

Poly(2,6-dimethyl-1,4-phenylene) oxide/atactic poly(styrene) fibers with nanoporous crystalline phase

Mohit Pathak^a, Anita Manzi^a, Mariateresa Lettieri^b, Christophe Daniel^{a,*}

^a Dipartimento di Chimica e Biologia "A. Zambelli" and INSTM Research Unit, Università degli Studi di Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano, (SA), Italy

^b CNR-SPIN c/o Università degli Studi di Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano, (SA), Italy

ARTICLE INFO

Keywords:

poly(2,6-dimethyl-1,4-phenylene) oxide (PPO)
Fibers
Nanoporous crystalline phases
Volatile organic compounds sorption

ABSTRACT

The preparation of poly(2,6-dimethyl-1,4-phenylene) oxide/atactic poly(styrene) (PPO/PS) fibers with nanoporous crystalline (NC) phase through guest-induced crystallization of melt-spun amorphous fibers is for the first time reported. These NC PPO/PS fibers display exceptional capacity to absorb volatile organic compounds from dissolved in water at very low concentrations. The equilibrium uptakes and sorption kinetics of perchloroethylene (PCE) exhibit significantly higher values and faster rates compared to the corresponding amorphous fibers. Furthermore, it is noteworthy that the equilibrium uptakes of NC PPO/PS fibers are considerably higher compared to NC PPO films. The fast pollutant uptake exhibited by these innovative NC PPO/PS fibers makes them highly promising potential applications in the field of water pollutant remediation.

1. Introduction

Like many other polymers [1], commercially available poly(2,6-dimethyl-1,4-phenylene)oxide (PPO) and syndiotactic polystyrene (sPS) thermoplastic polymers, can easily form co-crystalline phases with many low molecular-mass guest molecules [2]. However, PPO and sPS are unique among polymers due to their ability to form nanoporous-crystalline (NC) structures, when subjected to specific guest removal procedures [3–6].

The NC forms of sPS have been intensively studied due their sorption properties and their potential applications in various fields such as water and air purification, sensor technology, catalysis, and active packaging [7–10]. The discovery of two NC forms named α and β forms characterized with lower densities than the amorphous phase has been also established more recently for PPO [5,6]. Because of the high efficiency of PPO NC in absorbing gas and volatile organic compounds (VOCs) from air or water even at low concentrations, numerous publications have focused in the recent years on the study of the transport properties of PPO NC [11–16]. In addition to the degree of crystallinity (i.e. amount of nanopores) [14], it has been shown that the sorption properties of PPO materials with NC phases can depend on the matrix forms (i.e. powder, film, or aerogel) but also for the case of films on the orientation of the NC phase. For instance, it has been observed that NC film with crystalline polymer chains preferentially perpendicular to the film plane

can display sorption kinetics being one order faster diffusivity than for a NC film with crystalline polymer chains preferentially parallel to the film plane [13]. Recently, it has been also shown that VOCs sorption kinetics is further increased for NC films with a high surface area (up to 600 m²/g) characterized by amorphous mesopores in addition to the crystalline nanopores [15].

In this paper, the preparation of poly(2,6-dimethyl-1,4-phenylene) oxide/atactic poly(styrene) (PPO/PS) fibers with NC phase being obtained guest-induced crystallization of amorphous melt-spun PPO/PS fibers is reported for the first time. The use of a blend instead of neat PPO was necessary in order to improve the processability of PPO that is challenging as a result of its high glass transition temperature.

Among the different matrix forms, the fiber morphology is particularly suitable for filter sorption devices for VOC removal from water due to their moderate pressure drop, large water/polymer contact area, high volume packing, and safer macroscopic morphology than fine powder. In order to assess a possible use of PPO/PS fibers in filter sorption devices, we have investigated the sorption of perchloroethylene (PCE), a widespread groundwater contaminant, in amorphous and NC PPO/PS fibers.

The results reported here show that PCE uptakes both from vapor phase and from diluted aqueous solutions are significantly higher and faster for NC fibers than for amorphous fibers. Moreover, we surprisingly found that NC PPO/PS fibers present a much higher PCE uptake from

* Corresponding author.

E-mail address: cdaniel@unisa.it (C. Daniel).

<https://doi.org/10.1016/j.polymer.2024.126777>

Received 19 November 2023; Received in revised form 26 January 2024; Accepted 6 February 2024

Available online 14 February 2024

0032-3861/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

diluted aqueous solutions than for the benchmark high surface area NC films.

2. Experiment section

2.1. Materials and samples preparation

All the solvents (limonene (>99.9%), perchloroethylene (PCE, >99.5%) and acetonitrile (ACN, >99.95%)) were purchased by Sigma Aldrich and used without any purification. Poly(2,6-dimethyl-1,4-phenylene)oxide/atactic polystyrene (PPO/PS) pellets with a PPO/PS composition equal to 70/30 and a glass transition temperature $T_g = 167\text{ }^\circ\text{C}$ (see Fig. S1 of the Supporting Information) were supplied by SABIC.

The spinning of PPO/PS blend was realized with a homemade laboratory-scale spinning line of International Fibers Group (Linz-Austria) equipped with a Norris Extruder. The extrusion process was performed at a temperature of $330\text{ }^\circ\text{C}$, while the header temperature was carefully maintained at $300\text{ }^\circ\text{C}$. In these conditions, fibers with a diameter of c.a. $50\text{--}60\text{ }\mu\text{m}$, 30 dTex, and 12.5 cN/tex were obtained. It is worth noting that trials to obtain fibers with a 90/10 composition have been unsuccessful due to the high glass transition temperature ($T_g = 196\text{ }^\circ\text{C}$) of the blend.

PPO/PS fibers with co-crystalline phase were obtained by immersion in liquid limonene for 1 h at room temperature. Then, fibers with PPO nanoporous crystalline phase were obtained after complete limonene extraction by immersion of the co-crystalline fibers in liquid ACN for 30 min at room temperature.

Amorphous and high surface area NC PPO films with thickness of c.a. $40\text{--}50\text{ }\mu\text{m}$ were prepared according to the methodology reported given in reference 15.

2.2. Characterization techniques

Two-dimensional wide angle X-ray diffraction (2D-WAXD) patterns were obtained with a D8 QUEST Bruker diffractometer operating with a nickel-filtered $\text{Cu K}\alpha$ radiation, by sending the X-ray beam parallel to the fibers surface (EDGE patterns). Degree of planar orientation (f_c) of the obtained fibers were calculated by using the Hermans' orientation function [17].

$$f_c = \frac{3\langle \cos^2 \gamma \rangle - 1}{2}$$

where $\langle \cos^2 \gamma \rangle$ is the average cosine-squared value of the angle γ between the c crystallographic axis and the fibers axis. f_c is equal to +1, 0 and -0.5 when the c -axes of all crystallites are parallel, random, and perpendicular to the fiber's axis respectively.

Fourier-transform infrared spectra (FTIR) were obtained with a Vertex70 Bruker spectrometer. Pike Technologies' Easy Diff accessory benchmark was used to collect FTIR spectra in diffuse reflectance infrared Fourier transform mode (DRIFT). 32 scans were signal averaged to reduce the noise.

Scanning electron microscopy (SEM) analysis of the fibers was performed with a LEO Evo 50 (Carl Zeiss AG, Oberkochen, Germany). The SEM images were collected at an acceleration voltage of 10 kV, a working distance ranging from 9 to mm, and a beam current of $30\text{ }\mu\text{A}$. Before observation, the investigated samples were coated depositing approximately 20 nm of gold to provide conductive surfaces and prevent their charging.

Vapor sorption measurements of perchloroethylene (PCE) has been performed with a VTI-SA symmetrical vapor sorption analyser from TA Instruments. The vapor-phase sorption measurements were carried out at $35\text{ }^\circ\text{C}$ for relative pressure p/p_0 (p_0 is the saturated vapor pressure) of the organic adsorbates in the range 0.01–0.05.

PCE absorption tests in polymer fibers were conducted from 50 ppm,

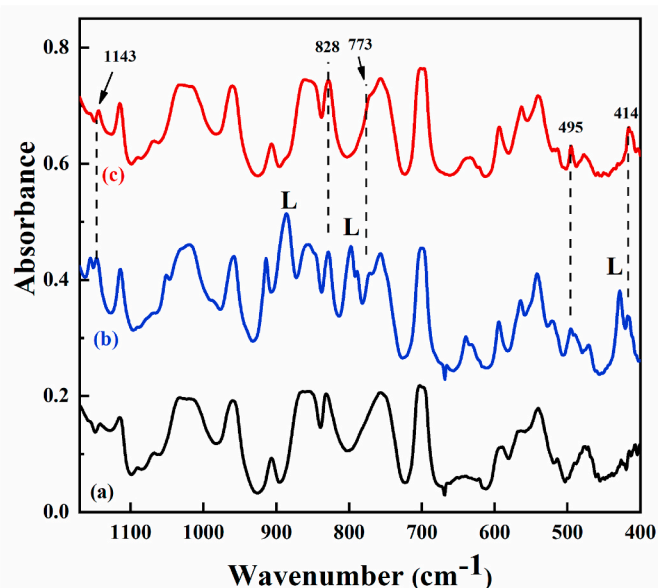


Fig. 1. FTIR spectrum of PPO/PS melt-spun fibers before (a) and after treatment with liquid limonene (b) and after successive limonene extraction with acetonitrile (c). In curve b, limonene bands are labelled with L. Curves b and c have been shifted vertically for the sake of presentation.

5 ppm and 500 ppb aqueous solutions at room temperature. The PCE uptake was monitored by the absorbance of the isolated PCE FTIR peaks at 800 cm^{-1} and 909 cm^{-1} . During sorption, the dilute aqueous solution was maintained homogeneous by continuous magnetic stirring. Calibration curves (see Fig. S2 of the Supporting Information) obtained from samples with a known amount of PCE determined by gravimetric analysis were used to determine PCE amount in the PPO/PS fibers.

3. Results and discussion

3.1. Characterization of NC PPO/PS fibers

The melt-spun PPO/PS fibers cannot be crystallized with typical solvents known to induce PPO co-crystallization such as toluene, benzene or carbon tetrachloride [18] that fully dissolve the fibers within a few minutes or less but are readily crystallized with limonene.

The FTIR spectra of the as-prepared melt spun PPO/PS fibers before (curve a) and after treatment with liquid limonene for 60 min (curve b) and after successive limonene extraction with acetonitrile (curve c) are reported in Fig. 1.

After treatment with limonene, the appearance of IR bands located at $1143, 828, 773, 495$ and 414 cm^{-1} typical of PPO co-crystalline phases in addition to limonene bands at $886, 798,$ and 428 cm^{-1} (labelled as L), indicates the solvent-induced crystallization of the fibers. After treatment with acetonitrile, the absence of the limonene bands and the maintaining of PPO crystalline bands shows a complete removal of the guest from the co-crystalline phase and the formation of a nanoporous phase. Moreover, the PPO crystalline bands located at $828, 773,$ and 414 cm^{-1} are characteristic of the NC α -form [6,18].

The SEM images of the PPO/PS fibers before and after limonene sorption/desorption are reported in Fig. 2.

The SEM images show that the fibrillary morphology is maintained after limonene sorption-desorption treatment. However, the occurrence of fiber etching and the formation of cracks are also clearly visible. The fiber etching occurring during the crystallization with limonene can be attributed to the dissolution of a small amount of polymer generating a weight loss of c.a. 7 wt %.

The 2D-WAXD patterns of the as-prepared PPO/PS fibers and of the

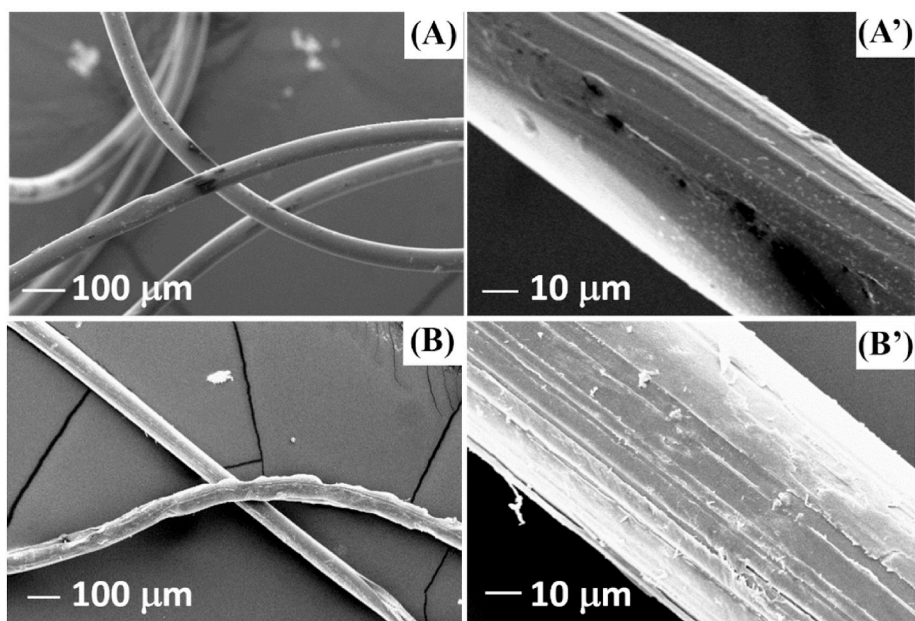


Fig. 2. SEM images of PPO/PS fibers before (A, A') and after (B, B') limonene sorption/desorption treatments.

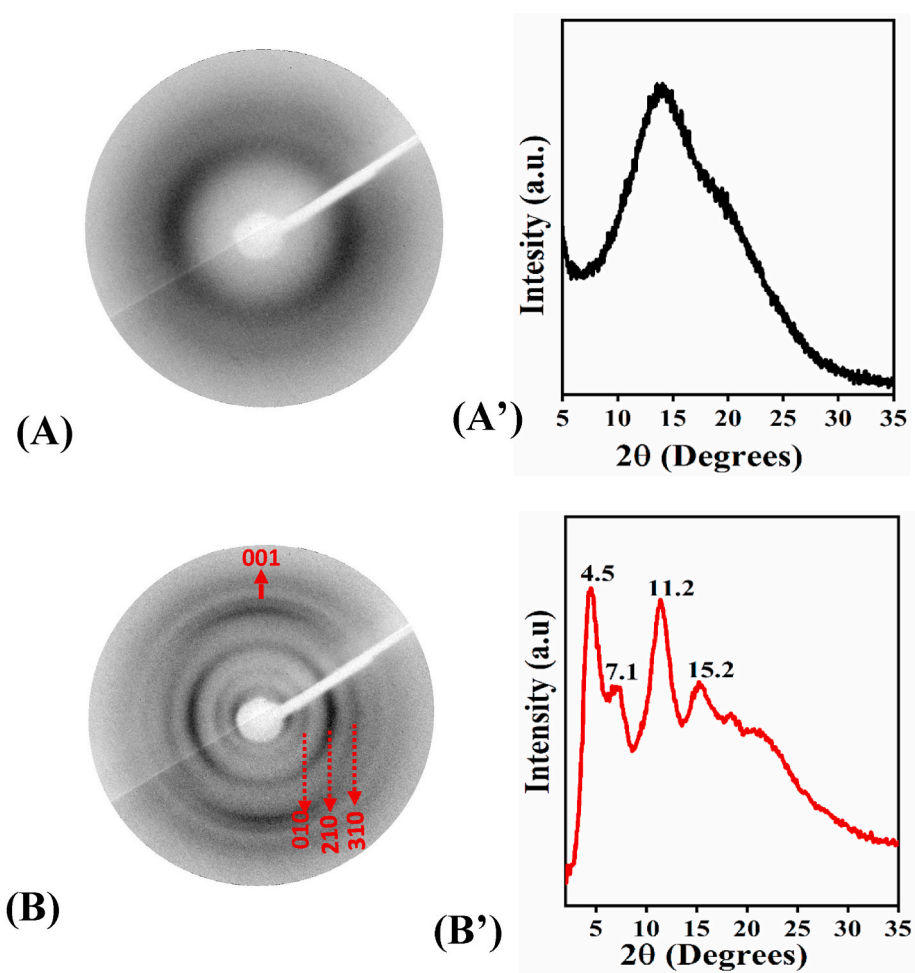


Fig. 3. (A, B) 2D WAXD patterns of as prepared PPO/PS melt-spun fibers (A) and PPO/PS fibers after co-crystallization with limonene and extraction with ACN (B). Fiber axis is vertical. (A', B') Equatorial intensity profiles of the corresponding 2D diffraction patterns.

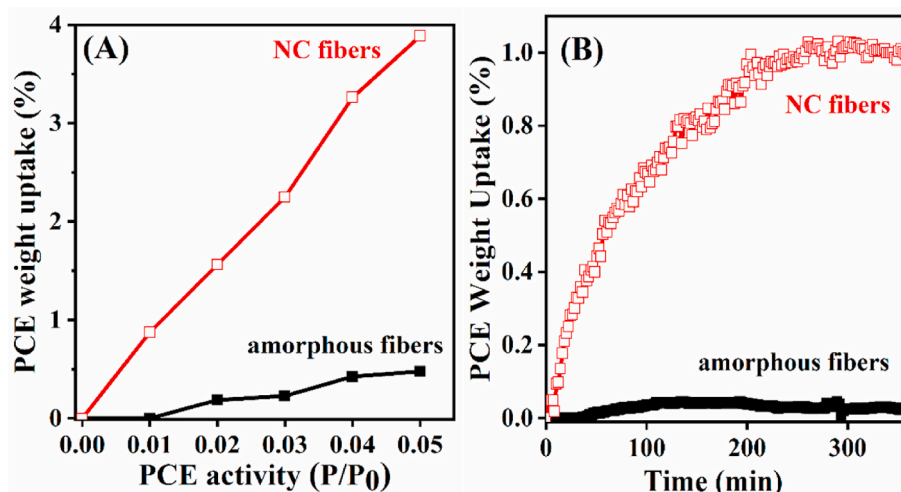


Fig. 4. PCE uptake values after 6 h for P/P₀ up to 0.05 (A) and sorption kinetics at 35 °C and relative pressure P/P₀ = 0.01 (B) for amorphous and NC PPO/PS fibers.

PPO/PS fibers after co-crystallization with limonene and extraction with ACN are shown in Fig. 3A and B, respectively while the corresponding equatorial intensity profiles are reported in Fig. 3A' and 3B'.

Fig. 3A and A' show that, as expected, the obtained melt-spun PPO/PS fibers are completely amorphous and unoriented.

The 2D pattern of the PPO/PS fibers after limonene sorption/desorption shows the presence of diffraction arcs (Fig. 3B), thus indicating the achievement of axial orientation of the crystalline phase without any mechanical stretching. The equatorial profile shown in Fig. 3B' is characterized by diffraction peaks at $2\theta_{\text{CuK}\alpha} \approx 4.5^\circ, 7.1^\circ, 11.2^\circ$ and 15.2° that clearly indicate the presence of the neat PPO nanoporous crystalline α -form [6,18] without inclusion of PS chains. This result is typical of miscible blends containing only one crystallizing component. In fact, during crystallization in such blend systems, the amorphous component diffuses away from the crystal growth front and is excluded from the crystalline phase [19]. The degree of crystallinity of the fibers evaluated from their melting enthalpy $\Delta H_m \approx 16.8 \text{ J/g}$ (see Fig. S1 of the Supplementary Material) and the enthalpy of the pure NC α form of PPO (i.e. $42 \pm 2 \text{ J/g}$ [20]) is $X_c \approx 38\%$.

It is worth adding that the guest-induced axially oriented crystallization has been previously observed for neat amorphous syndiotactic polystyrene (sPS) fibers [21]. The axial orientation of crystallites of unstretched sPS fibers during co-crystallization was attributed to the formation co-crystalline fibrils in confined space [21].

For NC PPO/PS fibers, the degree of orientation calculated from the (001) diffraction arc is c.a. 0.42 which is lower to the degree of orientation of NC sPS fibers that is in the range $0.7 < f_c < 0.8$ [21]. This lower degree of orientation may be due to a lower mobility of PPO chains due to the higher T_g of the PPO/PS blend with respect to neat sPS. Moreover, the entanglements of PPO with PS chains may also hinder the orientation of PPO crystalline phase.

3.2. Transport properties of amorphous and NC PPO/PS fibers

In order to gain valuable insights into the effectiveness of the NC fibers in removing VOCs from air and water, the perchloroethylene (PCE) uptake capacity and sorption kinetics of amorphous and NC PPO/PS fibers from vapor phase and from diluted aqueous solutions have been investigated. The choice of PCE was motivated by its widespread presence in contaminated aquifers due to its large use as a solvent for dry-cleaning and in many industrial activities such as degreasing, pesticide production, and chemical production. Due to its remarkable resistance to natural degradation processes, PCE can be retained in soil and groundwater for decades or even hundreds of years thereby presenting persistent environmental and health risks [22–24].

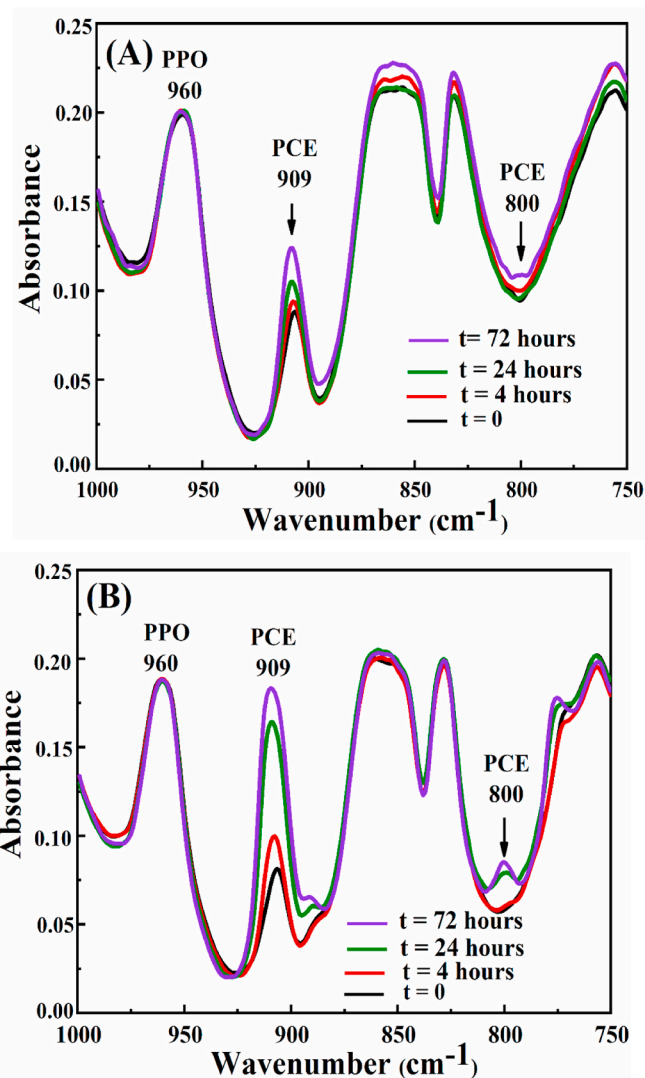


Fig. 5. FTIR spectra of the amorphous (A) and NC (B) PPO/PS fibers in the range of 1000–750 cm⁻¹ collected for different soaking times in a 50 ppm PCE aqueous solution. The spectra are normalized with respect to the PPO characteristic band at 960 cm⁻¹.

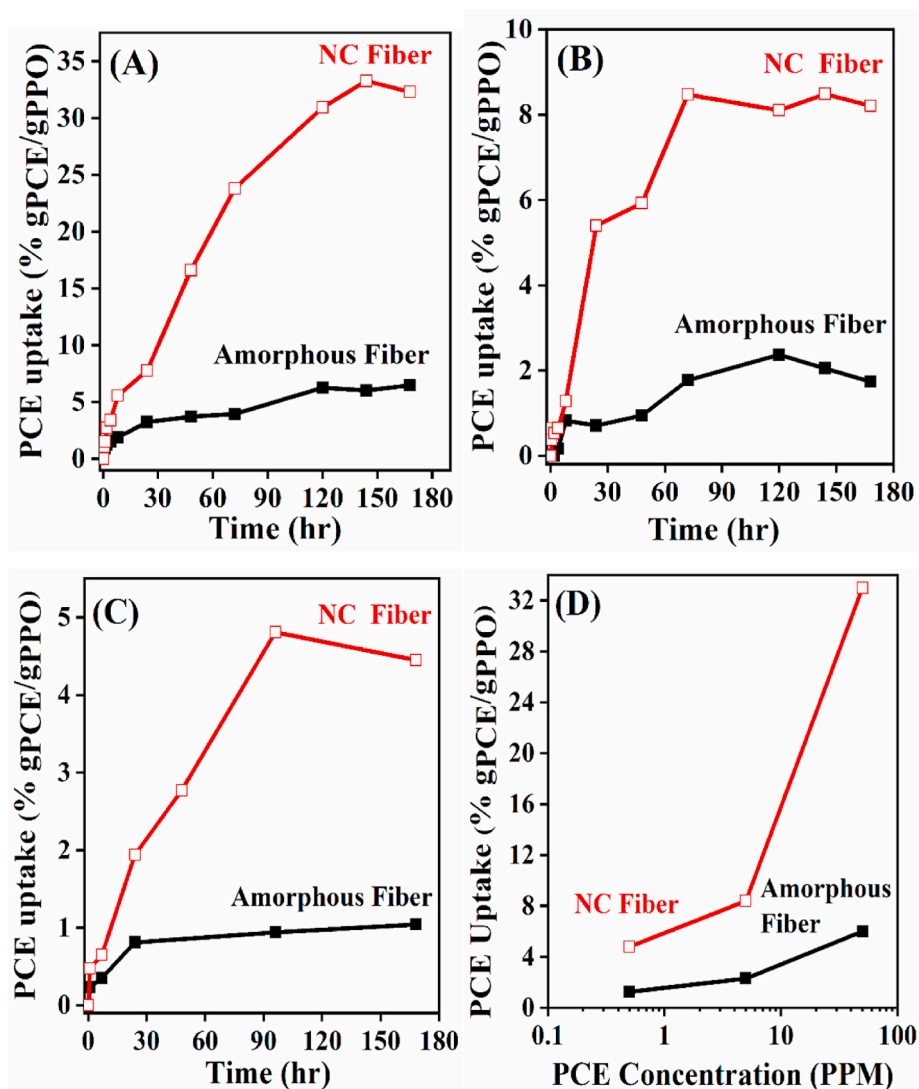


Fig. 6. Sorption kinetics of PCE from a (A) 50 ppm, (B) 5 ppm, and (C) 500 ppb aqueous solutions in amorphous and NC fibers. (D) PCE equilibrium uptake in PPO/PS fibers for 50 ppm, 5 ppm and 500 ppb aqueous solutions.

3.2.1. PCE sorption from vapor phase

The perchloroethylene (PCE) uptake after 6 h for relative pressure P/P_0 up to 0.05 and the PCE sorption kinetics at $P/P_0 = 0.01$ for the amorphous and NC PPO/PC fibers are reported in Fig. 4A and B, respectively.

Fig. 4A clearly shows the higher uptake capacity of the NC fibers with respect to the amorphous fibers for all the investigated range of PCE relative pressure. This difference is more important for the lower activities and in particular, at P/P_0 the uptake for amorphous fibers is nought. Moreover, it is also worth noting that, despite their large diameter of c.a. 60 μm , the NC fibers are characterized by a fast PCE sorption kinetics. The higher uptake of the NC fibers that is primarily due to the pores of PPO NC phase is consistent with previous works which have shown that the solubility of several VOCs and gas is significantly higher in semicrystalline nanoporous PPO than in the totally amorphous PPO [5,11–14].

3.2.2. PCE sorption from diluted aqueous solutions

The PCE sorption from diluted aqueous solutions in amorphous and NC fibers has been investigated with 50 ppm, 5 ppm and 500 ppb aqueous solutions by FTIR spectroscopy.

For example, the FTIR spectra in the range of 1000–750 cm^{-1} of amorphous and NC fibers collected for different soaking times in a 50

ppm aqueous PCE are shown in Fig. 5A and B, respectively.

We can observe both for amorphous and NC fibers an increase of the absorbance of the PCE bands located at 909 cm^{-1} and 800 cm^{-1} with soaking time due to the sorption of PCE in the fibers. The FTIR spectra also clearly show the higher absorbance of the PCE bands for the NC fibers that proves a higher PCE uptake of these fibers with respect to the amorphous fibers.

The amount of PCE in the fibers was evaluated using calibration curves obtained by thermogravimetric analysis of samples with a known amount of PCE and the PCE sorption kinetics for 50 ppm, 5 ppm and 500 ppb aqueous solutions in amorphous and NC fibers are reported in Fig. 6 A–C.

The results reported in Fig. 6 unequivocally demonstrate that, like for VOC sorption measurements from the vapor phase, the NC fibers exhibit significantly higher efficiency in VOC sorption from diluted aqueous solutions compared to the amorphous fibers.

For instance for the 50 ppm solution (Fig. 6 A), the amorphous fibers exhibit a PCE uptake of approximately 4 wt% after 48 h while the NC fibers demonstrate a significantly higher PCE uptake, reaching nearly 16%.

It is worth noting that the equilibrium uptake obtained for NC fibers with the 50 ppm solutions is much higher than the PCE uptake previously reported with PPO films. For the NC fibers, the PCE uptake is c.a.

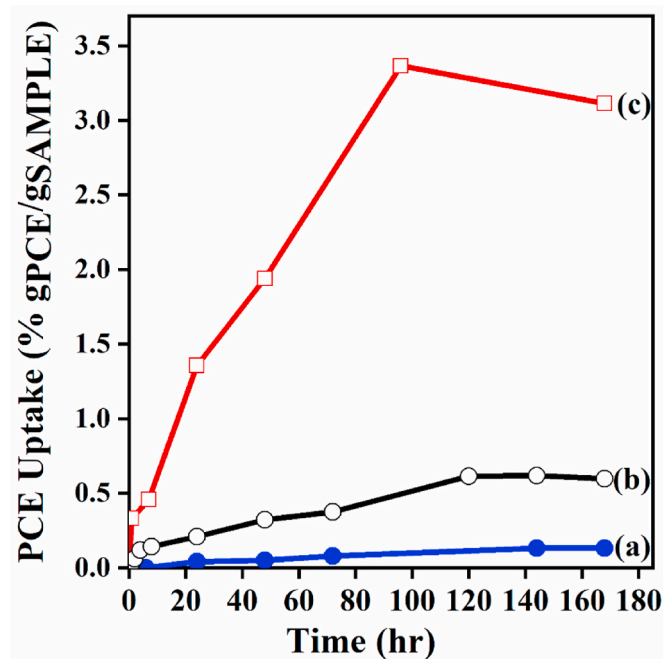


Fig. 7. PCE sorption kinetics at room temperature from 500 ppb aqueous solutions for amorphous PPO film (a), high surface area PPO film (b) and NC PPO/PS fibers (c). For the fibers, the PCE uptake is expressed taking in account the PPO/PS blend composition.

30 wt% while the highest PCE uptake obtained for NC PPO films was found to be c.a. 15–16 wt% [17,18].

In order to highlight the better PCE sorption capacity of the fibers with respect to PPO films for highly diluted solutions, a comparative study was undertaken. In particular, PCE sorption measurements of amorphous PPO film and high surface area NC PPO films from a 500 ppb solution have been carried out and the PCE sorption kinetics obtained for both PPO films and NC PPO/PS fibers are reported in Fig. 7.

The PCE sorption kinetics at 500 ppb reported in Fig. 7 clearly show the better sorption efficiency of NC PPO/PS fibers with respect to the high surface area NC PPO film that has shown the best VOC sorption properties among NC PPO samples [18]. Specifically, for this considered 500 ppb PCE concentration, the sorption capacity of the NC PPO/PS fibers is c.a. 5 times larger than the sorption capacity of the high surface area NC PPO film. This result showcases the outstanding performance of the NC fibers in efficiently capturing the PCE present in water even at highly diluted concentrations.

The higher equilibrium uptake observed with NC PPO/PS fibers with respect to NC PPO films can be due to the larger surface contact of the fibers with water and also to the formation of cracks (as shown by the SEM images reported in Fig. 1) that certainly improve the PCE diffusion within the fibers and therefore the equilibrium uptake. This feature has been observed with NC etched s-PS fibers that present higher VOC sorption uptake from aqueous solutions than NC than NC unetched fibers [10].

4. Conclusions

Poly(2,6-dimethyl-1,4-phenylene) oxide/atactic poly(styrene) fibers with nanoporous crystalline phase have been successfully prepared by limonene sorption/desorption treatment of amorphous PPO/PS fibers obtained by melt-spinning. The NC fibers with the nanoporous α -form are characterized by an axial orientation of the crystalline phase. Sorption measurements of perchloroethylene (PCE) both from vapor phase and aqueous solutions clearly show the higher sorption capacity of NC fibers with respect to the amorphous fibers. Particularly significant

are the sorption results obtained with diluted PCE aqueous solutions showing a much higher sorption capacity of NC fibers with respect to the benchmark high surface NC PPO films.

In summary, the excellent sorption properties, associated with safe and manageable morphology as well as simple preparation procedures with eco-friendly solvent, make NC PPO/PS fibers particularly suitable as filter sorption medium to remove traces of pollutants from water.

Notes

The authors declare no competing financial interest.

CRediT authorship contribution statement

Mohit Pathak: Writing – original draft, Investigation, Data curation. **Anita Manzi:** Investigation. **Mariateresa Lettieri:** Investigation. **Christophe Daniel:** Writing – review & editing, Writing – original draft, Supervision, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Financial support of Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR), Italy is acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2024.126777>.

References

- [1] J.M. Guenet, *Polymer-solvent Molecular Compounds*, first ed., Elsevier, Oxford, 2008.
- [2] G. Guerra, C. Daniel, P. Rizzo, O. Tarallo, Advanced materials based on polymer cocrystalline forms, *J. Polym. Sci. B Polym. Phys.* 50 (5) (2012) 305–322.
- [3] C. De Rosa, G. Guerra, V.o. Petraccone, B. Pirozzi, Crystal structure of the emptied clathrate form (δ e form) of syndiotactic polystyrene, *Macromolecules* 30 (14) (1997) 4147–4152.
- [4] V. Petraccone, O. Ruiz de Ballesteros, O. Tarallo, P. Rizzo, G. Guerra, Nanoporous polymer crystals with cavities and channels, *Chem. Mater.* 20 (11) (2008) 3663–3668.
- [5] C. Daniel, S. Longo, J.G. Vitillo, G. Fasano, G. Guerra, Nanoporous crystalline phases of poly(2,6-dimethyl-1,4-phenylene)-oxide, *Chem. Mater.* 23 (13) (2011) 3195–3200.
- [6] B. Nagendra, A. Cozzolino, C. Daniel, P. Rizzo, G. Guerra, F. Auriemma, Two nanoporous crystalline forms of poly(2,6-dimethyl-1,4-Phenylene)oxide and related Co-crystalline forms, *Macromolecules* 52 (24) (2019) 9646–9656.
- [7] P. Pilla, A. Cusano, A. Cutolo, M. Giordano, G. Mensitieri, P. Rizzo, L. Sanguigno, V. Venditto, G. Guerra, Molecular sensing by nanoporous crystalline polymers, *Sensors* 9 (2009) 9816–9857.
- [8] M. Erdogan, Z. Özbek, R. Çapan, Y. Yagci, Characterization of polymeric LB thin films for sensor applications, *Appl Polym Sci* 123 (4) (2012) 2414–2422.
- [9] A. Buonerba, C. Cuomo, S. Ortega Sánchez, P. Canton, A. Grassi, Gold nanoparticles incarcerated in nanoporous syndiotactic polystyrene matrices as new and efficient catalysts for alcohol oxidations, *Chem. Eur J.* 18 (3) (2012) 709–715.
- [10] C. Daniel, P. Antico, G. Guerra, Etched fibers of syndiotactic polystyrene with nanoporous-crystalline phases, *Macromolecules* 51 (15) (2018) 6138–6148.
- [11] M. Galizia, C. Daniel, G. Fasano, G. Guerra, G. Mensitieri, Gas sorption and diffusion in amorphous and semicrystalline nanoporous poly(2,6-dimethyl-1,4-phenylene)oxide, *Macromolecules* 45 (2012) 3604–3615.
- [12] M. Galizia, C. Daniel, G. Guerra, G. Mensitieri, Solubility and diffusivity of low molecular weight compounds in semi-crystalline poly-(2,6-dimethyl-1,4-phenylene)oxide: the role of the crystalline phase, *J. Membr. Sci.* 443 (2013) 100–106.
- [13] A. Cozzolino, B. Nagendra, P. Rizzo, C. Daniel, G. Guerra, Fast uptake of organic pollutants from dilute aqueous solutions by nanoporous-crystalline PPO films with c-perpendicular orientation, *Eur J Polym* 161 (2021) 110864.
- [14] A.Y. Alentiev, I.S. Levin, M.I. Buzin, N.A. Belov, R.Y. Nikiforov, S.V. Chirkov, I. V. Blagodatskikh, A.S. Kechevyan, P.A. Kechevyan, V.G. Bekeshev, V.E. Ryzhikh, Y.

- P. Yampolskii, Gas transport parameters, density and free volume of nanocrystalline poly-2,6-dimethylphenylene oxide, *Polymer* 226 (2021) 123804.
- [15] B. Nagendra, A. Cozzolino, C. Daniel, P. Rizzo, G. Guerra, High surface area nanoporous-crystalline polymer films, *Macromolecules* 55 (7) (2022) 2983–2990.
- [16] A.Y. Alentiev, I.S. Levin, N.A. Belov, R.Y. Nikiforov, S.V. Chirkov, D.A. Bezgin, V. E. Ryzhikh, J.V. Kostina, V.P. Shantarovich, L.Y. Grunin, Features of the gas-permeable crystalline phase of poly-2,6-dimethylphenylene oxide, *Polymers* 14 (2022) 120.
- [17] P. Rizzo, A. Spatola, A. De Girolamo Del Mauro, G. Guerra, Polymeric films with three different uniplanar crystalline phase orientations, *Macromolecules* 38 (24) (2005) 10089–10094.
- [18] M. Golla, B. Nagendra, F. Fierro, P. Rizzo, C. Daniel, G. Guerra, Axially oriented nanoporous crystalline phases of poly(2,6-dimethyl-1,4-phenylene)oxide, *ACS Appl. Polym. Mater.* 2 (8) (2020) 3518–3524.
- [19] G. Groeninckx, M. Vanneste, V. Everaert, in: L.A. Utracki (Ed.), *Polymer Blends Handbook*, Springer, Dordrecht, 2003, pp. 2023–2294.
- [20] F.E. Karasz, J.M. O'Reilly, H.E. Bair, R.A. Kluge, R.S. Porter, in: J.E. Johnson (Ed.), *Analytical Calorimetry*, vol. 1, Plenum Press, NY, 1968, p. 59.
- [21] A. Cozzolino, P. Rizzo, C. Gallo, R. Bianchi, C. Daniel, G. Guerra, Axially oriented guest induced crystallization in syndiotactic polystyrene unstretched fibers, *Polymer* 228 (2021) 123908.
- [22] D.-K. Lee, I.-C. Cho, Reaction pathways of photocatalytic oxidation of PCE in water with the TiO₂ film on glass, *Stud. Surf. Sci. Catal.* 133 (2001) 303–308.
- [23] M.A. Kumar, S. Bae, S. Han, Y. Chang, W. Lee, Reductive dechlorination of trichloroethylene by polyvinylpyrrolidone stabilized nanoscale zerovalent iron particles with Ni, *J. Hazard Mater.* 340 (2017) 399–406.
- [24] K.-S. Lin, N.V. Mdlovu, C.-Y. Chen, C.-L. Chiang, K. Dehvari, Degradation of TCE, PCE, and 1,2-DCE DNAPLs in contaminated groundwater using polyethylenimine-modified zero-valent iron nanoparticles, *J. Clean. Prod.* 175 (2018) 456–466.