



Transitions between Nanoporous crystalline α and β forms of poly(2,6-dimethyl-1,4-phenylene) oxide (PPO)

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ABSTRACT

Nanoporous-crystalline (NC) α and β forms of Poly(2,6-dimethyl-1,4-phenylene) oxide (PPO), exhibit two different large helix conformations, both being suitable for intrahelical low-molecular-mass guest inclusion. $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions can be achieved by sorption of liquid β -guests and α -guests (i.e., of guest inducing β and α forms by solution casting and by sorption in amorphous PPO), respectively. Both $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions occur with complete loss of possibly present crystalline phase orientations (both axial and planar). Moreover, the reported data show that transitions between the two phases and the associated loss of crystalline phase orientation occur only for guests being good PPO solvents. These observations rule out the possibility of solid–solid transitions while can be rationalized by mechanisms involving a local dissolution of the NC phases. This local polymer dissolution is followed by host/guest co-crystallization with the helical conformation being different from the starting one and more suitable to host the used guest. These data fully confirm complete separation between the two NC phases while rule out the hypothesis of a continuum of NC phases between two limit ones.

1. Introduction

Poly(2,6-dimethyl-1,4-phenylene) oxide (PPO) is a commercial engineering plastic, being amorphous after melt processing [1–11]. It is well known that this amorphous polymer can be crystallized by suitable solvent treatments [12–21], generally leading to co-crystalline (CC) forms with low-molecular-mass guest molecules [16–21]. CC forms of PPO were divided in two Classes: *i*) with few specific guest molecules (decalin, tetralin and α -pinene) leading to highly ordered and large crystallites (even single crystals) and exhibiting small diameter 4/1 polymer helices with *inter-helical guest location* [16–18]; *ii*) with most organic guest molecules leading to poorly ordered and small crystallites and exhibiting large diameter helices with *intra-helical guest location* [19–21].

Guest removal from CC PPO phases of Class *i* leads to polymer amorphization while guest removal from CC PPO phases of Class *ii* leads to nanoporous-crystalline (NC) phases, i.e. crystalline phases with density lower than for the corresponding amorphous phase [19–21]. These NC phases exhibit high uptakes in their crystalline channels of organic guest molecules, even when present in traces in air or water [21–30].

Detailed studies, mainly based on wide-angle X-ray diffraction (WAXD) and Fourier Transform Infrared (FTIR) characterizations, have shown the presence of two sub-classes of Class *ii* CC forms, named α and β [21,31,32]. These α and β CC forms, after guest removal, are transformed in two NC forms also named α and β , respectively [20,21]. NC α and β -forms of PPO exhibit large diameter helices [32] with slightly different chain conformations, with layer-line periodicity of 0.53 nm and of 0.55 nm, respectively [20,21]. Guest molecules that can induce crystallization in α or β CC forms of PPO (by sorption in amorphous films and by solution casting) were defined as α or β -guests, respectively. A list of α and β -guests of PPO is reported in Table 1 of Ref.31.

Thermal transitions between these two NC forms of PPO are not observed, because both NC forms remain stable up to their melting [33,34]. Sorption/desorption procedures of liquid α guests are instead able to induce transition [35] from the lower melting NC β -form ($T_{m,\beta} \approx 245^\circ\text{C}$) toward the higher melting NC α -form ($245^\circ\text{C} < T_{m,\alpha} < 265^\circ\text{C}$) [34].

In this paper, an extended study on sorption of liquid α and β guests in PPO unoriented and oriented films exhibiting NC β and α phases, respectively, is reported. This study not only allows establishing suitable conditions for guest induced $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions but also gives

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Table 1

A list of guest molecules that can induce formation of CC and NC β -forms by sorption in amorphous PPO films (β -guests). Sorption of liquid β -guests, being good PPO solvents, induce $\alpha \rightarrow \beta$ transition as well as loss of crystal phase orientations.

β Guest molecules	α to β transition α form film immersion in the liquid at room temperature	Loss of crystal phase orientation	PPO solubility
Dichloromethane	Film dissolution		Yes at rt ^b
Dichloromethane/acetone (1/1)	Yes	Yes	
CHCl ₃	Film dissolution		Yes at rt ^b
CHCl ₃ /acetone (1/1)	Yes	Yes	–
Benzene	Film dissolution		Yes at rt ^b
Benzene/acetone (1/1)	Yes	Yes	–
Perchloroethylene	Film dissolution		Yes at rt ^b
Perchloroethylene/acetone (1/1)	Yes	Yes	–
Dichloroethane	Film dissolution		Yes at rt ^b
Dichloroethane/acetone (1/1)	Yes	Yes	–
2-Methyl tetrahydrofuran	Yes	Yes	Yes at 60–65 °C
Ethyl benzene	Yes	Yes	Yes at 40–45 °C
1,4-Dioxane	Yes	Yes	Yes at 60–65 °C
1,2-dichloro propane	Yes	Yes	Yes at 60–65 °C
Methyl phenyl ether	Yes	Yes	Yes at 50–55 °C
Methyl ethyl ketone	No ^a	No ^a	No for T \leq T _b ^c
Acetone	No ^a	No ^a	No for T \leq T _b ^c
Hexanal	No	No	No for T \leq T _b ^c
Ethyl acetate	No	No	No for T \leq T _b ^c
Diethyl ether	No	No	No for T \leq T _b ^c

^a No at room temperature and yes at 60 °C.

^b rt is room temperature.

^c T_b is the boiling temperature.

relevant information on their mechanism.

2. Experimental section

PPO (Ultra High P6130 grade; $M_w = 350 \text{ kg mol}^{-1}$) was kindly supplied by Sabic, the Netherlands. All used solvents (of Tables 1 and 2) were purchased from Sigma Aldrich and used without further

Table 2

A list of guest molecules that can induce formation of CC and NC α -forms by sorption in amorphous PPO films (α -guests). Sorption of liquid α -guests, being good PPO solvents, generally induce $\beta \rightarrow \alpha$ transition as well as loss of crystal phase orientations.

α Guest molecules ^a	β to α Transition β form film immersion in the liquid at rt	Loss of crystal phase orientation	PPO Solubility
CCl ₄	Yes	Yes	Yes, at 30–35 °C
1,1,1-trichloroethane	Yes	Yes	Yes at 40–50 °C
Mesitylene	Yes	Yes	Yes at 60–65 °C
Dibenzyl ether	No ^b	No ^b	Yes at 70–75 °C
Carvacrol	No ^b	No ^b	Yes at 75–80 °C
Carvone	No ^b	No ^b	Yes at 80–90 °C
Eugenol	No ^b	No ^b	Yes at 80–90 °C
Limonene	No ^b	No ^b	No, for T < 90 °C

^a Other α guests, like toluene, o-xylene, chlorobenzene, 1,2-dichloro benzene and 1,1,2-trichloroethylene lead to complete film dissolution at rt.

^b No at rt and Yes at 60 °C.

processing.

All NC PPO films were prepared by guest extraction by sorption/desorption of acetonitrile from CC films. Unoriented CC α form films were prepared by casting at room temperature of 0.5–1 wt% PPO solutions in trichloroethylene. CC α form films with c_{\perp} orientation [36] were prepared by guest induced crystallization of amorphous PPO films, by immersion in liquid limonene for 12 h at room temperature. CC α form films with axial orientation were prepared by limonene induced crystallization (immersion in liquid, for 3 h at room temperature) of axially stretched amorphous PPO films. Amorphous films with a thickness of nearly 150 μm were stretched at 220 °C up to draw ratio of nearly 3, at a stretching rate of 10 mm/min. Amorphous PPO films, were obtained by casting at 60 °C of 0.5–1.0 wt% polymer solutions in CHCl₃. CC β form films with $c_{//}$ orientation [36] were prepared by casting at room temperature of 0.5–1.0 wt% polymer solutions in benzene.

Sorption of β guests in α -form films as well as sorption of α guests in β -form films were conducted by immersion in pure liquids, at room temperature or at 60 °C, for 10–240 min. For some guests being very strong solvents for PPO, also test with 50/50 vol/vol guest/acetone solutions were used, to avoid film dissolution.

To study kind and degree of planar orientation in the films, two-dimensional wide angle X-ray diffraction (2D-WAXD) patterns were obtained by a D8 QUEST Bruker diffractometer (CuK α radiation), by sending the X-ray beam parallel to the film surface (EDGE patterns). For films with orientation of the chain axes of the crystalline phases preferentially parallel and perpendicular to the film plane (named $c_{//}$ and c_{\perp} orientations, respectively), the degree of orientation $\chi_{(001)}$, was formalized on a quantitative numerical basis using the usual Hermans orientation function:

$$\chi_{(001)} = \frac{(3\overline{\cos^2\gamma} - 1)}{2} \quad (1)$$

where $\overline{\cos^2\gamma}$ was experimentally evaluated by intensity of the azimuthal distribution of 001 reflection. In these assumptions, when $\chi_{(001)}$ is equal to 0, there is a random crystallite orientation while when $\chi_{(001)}$ is equal to -0.5 or $+1$, c axes of all crystallites are perfectly perpendicular or parallel to the film surface, respectively.

Fourier Transform Infrared Spectroscopy (FTIR) was obtained at 2.0 cm^{-1} resolution with a Vertex 70 Bruker spectrophotometer. It is equipped with a deuterated triglycine sulfate (DTGS) detector and Ge/KBr beam splitter. For polarized infrared spectra, it is fitted with SPE-CAC 12000 wire grid polarizer. 32 scans were averaged to reduce the noise level.

For the kinetics study of Fig. 7, c_{\perp} NC α PPO films with a thickness of nearly 50 μm were immersed in liquid THF at room temperature for 0–5 min. These films were removed from liquid THF at different times and then rapidly dipped in ACN. This step was needed to quench further crystallization.

Differential scanning calorimetry (DSC, TA Q2000 equipment) was

used to evaluate melting enthalpies of the NC PPO films. The heating/cooling scans were conducted under the control program, at a rate of 10 °C/min. Degree of crystallinity (X_c) of NC PPO samples was determined based on the following formula:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \quad (2)$$

where ΔH_m is the melting enthalpy and ΔH_m^0 is the melting enthalpy of a fully crystalline α -form PPO sample ($42 \pm 3 \text{ J g}^{-1}$) [29].

3. Results and discussion

3.1. $\alpha \rightarrow \beta$ transitions as induced by β -guests

A WAXD pattern of an unoriented NC α -form PPO film is shown in Fig. 1a and exhibits the typical 100 and 010 peaks located at $2\theta_{\text{CuK}\alpha} = 4.5^\circ$ and 7.2° [20], respectively. The WAXD pattern of this film after sorption at room temperature of a liquid β -guest (THF) followed by guest removal by sorption/desorption of acetonitrile, is shown in Fig. 1b. This pattern shows hk0 peaks located at $2\theta_{\text{CuK}\alpha} = 5.2^\circ$ and 7.7° , typical of the NC β form [20]. The occurrence of a THF induced $\alpha \rightarrow \beta$ transition is confirmed by the corresponding FTIR spectra reported in Fig. 1a' and 1b'. In fact, the untreated film shows the typical peaks of the α form (e.g., at 773 cm^{-1} and 414 cm^{-1}) while the THF treated film shows the typical peaks of the β form (e.g., at 777 cm^{-1} and 418 cm^{-1}).

The THF induced $\alpha \rightarrow \beta$ transition also occurs for oriented α form films, both exhibiting axial orientation (2D pattern of Fig. 2a) as well as planar orientations (as shown for c_\perp orientation in the 2D pattern of Fig. 3a). This $\alpha \rightarrow \beta$ transition is clearly shown by the angles of the observed diffraction peaks, more clearly apparent in the equatorial profiles of Fig. 2a',b' and 3a',b'. Beside $\alpha \rightarrow \beta$ transitions, the 2D patterns of Figs. 2 and 3 also show complete loss of crystal phase orientation. In fact, the diffraction arcs of Fig. 2a and 3a, after $\alpha \rightarrow \beta$ transitions, are all replaced by uniform diffraction rings (Fig. 2b and 3b).

The occurrence of a THF induced $\alpha \rightarrow \beta$ transition in oriented films is confirmed by the corresponding FTIR spectra reported in Fig. 4. In fact, the untreated oriented films show the typical peaks of the α form (e.g., at 773 cm^{-1} and 414 cm^{-1}) while the corresponding THF treated films shows the typical peaks of the β form (e.g., at 777 cm^{-1} and 418 cm^{-1}).

Polarized FTIR spectra of an axially stretched NC α PPO film and of the derived NC β PPO film, are shown (for the of $790\text{--}730 \text{ cm}^{-1}$ range) in Fig. 5a and 5b, respectively. It is apparent that the crystalline α peak at

Axial oriented NC α -form

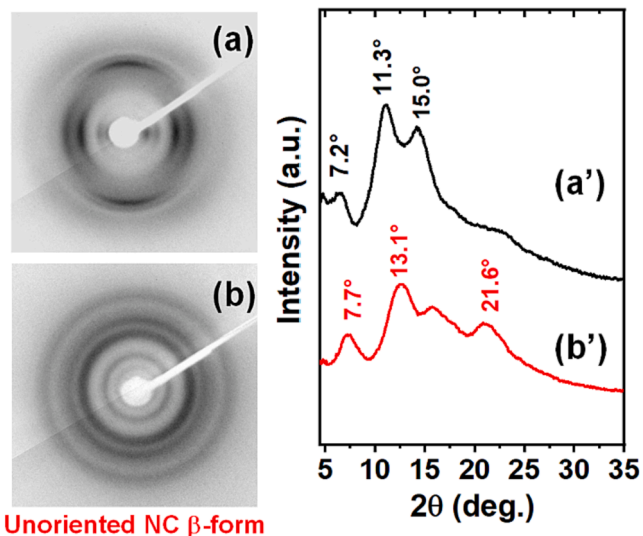


Fig. 2. 2D WAXD patterns of a NC α -form film with axial orientation before (a) and after sorption of liquid THF (b) at room temperature, showing complete loss of orientation. The corresponding equatorial profiles shown in (a') and (b') indicate the transition from the NC α -form to the NC β form.

773 cm^{-1} is highly dichroic (Fig. 5a) whereas the crystalline β peak at 777 cm^{-1} , observed after $\alpha \rightarrow \beta$ transition as induced by liquid THF sorption, does not exhibit linear dichroism (Fig. 5b). This confirms that the $\alpha \rightarrow \beta$ transition occurs with complete loss of crystalline phase orientation.

Behaviors strictly like that one observed for THF sorption ($\alpha \rightarrow \beta$ transition associated with complete loss of crystal phase orientation, Figs. 1-5) are observed for other β -guests, being able to dissolve PPO, which are listed in the upper part of Table 1. β -guests being poor PPO solvents, which are listed in the lower part of Table 1, on the contrary lead to CC α forms (rather than CC β forms), with maintenance of crystal phase orientation. For the last three guests of Table 1, the formation of CC α forms and maintenance of their possible crystal phase orientations, even occurs for their sorption at 60°C .

It is worth adding that, the first five β -guests of Table 1 are very strong solvents and fully dissolve α -form PPO films. To study the

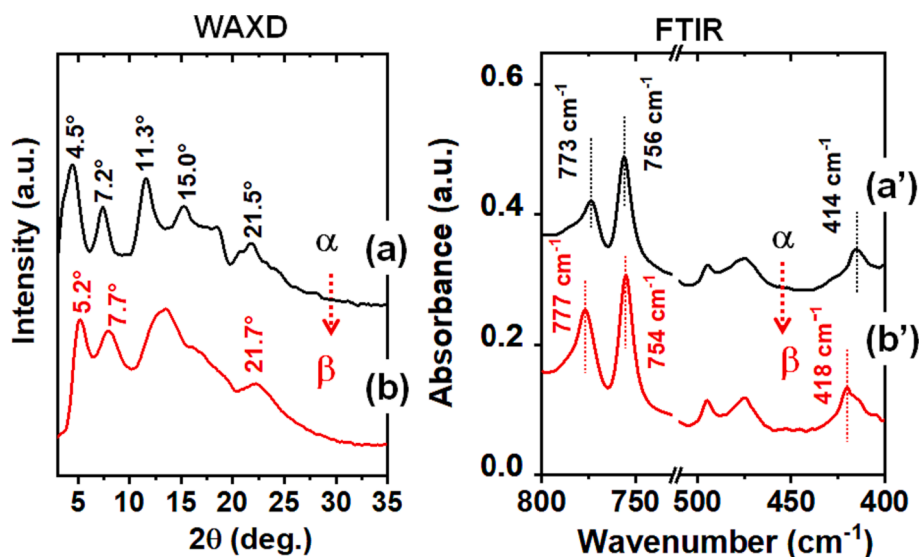


Fig. 1. WAXD patterns (a,b) and FTIR spectra (a',b') of an unoriented NC α -form PPO film, before (a,a') and after (b,b') temporary sorption of THF (β -guest). Both WAXD patterns and FTIR spectra indicate the transition to the NC β -form.

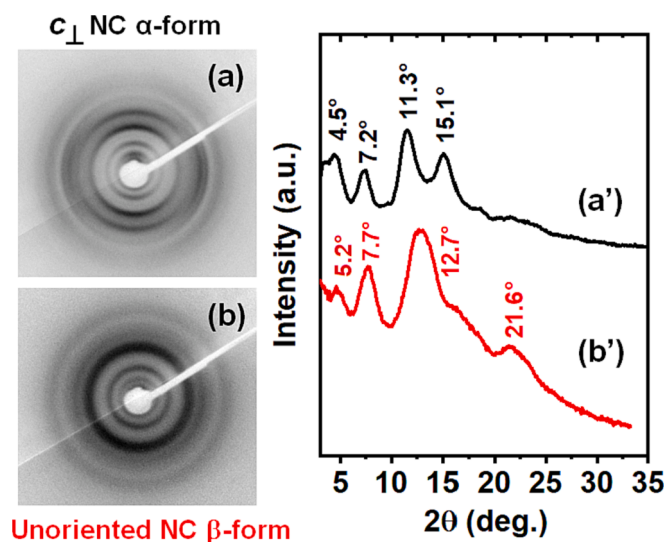


Fig. 3. 2D WAXD EDGE patterns of a NC α -form film with c_{\perp} orientation before (a) and after sorption of liquid THF (b) at room temperature, showing complete loss of orientation. The corresponding meridional profiles shown in (a') and (b') indicate the transition from the NC α -form to the NC β form.

possible ability of these β -guests to induce $\alpha \rightarrow \beta$ transition, tests were conducted by using 50/50 by volume solutions with acetone, i.e., with a β -guest which is a poor PPO solvent (lower part of Table 1). As reported in the upper part of Table 1, the five considered β -guest/acetone 50/50 by volume solutions induce $\alpha \rightarrow \beta$ transition, again associated with complete loss of crystal phase orientations. Strictly similar phenomena are observed for β -guest/acetone solutions, with 75/25 vol ratio.

3.2. $\beta \rightarrow \alpha$ transitions as induced by α -guests

$\beta \rightarrow \alpha$ transitions were described in a previous paper for two α guests: dibenzyl ether and limonene (by sorption at 60 °C) [35]. In this paper we extend our analysis to other α guests (listed in Table 2), by also conducting liquid sorption tests on β form films exhibiting crystal phase orientations. Our analysis was mainly conducted on NC β PPO films exhibiting the $c_{//}$ orientation, i.e., with the crystalline chain axes

preferentially parallel to the film plane, which are generally obtained by solution casting with β guests [36].

WAXD EDGE patterns of a NC β -form film with $c_{//}$ orientation before and after sorption of a liquid α -guest (CCl_4) are shown in Fig. 6a and 6b, respectively. The $hk0$ diffraction rings being polarized on the equator and the 001 peak being polarized on the meridian of the pattern of Fig. 6a, clearly indicate the presence of $c_{//}$ orientation. In particular, the intensity distribution for the 001 peak allows evaluating a degree of orientation $\chi_{(001)} \approx 0.3$. The presence of only uniform diffraction rings in Fig. 6b clearly indicates that also $\beta \rightarrow \alpha$ transition occurs with complete loss of crystal phase orientation. The corresponding equatorial profiles, shown in Fig. 6a' and 6b', clearly show the occurrence of a $\beta \rightarrow \alpha$ transition.

Behaviors like that one observed for CCl_4 sorption ($\beta \rightarrow \alpha$ transition associated with complete loss of crystal phase orientation, Fig. 6) are observed for other β -guests, being able to dissolve PPO, which are listed in the upper part of Table 2. Sorption of liquid α -guests being poor PPO solvents, which are listed in the lower part of Table 2, on the contrary lead to CC β forms (rather than CC α forms), and to NC β form after guest removal, with maintenance of crystal phase orientation.

It is worth adding that also the α guests being poor PPO solvents (lower part of Table 2) can induce $\beta \rightarrow \alpha$ transition associated with complete loss of crystal phase orientation, if guest sorption is conducted at 60 °C.

3.3. Sorption of guests leading to CC phases with maintenance of helical conformation and of crystalline phase orientations

As described in the two previous sections, sorption of some guests being poor solvents of PPO (lower rows in Tables 1 and 2) can lead to CC phases, without inducing $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$ transitions and with maintenance of crystalline phase orientations.

Also sorption of liquid α and β guests by NC α and β form films leads to CC α and β forms, respectively, with maintenance of the possibly present crystalline orientation. In fact, axial orientation as well as both kinds of planar orientations (c_{\perp} and $c_{//}$) [36] remain essentially unaltered [35]. Analogous polymorphic behavior was observed for transitions between PPO CC forms of Class i (i.e., of CC forms with decalin, tetralin and α -pinene). In fact, both the observed uniplanar orientations are fully retained after guest exchange procedures [37].

It is also interesting the polymorphic behavior observed for two

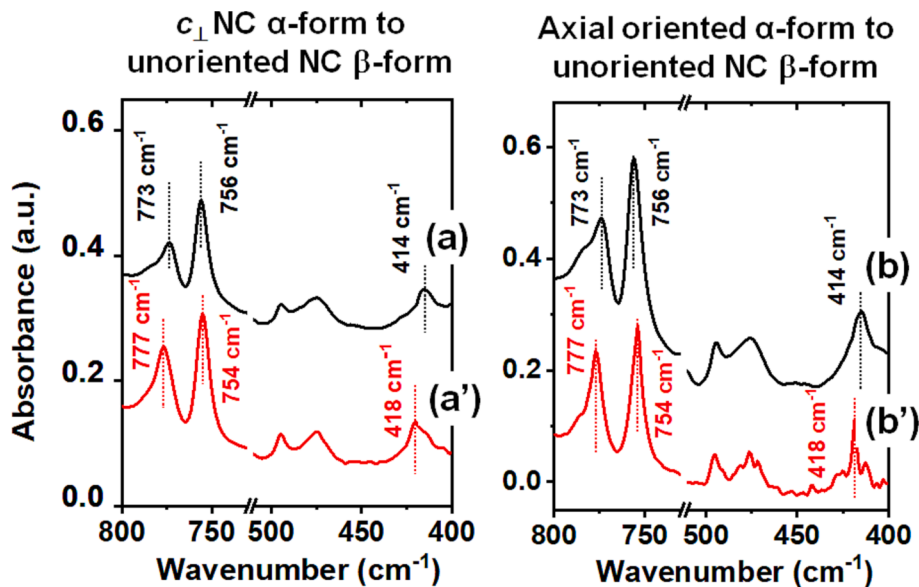


Fig. 4. FTIR spectra of NC α -form films with c_{\perp} orientation (a, a') or with axial orientation (b, b'), before (a, b; black spectra) and after sorption (a', b'; red spectra) of liquid THF.

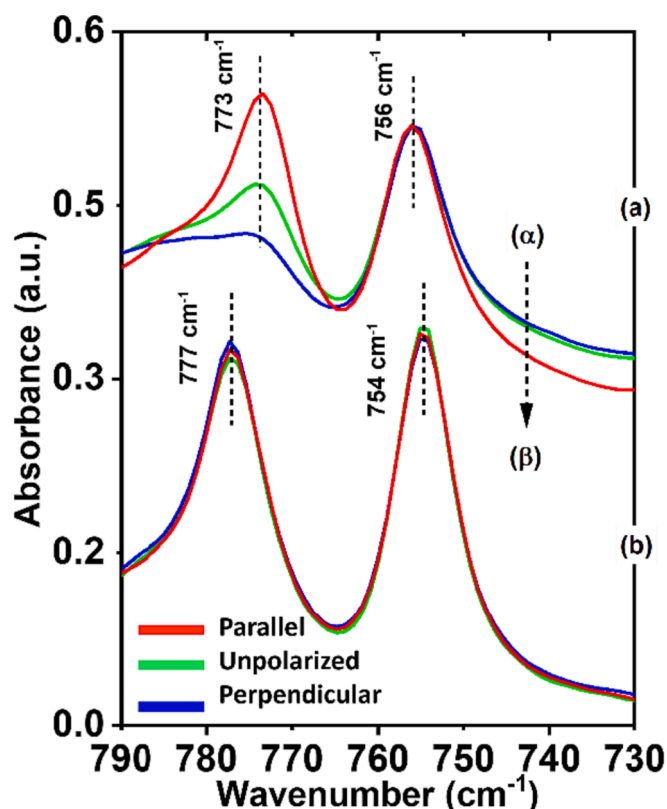


Fig. 5. Polarized FTIR spectra (in the range of 790 cm^{-1} to 730 cm^{-1}) of an axially oriented NC α form film before (a) and after sorption of liquid THF guest at room temperature (b). Green line spectra refer to unpolarized light, while red and blue lines spectra were collected with polarized light being parallel and perpendicular to the film stretching direction, respectively. The high dichroism of the crystalline α peak at 773 cm^{-1} and the absence of dichroism for the crystalline β peak at 777 cm^{-1} , are clearly apparent.

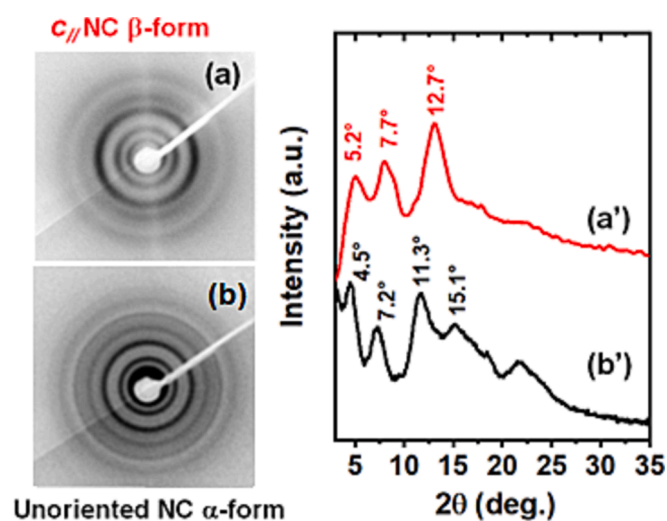


Fig. 6. 2D WAXD EDGE patterns of a NC β -form film with $c_{//}$ orientation before (a) and after sorption of a liquid α -guest (CCL_4) (b), showing the loss of orientation ($\chi_{(001)}$ decreases from 0.3 to zero). The corresponding equatorial profiles shown in (a') and (b') indicate the transition from the NC β -form to the NC α form.

specific guests (methylbenzoate and 1,3,5-trichlorobenzene), which are good PPO solvents but cannot be defined neither α nor β guests. In fact, both guests lead to CC β phase by amorphous film immersion at rt while

lead to CC α phase by solution casting at $60\text{ }^\circ\text{C}$. Immersion of NC α and β form films in both guests at rt leads to CC α and β form films, respectively, with maintenance of helical conformation as well as of crystalline phase orientation. The maintenance of the crystalline helical conformation as well as of their packing (α or β) can be explained by the similar thermodynamic stability of CC α and β form crystallites, for these two specific guests.

3.4. Mechanism of $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions

Data reported in the previous sections show that transitions between the two PPO phases (both $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$) are always associated with complete loss of crystalline phase orientations, which are possibly present in the films. These observations rule out the possibility that $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ could be solid-solid phase transitions.

The reported data also show that $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions occur by sorption of β and α guests, respectively, only when they are good PPO solvents. This indicates transition mechanisms that involve dissolution of a NC phase followed by formation of a host/guest CC phase with change of chain conformation. In this respect, it is worth noting that both α and β forms (NC as well as CC) exhibit large helices, being suitable for intrahelical guest inclusion, but with different helix diameters (larger for α form than for β form) [32].

To get additional information on the mechanism of these transitions, kinetics were studied by FTIR. Just an example, variations of the FTIR spectra in the range $785\text{--}745\text{ cm}^{-1}$, as a consequence of THF sorption at room temperature in a α form PPO film having a thickness of nearly $50\text{ }\mu\text{m}$, are shown in Fig. 7. A change of α form to β form is clearly shown by the gradual shift of the 773 cm^{-1} peak up to 777 cm^{-1} (already complete after 1 min of guest sorption), which is mainly due to the change of chain conformation, leading to a reduction of the crystalline polymer helix diameter. Correspondingly the intensity of the crystalline peak at $756\text{--}754\text{ cm}^{-1}$, and hence the degree of crystallinity, remains essentially

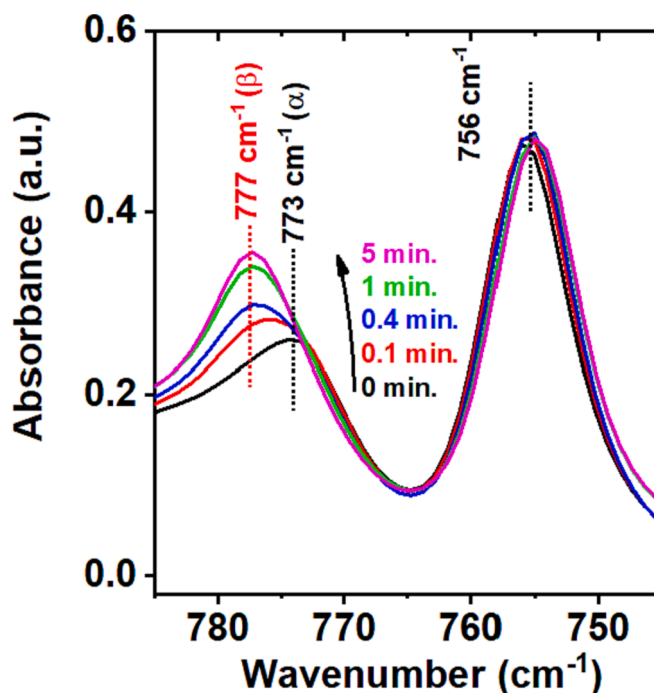


Fig. 7. FTIR spectra of a NC α -form film ($50\text{ }\mu\text{m}$ thick) after different times of sorption of liquid THF at room temperature: 0 min (black line), 0.1 min (red line), 0.4 min (blue line), 1 min (green line), and 5 min (pink line). A complete transformation from α form to β form (as pointed out by the peak shift from 773 cm^{-1} up to 777 cm^{-1}) occurs, without any significant change of degree of crystallinity (constant intensity of the $756\text{--}754\text{ cm}^{-1}$ peak).

unaltered, for the entire transition kinetics. The invariance of degree of crystallinity is confirmed by the unaltered intensity of other crystalline peaks (like, e.g., those observed at 495 cm^{-1} and 414 cm^{-1}).

The maintenance of the degree of crystallinity is further confirmed by evaluating melting enthalpies (ΔH_m) of NC PPO films before and after phase transition, by DSC scans like those shown in Fig. S2. ΔH_m of NC PPO films after different times of sorption of liquid THF are all similar, within a narrow range (20.0–21.5 J/g). Correspondingly, the degree of crystallinity of NC PPO films is in the range 47.5–51.0 %.

Gradual crystal phase transitions, with poor variation of degree of crystallinity, can be rationalized by recrystallization kinetics faster than kinetics of advancement of the guest front in thick PPO films.

Hence, the observed phase transition kinetics, with maintenance of degree of crystallinity for the entire recrystallization time and with complete loss of orientation of the crystalline phase, can be rationalized by local dissolution of NC α or β phases (controlled by kinetics of guest diffusion in the polymer film) and faster local recrystallizations leading to CC β or α phases, which after guest removal lead to NC β or α phases, respectively.

It is worth adding that the complete loss of orientation, as observed for both $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions, fully confirms complete separation between the two NC phases (as suggested by more recent structural data) [20] while rules out the previous hypothesis [19] of occurrence of many (if not a continuum of) modifications between two limit ones.

A comparison with the polymorphic behavior of syndiotactic polystyrene (sPS), i.e. the only other polymer being able to form NC phases, is also informative. For sPS, differently from PPO, crystalline phase orientations are maintained for all crystalline phase transitions involving CC and NC phases. In fact, axial, uniplanar [38,39] and uniplanar-axial [40] orientations of the NC and CC δ form [41], can be maintained not only for NC \rightarrow CC and CC \rightarrow NC transitions but also for transitions toward CC and NC ϵ phases [42,43] as well as toward the dense γ phase [38]. Crystalline phase orientations are also maintained after guest-exchange procedures [39], which transform a CC phase with a given guest into a CC phase with a different guest [44–46]. The maintenance of crystalline phase orientation, for crystal phase transitions of sPS, can be rationalized by the presence for all these crystalline forms (NC and CC δ , NC and CC ϵ , and γ) of the same helical conformation ($s(2/1)2$) [41,42,47]. The opposite behavior observed for $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions of PPO, i.e. complete loss of crystalline phase orientation, can be rationalized by the presence for α and β phases of two different helical conformations.

4. Conclusions

An extended study on sorption of liquid guests, in PPO films exhibiting NC α and β phases, is reported. Sorption of some α and β guests in NC β and α -form PPO samples induces formation of CC α and β forms (and of the corresponding NC α and β forms, after guest removal), respectively. Sorption of other guests in NC PPO samples instead leads to their inclusion in the available NC form, thus inducing formation of the corresponding CC form.

When sorption of liquid guests is by oriented samples (e.g., films with axial or planar orientations), maintenance of crystalline form occurs with maintenance of crystalline phase orientation while $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions occur with complete loss of crystalline phase orientation. These observations rule out the possibility that $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ could be solid–solid phase transitions.

Collected data for many guest molecules show that transitions between the two phases (both $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$), and the associated loss of crystalline phase orientation, occur only for guests being good PPO solvents. Moreover, these transitions occur with maintenance of degree of crystallinity, for the entire transition kinetics. This indicates the occurrence of only local dissolution of a NC α or β phases and local recrystallizations leading to CC β or α phases (which after guest removal lead to NC β or α phases), respectively.

Moreover, the complete loss of crystal phase orientation, as observed for both $\alpha \rightarrow \beta$ and for $\beta \rightarrow \alpha$ transitions, fully confirms complete separation between the two NC phases while rules out the previous hypothesis of occurrence of a continuum of modifications between two limit ones.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2023.112532>.

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