The solvent was removed from the crystallized films by the above-described extraction procedure with supercritical carbon dioxide. The density of film samples was determined by flotation, at room temperature, in aqueous solutions of $CaCl_2$.

Characterization Techniques. X-ray diffraction patterns were obtained on a Bruker D8 Advance automatic diffractometer operating with a nickel-filtered CuKα radiation. The degree of crystallinity of powders and films was obtained from the X-ray diffraction data, by applying the standard procedure of resolving the diffraction pattern into
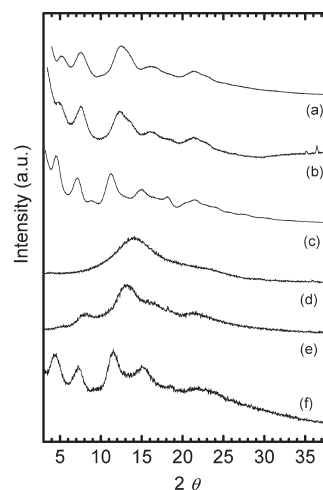

Figure 1. X-ray diffraction patterns of PPO samples, after complete solvent extraction by supercritical carbon dioxide: (a–d) powders, as obtained from gels in benzene (a), DCE (b), CCl$_4$ (c), and decalin (d); (e–f) films, as obtained by compression molding and crystallized by sorption of benzene (e) or CCl$_4$ (f).

two areas corresponding to the contributions of the crystalline and amorphous fractions (for the 2θ range $6°-35°$).

Fourier Transform Infrared (FTIR) spectra were obtained at a resolution of $2.0\ cm^{-1}$ with a Vertex 70 Bruker spectrometer equipped with deuterated triglycine sulfate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to $0.01\ cm^{-1}$ using a He–Ne laser. A total of 32 scans were signal averaged to reduce the noise.

The content of the guest molecules in the films was determined by the intensity of FTIR guest peaks, as calibrated by thermogravimetric measurements. Thermogravimetric measurements (TGA) were performed with a TG 209 F1 equipment from Netzsch.

The vapor sorption measurements have been carried out at $35\ ^\circ C$ with a VTI-SA symmetrical vapor sorption analyzer from TA Instruments.

Surface area, pore volume, and pore size distribution were obtained by N_2 adsorption measurements carried out at 77 K on a Micromeritics ASAP 2020 sorption analyzer. All the samples were outgassed for 24 h at $30\ ^\circ C$ before the analysis. The specific surface area of the polymers was calculated using the Brunauer–Emmet–Teller (BET) method,[26] while the pore diameter and the pore size distribution were evaluated using the DFT (Density Functional Theory) method on the basis of the cylindrical pore model proposed by Jaroniec et al.[27] The micropore volume has been determined with the t-plot method,[28] adopting the equation of thickness reported in ref 29.

■ RESULTS AND DISCUSSION

PPO Powders and Films Exhibiting Different Crystalline Phases. As already described for PPO films cast from dilute solutions,[23b] the X-ray diffraction patterns and hence the structures of crystalline phases of PPO are extremely variable, depending on the crystallization procedure and mainly on the crystallization solvent.

The X-ray diffraction patterns of powders, as obtained by PPO gels in benzene, 1,2-dichloro-ethane (DCE) and CCl$_4$, after complete solvent extraction by supercritical carbon dioxide, are shown in Figures 1a, b, and c, respectively.

The X-ray diffraction patterns of the powders from benzene, DCE, and CCl$_4$ gels exhibit high degrees of crystallinity (in the range 55–60%) and present peaks being located at definitely

Table 1. Diffraction Angles (2θ), Bragg Distances (d), and Relative Intensities (I) of the Reflections Observed in the X-ray Diffraction Pattern of the PPO Semicrystalline Powders of Figure 1a−c, As Obtained by Complete Solvent Extraction from Gels[a]

PPO from benzene gels (Figure 1a)			PPO from DCE gels (Figure 1b)			PPO from CCl₄ gels (Figure 1c)		
2θ (deg)	d (nm)	I	2θ (deg)	d (nm)	I	2θ (deg)	d (nm)	I
5.15	1.70	m	4.85	1.80	w	4.55	1.95	s
7.65	1.15	s	7.55	1.15	s	7.15	1.25	s
						9.0	1.05	vw
12.5	0.70	vs	12.5	0.70	s	11.0	0.80	s
16.0	0.55	vw	16.0	0.55	w	15.0	0.60	m
			18.5	0.50	vw	18.0	0.50	w
						20.5	0.45	vw
21.5	0.40	w	21.5	0.40	w	21.5	0.40	w

[a] w = weak, m = medium, s = strong, v = very.

different diffraction angles, as listed in Table 1 columns 1−3, 4−6 and 7−9, respectively.

The X-ray diffraction patterns of the powders from decalin gels present only broad amorphous halos (Figure 1d) and clearly indicate the formation of fully amorphous PPO.

The X-ray diffraction patterns of amorphous PPO films (obtained by cooling from the melt, in a compression molding process), after crystallization induced by sorption of benzene at room temperature or carbon tetrachloride at 80 °C, followed by complete solvent removal, are shown in Figures 1e and 1f, respectively. These spectra are similar (although with lower degrees of crystallinity) to those of the powders obtained from gels with the same solvents, which are shown in Figures 1a and 1c, respectively.

It is worth adding that the patterns of Figure 1a,e (and of columns 1−3 of Table 1) are also similar to those of films cast from dilute PPO solutions in benzene or CS₂[23b] On the other hand, the patterns of Figure 1c,f (and of columns 7−9 of Table 1) are similar to those of films cast from dilute PPO solutions in chloro-benzene and bromo-benzene.[23b]

The whole set of the data of Figure 1 and Table 1 indicates that PPO can crystallize in markedly different crystalline phases. Additional results indicate that there is nearly a continuum of crystalline phases between two limit structures exhibiting highest and lowest 2θ values (columns 1−3 and 7−9 of Table 1). In fact, for instance, powders from gels subjected to complete solvent removal present a progressive shift of the diffraction peaks to lower 2θ values, along the sequence benzene ≈ tetralin > methylene chloride > 1,2-dichloroethane > α-pinene > trichlorobenzene > chlorodecane ≈ CCl₄.

Equilibrium Guest Sorption from Amorphous and Semicrystalline PPO Samples. Benzene and CCl₄ sorption experiments at 35 °C at pressures lower than 0.08 P/P_0 on amorphous and semicrystalline PPO powders have been conducted, and the main results have been reported in Figures 2A and 2B, respectively. In particular, semicrystalline powders obtained from gels in benzene (of Figure 1a) or in CCl₄ (of Figure 1c) and amorphous powder from decalin gel (of Figure 1d) have been compared. It is clearly apparent that large solvent uptakes occur for all PPO samples already at very low solvent activities, clearly confirming the presence of nanopores (microporosity). However, surprisingly, the lowest solvent equilibrium uptakes occur for the amorphous powder while the guest uptake of the two highly crystalline PPO powders is roughly double with respect to those of the amorphous powder. It is worth noting that the two highly crystalline powders, as obtained by benzene and CCl₄ gels,

although exhibiting the two limit crystalline structures of Figures 1b and 1d (of columns 1−3 and 7−9 of Table 1, respectively) present very similar and maximum vapor uptake.

For the sake of comparison, the benzene uptake from a δ nanoporous crystalline powder of s-PS, with a degree of crystallinity close to 30% is also shown, as gray curve and circles, in Figure 2A. The benzene sorption from the δ form s-PS sample, which for low activities absorbs guest molecules essentially only in the nanoporous crystalline phase,[7b,8c,10a,10b,12b,12c] is close to that one of the amorphous PPO sample and nearly one-half of the sorption from the semicrystalline PPO samples.

The extremely high sorption capability of these crystalline PPO phases is clearly confirmed by experiments of guest uptake from dilute aqueous solutions. The FTIR spectra of PPO films after equilibrium sorption of benzene, from a 10 ppm aqueous solution at room temperature, are compared in Figure 3 for an amorphous film and for the CCl₄-crystallized PPO film of Figure 1f. From the intensity of the benzene peaks, like that one at 676 cm^{-1} in Figure 3, it is immediately apparent that the benzene sorption from the semicrystalline film is nearly triple that for the amorphous film. A gravimetric calibration curve allows establishing that the equilibrium benzene sorption in the semicrystalline sample is close to 10 wt %. This benzene uptake corresponds to a concentration increase of 10 000 times and is also more than double that from an s-PS sample exhibiting the nanoporous δ phase.

The occurrence of a sorption capability of the PPO crystalline phases higher than for the amorphous phase is confirmed by classical BET experiments. The N₂ isotherms obtained for the PPO semicrystalline (from CCl₄ gel) and amorphous (from decalin gel) powders are compared in Figure 4, and their surface area, total pore volume, and micropore volume are reported in Table 2. The large surface area and pore volume possessed by the two PPO specimens are noteworthy, with an important contribution due to the presence of micropores (Table 2). Particularly impressive is the result that the semicrystalline sample possesses porosity and microporosity nearly double that of the fully amorphous sample.

Nanoporous and co-Crystalline Phases of PPO. The whole set of data of Figures 1−4 clearly indicates that the crystalline phases of PPO are nanoporous. In particular, in the usual approximation of the two-phase model of semicrystalline polymer samples, because the crystalline phases constitute roughly only 60% of the semicrystalline powders, the data of Figure 2
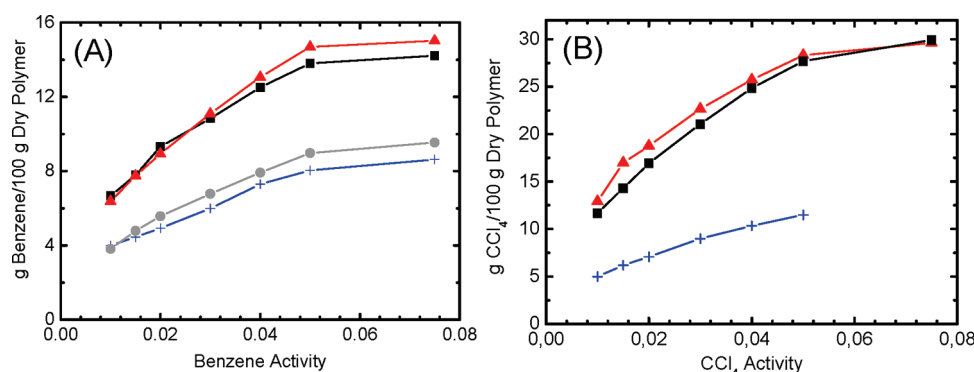
Figure 2. Benzene (A) and CCl_4 (B) gravimetric sorption isotherms, at 35 °C and at pressures lower than 0.08 P/P_0, on PPO samples: amorphous (blue plus symbols); benzene-crystallized (black solid squares), and CCl_4–crystallized (red solid triangles). Benzene uptake from an s-PS powder exhibiting the δ nanoporous crystalline phase (gray solid circles).
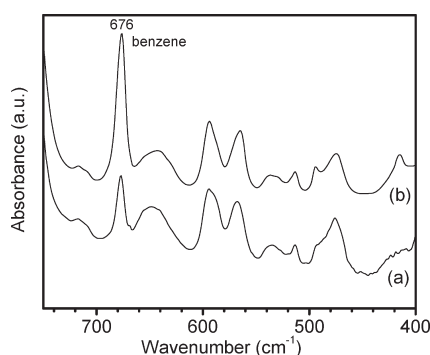

Figure 3. FTIR spectra in the wavenumber range 750–400 cm^{-1} of PPO films after equilibrium benzene sorption from 10 ppm aqueous solutions: (a) amorphous; (b) CCl_4–crystallized.
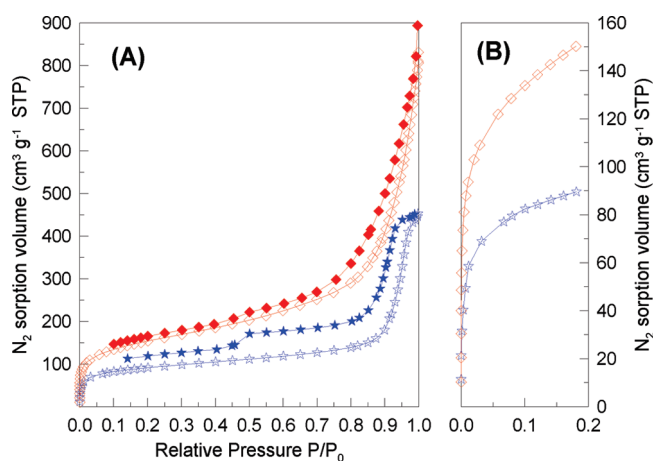

Figure 4. Volumetric N_2 adsorption isotherms recorded at 77 K on the amorphous (stars, blue) and semicrystalline PPO (diamonds, red). Empty and filled symbols refer to the adsorption and desorption branches, respectively. B shows the detail of the adsorption branch reported in A, for low pressures.

indicate that the crystalline forms present a guest solubility much higher than for the (also nanoporous) PPO amorphous phase.

For instance, for $P/P_0 = 0.075$, the benzene uptake is 8.5 wt % for the fully amorphous sample, 15 wt % for the semicrystalline

Table 2. Surface Area (m^2 g^{-1}) and Pore Volume (cm^3 g^{-1}) of the Polymers

	S_{BET}[a]	S_{micro}[a]	V_{tot}[b]	V_{micro}[c]
PPO/CCl_4	549	214	0.64	0.12
PPO amorphous	320	102	0.28	0.06

[a] Total area evaluated following the BET model in the standard 0.05 < P/P_0 < 0.25 pressure range. [b] Total pore volume calculated as volume of the liquid at $P/P_0 \approx 0.90$. [c] Micropore volume obtained from the t-plot.

sample (Figure 2A), and 19 wt % as calculated for the crystalline phase. This phenomenon becomes also more impressive for the sorption of the bulkier CCl_4 molecules (Figure 2B). In fact, for instance, the CCl_4 solubility for $P/P_0 = 0.075$ is nearly 13 wt % for amorphous PPO, higher for the highly crystalline powder (30 wt %), and is calculated to be very high for the nanoporous crystalline phase (41 wt %). It is also worth adding that although this weight uptake of the two guests in the crystalline phase is widely different, the corresponding molar uptake is similar, that is, for $P/P_0 = 0.075$, not far from 1 guest molecule per 3 monomeric units.

The nanoporous nature of these crystalline phases is confirmed by density measurements by flotation of film samples. In fact, the density of the semicrystalline film of Figure 1e (1.009 ± 0.002 g/cm^3) is lower than the density of fully amorphous PPO films (1.016 ± 0.004 g/cm^3). These data, by assuming a degree of crystallinity of 30%, as evaluated from the X-ray diffraction pattern of Figure 1e, allow predicting a density of the crystalline phase of roughly 0.99 g/cm^3.

A density of the crystalline phase lower than for the corresponding amorphous phase has been until now observed only for s-PS. In particular, s-PS samples exhibiting the nanoporous δ-form or ε-form present a density slightly lower than for fully amorphous samples (1.04 vs 1.05 g/cm^3),[8a,12a] corresponding to crystalline phase densities of 0.98 g/cm^3.[8b,9b]

It is worth adding that the described nanoporous crystalline modifications of PPO, as well as their sorption ability, present long-term stability also after many repeated guest sorption–desorption cycles. Moreover, we have verified that the guest sorption at room temperature of these semicrystalline polymer samples remains essentially unaltered after several hours of thermal treatments in air, at least up to 100 °C.

Additional X-ray diffraction experiments have been conducted to establish if the sorption of guest molecules into these nanoporous
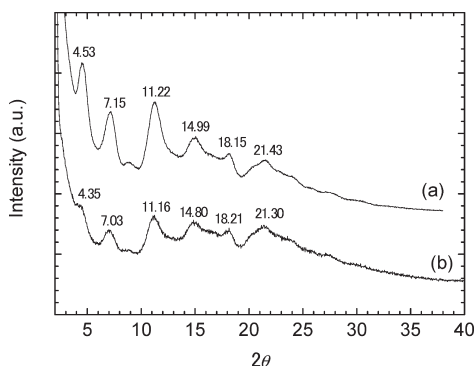
Figure 5. X-ray diffraction patterns of PPO powders, as obtained by solvent extraction from gel in CCl_4, before (a) and after (b) sorption of CCl_4 at room temperature (RT) and at $P/P_0 = 0.05$; CCl_4 content of nearly 28 wt %.

crystalline phases leads to the formation of co-crystalline phases, between the polymer-host and the low-molecular mass guest molecules. The X-ray diffraction patterns of the PPO semicrystalline powders of Figure 1a–c, as a consequence of also large guest uptakes, do not show any significant peak shift and only show reversible but minor changes of the relative intensity of the diffraction peaks. For instance, the X-ray diffraction patterns of the PPO semicrystalline powders of Figure 1c (CCl_4-crystallized) before and after CCl_4 equilibrium sorption at $P/P_0 = 0.05$ are compared in Figure 5a and 5b, respectively. The patterns show that the large CCl_4 uptake (overall: 28 wt %; calculated for the crystalline phase: 37 wt %) only leads to a decrease of the intensity of the low 2θ peaks ($<14°$) with respect to the high 2θ peaks.

This suggests that the location of the guest molecules into the empty space of the PPO nanoporous crystalline phases is characterized (at least for the considered guests) by a high degree of disorder.

■ CONCLUSIONS

The formation of highly crystalline or fully amorphous PPO powders can be obtained by solvent removal from gels, by making suitable selection of the solvent. Moreover, the choice of the gel solvent allows controlling the nature of the crystalline phase. In particular, X-ray diffraction patterns indicate the presence of many (if not a continuum of) modifications between two limit ones, exhibiting diffraction peaks at lowest (column 7 of Table1) or highest (column 1 of Table1) angles. Similar crystalline phases, although generally exhibiting lower degrees of crystallinity, can be also obtained by solvent induced crystallization in amorphous films.

As widely recognized, amorphous PPO is a high free volume, ultrapermeable phase, which exhibits very high guest solubility, already for low guest activity. Surprisingly, the semicrystalline PPO samples present a much higher solubility of many guests (e.g., benzene, CCl_4). These sorption results, as well as density measurements and classical BET experiments, clearly indicate that the PPO crystalline phases are nanoporous.

Preliminary X-ray diffraction data indicate that the considered guest molecules present a high degree of disorder into the empty space of PPO nanoporous crystalline phases.

Complete structural analyses, possibly based on X-ray diffraction data of oriented semicrystalline samples, will be needed. In fact, for the nanoporous crystalline phases, a precise knowledge of the cavities should allow to optimize their use for molecular

separations while for the co-crystalline phases a precise knowledge of active-guest location and orientation, with respect to the unit cell, should allow to optimize their use for functional materials.

Applications of polymeric nanoporous crystalline phases, until now only based on s-PS, are expected to be widely expanded in the near future. In fact, many applications are predictable for PPO nanoporous crystalline phases, which present with respect to nanoporous crystalline phases of s-PS the advantage of faster guest sorption kinetics, because of the nanoporous nature also of the amorphous phase, as well as the advantage of higher thermal stability.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +39-089-969558. Fax: +39-089-969603. E-mail: gguerra@unisa.it.

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