Absorption and Isomerization of Azobenzene Guest Molecules in Polymeric Nanoporous Crystalline Phases

Nicola Coscia, Antonietta Cozzolino, Manohar Golla and Paola Rizzo

Abstract: PPO co-crystalline (CC) films including azobenzene guest molecules have been prepared and characterized by WAXD, FTIR and UV-Visible measurements. Isomerization reactions of azobenzene (photo-induced trans to cis and spontaneous cis to trans) included in α and β nanoporous-crystalline (NC) phases leading to CC phases, or simply absorbed in amorphous phase have been studied on thick and thin films. Spectroscopic analysis shows that photo-isomerization of azobenzene occurs without expulsion of azobenzene guest molecules from crystalline phases. Sorption studies of α and β NC films immersed into photo-isomerized azobenzene solution reveal a higher selectivity of the β NC phase toward cis azobenzene isomer than the α NC phase, inducing us to propose the β NC phase as particularly suitable for absorbing spherically bulky guest molecules.

Keywords: poly(2,6-dimethyl-1,4-phenylene)oxide; co-crystalline phase; confined isomerization; FTIR spectra; UV-Vis spectra

1. Introduction

Nanoporous crystalline (NC) phases can be easily achieved for a large variety of chemical compounds: inorganic (e.g., zeolites) [1,2], metal-organic [3–6] as well as organic [7–10]. As for polymers, usually the removal of low-molecular-mass guest molecules from co-crystalline (CC) phases generates amorphous or dense crystalline phases with the only exception represented by two relevant commercial polymers: syndiotactic polystyrene (s-PS) [11] and poly(2,6-dimethyl-1,4-phenylene)oxide (PPO) [12].

In particular, starting from s-PS or PPO CC phases, by using simple extraction procedures, NC phases presenting crystalline density lower than those of corresponding amorphous phases (named δ and ε for s-PS [13,14] or α and β for PPO [15,16]) can be obtained. As for PPO, the two NC phases (α and β), showing crystalline density of 0.93 g/cm³ and 0.95 g/cm³ lower than that of the corresponding amorphous phase (1.04 g/cm³) [17], are particularly interesting since they present a higher sorption and diffusivity of most suitable guest molecules with respect to δ and ε NC phases of s-PS. This behavior can be assigned mainly to the contribution of NC phases but also to the high free volume of the PPO amorphous phase [12].

It is well to highlight that polymeric nanoporous crystalline (NC) phases present many advantages with respect to nanoporous amorphous polymers as well as with respect to inorganic and organometallic nanoporous materials. Particularly relevant are simple processing conditions (low pressures and temperatures) and processing techniques (both from melt and solutions) [18], leading to a large variety of morphologies like fibers, sheets, films, membranes, foams, gels and aerogels [19–23]. Moreover, NC polymers present the further advantage of showing identical cavities that allow molecular selectivity [24–30] comparable to those of NC inorganic and organometallic materials. An additional interesting, rather unique characteristic of NC polymers is their capability to control the orientation of their guest molecules at macroscopic level. In particular, by using different
crystallization procedures, the orientation of both host polymeric co-crystalline phases and guest molecules can be easily realized [31].

The polymeric NC phases are also particularly relevant since they can absorb suitable guest molecules, even at low activity from water and air, and can be useful for many application fields like water and air purification [24,32–39], molecular separation [40] as well as molecular sensors [41–44].

It is known that inclusion of chromophores as well as of photoreactive guest molecules in confined lattices is increasingly taken into account for developing advanced materials with new electronic and optical properties [45–48]. As for s-PS, intramolecular solid-state reactions [49] have been performed involving guest molecules absorbed in NC phases (leading to CC phases). In particular, photo-isomerization of norbornadiene to quadricyclane occurred into the δ co-crystalline phase (CC) [49] as well as the photo-isomerization of azobenzene guest molecules included inside the δ and ε CC phases occurred without expulsion of guest molecules from s-PS co-crystalline lattices [50]. In the case of irradiation-induced polymerization of benzyl methacrylate in the s-PS co-crystalline phase [51], instead, it was evidenced that polymerization products were expelled from the crystalline host lattice leading to a rearrangement of the crystalline phase that became a mesomorphic phase.

As is well known, photochromic molecular switches such as azobenzene [52], spiropyran [53], or arylazopyrazole [54] are responsive molecules that isomerize upon irradiation with light. Achieving fine control of these compounds’ isomerization is important since they can be crucial components for the development of functional photoresponsive materials [55,56], light-powered molecular machines [57–59], and in photopharmacology [60], where spatiotemporal control of molecular transitions/reactions is needed. In particular, azobenzene, represents a very interesting example of molecular switch, its reversible trans→cis isomerization has been largely studied in solution [61], in the gas phase [62–64], as well as in amorphous and crystalline phases [65–67] and it is still actually investigated for many applications, from the development of active materials to the design of stimuli-responsive molecular systems and light-powered molecular machines [68–70].

To fully understand its potential, it becomes important to control the mechanism and kinetics of photo-induced isomerization; one possible strategy involves the confinement of photo-responsive switches such as azobenzene molecules within confined molecular environments, which may allow control over their light induced conversion.

In this paper the formation of co-crystalline phases of azobenzene with PPO have been studied.

Isomerization reactions (both photo-induced trans→cis and spontaneous cis→trans) of azobenzene as a guest of PPO co-crystalline phases or simply absorbed in the amorphous phase have been analyzed by FTIR and UV-Visible measurements on thick and thin films. Sorption studies on photo-isomerized azobenzene solution have been also performed in order to evaluate a possible selectivity of α or β NC phases toward cis or trans azobenzene isomers.

2. Experimental Section

2.1. Materials

Poly(2,6-dimethyl 1,4-phenylene)oxide (PPO), with weight-average molecular mass (M_w) of 350 Kg/mol was supplied by SABIC.

Carbon tetrachloride, benzene, chloroform, mesitylene, acetonitrile, methyl-ethyl ketone, methanol and azobenzene were supplied by Aldrich and used without any purification.

Semicrystalline PPO films with a thickness of nearly 50 µm, presenting α and β co-crystalline (CC) phases both with c// orientation were obtained by casting procedure at room temperature from 1.5 wt% carbon tetrachloride and benzene solution, respectively.

By immersion of CC PPO films in pure acetonitrile for 1 h, followed by acetonitrile desorption, carbon tetrachloride and benzene guest molecules were removed leading to PPO films showing α and β nanoporous crystalline (NC) phases.
Amorphous PPO films were achieved from 1.5 wt% chloroform solution at 60 °C, followed by solvent removal.

All cast films, semicrystalline and amorphous, have been immersed in 2% azobenzene/methanol solution for 30 min.

Axially amorphous oriented films were obtained by stretching PPO amorphous films in the temperature range 220–230 °C up to draw ratio 4–5. Films exhibiting axial orientation of α NC phase were obtained by axial stretching of PPO/mesitylene CC films at 170–175 °C up to draw ratio 4 and by subsequent mesitylene removing through sorption/desorption procedures of acetonitrile at room temperature for 2 h [71]. PPO/mesitylene CC films, with thickness of nearly 150 µm, were obtained by casting from 3.5 wt% mesitylene solution at room temperature. Film stretching experiments were conducted by a dynamometer INSTRON 4301, with controllable speed and temperature, up to draw ratio \( \lambda = l/l_0 \) (where \( l \) is the final length of the film) of 4–5 and by using elongation rate in the range 3–10 mm/min.

Amorphous and NC axially stretched films were immersed in a 0.2 wt% azobenzene/methanol solution for 48 h leading to amorphous and CC films with 1.5 wt% and 6 wt% of azobenzene content, respectively. NC axially stretched films were also immersed in a 2 wt% azobenzene/methanol solution for 12 h at room temperature leading to CC film with 12 wt% of azobenzene.

Amorphous PPO films with thickness of nearly 0.1 µm were obtained by spin-coating of PPO chloroform solution (1.5 wt%) onto quartz surfaces at a spin-rate of 1500 rpm. PPO α and β NC films were obtained by exposure of amorphous PPO films to carbon tetrachloride and methyl-ethyl ketone vapors at 60 °C for 30 min, respectively, then all films have been immersed in 0.2 wt% azobenzene/methanol solution for 30 min.

The content of azobenzene molecules was evaluated by thermogravimetric measurements (TGA), with a TA instrument TGA Q500 with heating rate of 10 °C/min, in the temperature range of 20–600 °C, under nitrogen gas flow.

2.2. X-ray Diffraction

Two-dimensional (2D) Wide Angle X-ray Diffraction (WAXD) patterns were performed by D8 QUEST Bruker diffractometer and the equatorial profiles were collected along the equatorial direction of the 2D patterns.

2.3. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were conducted at 2.0 cm\(^{-1}\) resolution with a Vertex 70 Bruker spectrophotometer. A total of 32 scans were performed and averaged to reduce the noise level. Polarized infrared spectra were obtained by using a SPECAC 12,500 polarizer.

As described in detail in a previous report [36], satisfactory evaluation of the degree of crystallinity (\( X_c \)) for PPO samples, can be obtained by FTIR spectral subtraction procedures based on the use of the 475 cm\(^{-1}\) band, according to the following relationship:

\[
K = (1 - X_c) l/l' \tag{1}
\]

where \( l \) and \( l' \) are the thickness of the sample and of an amorphous PPO film, respectively.

The degree of orientation of the chain axes of the host crystalline helices with respect to the draw direction was evaluated by using the axial orientation factor as reported in [17]:

\[
f_{c,IR} = S_h (2 \cot^2 \theta + 2)/(2\cot^2 \theta - 1) \tag{2}
\]

where \( \theta \) is the angle between the chain axis and the transition moment vector of the vibrational mode and \( S_h \) is the order parameter of the host crystalline phase as calculated by the formula:

\[
S_h = (R - 1)/(R + 2) \tag{3}
\]

where \( R = A_{//}/A_\perp \) is the dichroic ratio, and \( A_{//} \) and \( A_\perp \) are the measured absorbance for polarization plane parallel and perpendicular to the draw direction, respectively.
2.4. UV-Vis Spectroscopy

UV-Visible spectra were recorded on Varian Cary 50 spectrophotometer in the range 200–600 nm with a scan rate of 600 nm/min.

2.5. Trans → Cis Photo-Isomerization

PPO/azobenzene co-crystalline samples were irradiated by a xenon lamp (BLX equipment from BioLink) at 365 nm, with a power of 65 W and an energy of 99.66 mJ/cm² at room temperature.

3. Results and Discussion

3.1. Formation of PPO/Azobenzene Co-Crystalline Phases

PPO co-crystalline (CC) films including azobenzene guest molecules were prepared by dipping α or β nanoporous crystalline (NC) films (~50 µm thick) in azobenzene solutions, using methanol as carrier. In particular, FTIR spectra in the wavenumber range 1100–400 cm⁻¹ of α and β NC as well as of amorphous films, before (gray lines) and after immersion in 2 wt% azobenzene/methanol solution for 30 min are reported in Figure 1 (red, blue and black lines, respectively).

FTIR spectra present typical peaks at 828, 773, 756 and 414 cm⁻¹ for α phase (red line), at 825, 777, 756 and 418 cm⁻¹ for β crystalline phase (blue line) and at 831 and 755 cm⁻¹ for amorphous (black line) [15,63,72]. Peaks located at 1070, 929, ~775, ~755, 690, 545, 524 cm⁻¹ associated to vibrational modes of azobenzene trans isomer are also shown [73,74].

It is apparent that the amount of azobenzene absorbed in α and β NC films was higher than that absorbed in amorphous sample and, by thermogravimetric measurements, it was evaluated close to ≈8.8 wt%, ≈9.6 wt% and ≈4 wt% for α, β and amorphous films, respectively.
The degree of crystallinity, evaluated by FTIR measurements, for α and β films was ~42% and ~46%, respectively.

X-ray diffraction patterns of PPO CC films of Figure 1A,B, taken with a two-dimensional diffractometer, are shown in Figure 2A,B; for comparison, patterns of α and β nanoporous crystalline phases are also reported in Figure 2A',B' respectively. Equatorial EDGE profiles are shown in Figure 2a,b,a',b'.

![Figure 2. 2D WAXD patterns (A, A', B, B') and corresponding equatorial intensity profiles (a, a', b, b') of PPO films presenting: CC α phase with ~8.8 wt% of azobenzene (A,a), nanoporous α phase (A',a'); CC β phase with ~9.6 wt% of azobenzene (B,b) and nanoporous β phase (B',b'). A dashed red line shows the direction of equatorial profiles.](image)

It is apparent that diffraction profiles of PPO films with azobenzene (red and blue lines) exhibited 2θ values similar to NC films (black lines), however, variations in relative intensity of diffraction peaks, indicating the formation of PPO/azobenzene CC phases, were visible [72].

Moreover, patterns in Figure 2 presented diffraction arcs centered on the equator for 2θ < 16° and on the meridional for 2θ > 16°, indicating the occurrence of c// orientation for PPO films [72]. The degree of c// orientation, evaluated by azimuthal scan of the 001 reflection (χ (001)) of the EDGE pattern of Figure 2, was close to 0.6 for both CC and NC α form films and it was close to 0.5 for CC and NC β form films.

Additional information relative to PPO/azobenzene CC phases could be obtained from axially stretched films. In particular, two-dimensional WAXD patterns (A, B, C) and the corresponding equatorial EDGE profiles of axially stretched PPO films, exhibiting NC α phase before (A,a) and after sorption of different amount of azobenzene ~6 wt% (B,b) and 12 wt% (C,c), are shown in Figure 3.

Diffraction profiles of films with azobenzene (3b,3c) exhibited 2θ values similar to NC films (3a); however, a strong reduction of relative intensity for 100 peak as well as an intensity enhancing for 310 peak, by increasing the azobenzene content, confirmed the formation of the PPO/azobenzene CC phase with inclusion of azobenzene guest molecules into the nanoporous α crystalline phase.

Axially stretched co-crystalline PPO films were also characterized by infrared linear dichroism measurements.

FTIR spectra in the wavenumber range 1100–400 cm⁻¹, taken with polarization plane parallel (thin blue line) and perpendicular (thick red line) to the draw direction of PPO films presenting an α NC phase (A), CC phase with ~6 wt% of azobenzene (B) and amorphous phase with ~1.5 wt% of azobenzene (C) are reported in Figure 4, respectively. Azobenzene peaks labelled with (*) are also shown.
Vibrational peaks of the host crystalline phase were dichroic: 773 (II), 756 (⊥), 594 (II), 495 (II) and 414 cm\(^{-1}\) (II) [17,72]. The degree of orientation (\(f_{c,IR}\)) of \(\alpha\) stretched film, evaluated on the dichroism of the isolated peak at 495 cm\(^{-1}\), was \(\sim 0.45\).

Vibrational peaks associated to trans azobenzene isomer absorbed in \(\alpha\) film are also apparent in Figure 4B and were dichroic, (see for instance peaks at 1070 (⊥), 690(⊥), 545(⊥), 524 (II) cm\(^{-1}\)), confirming the inclusion of trans azobenzene isomer as guest in the \(\alpha\) phase, while they were merely detectable and not dichroic if absorbed in amorphous stretched films, (see peak at 690 in Figure 4C).

The order parameter \(S_2\), evaluated on vibrational peaks at 690 and 524 cm\(^{-1}\) of trans azobenzene isomer absorbed in CC films, associated to torsion \(\tau\) (C-C) and to out of plane \(\gamma\) (C-H) (at 690 cm\(^{-1}\)) or to in plane bending \(\delta\) (C-N), \(\delta\) (C-C), and \(\delta\) (N=N) (at 524 cm\(^{-1}\)) [73],
are \( S_{g,690} = -0.05 \) and \( S_{g,524} = +0.21 \), respectively. The obtained results also let us affirm that trans azobenzene guest molecules were included as guest in the \( \alpha \) PPO CC phase.

3.2. Trans \( \rightarrow \) Cis Photo-Isomerization of Azobenzene Molecules

Isomerization, photo-induced trans \( \rightarrow \) cis or spontaneous cis \( \rightarrow \) trans, of azobenzene being guest of PPO co-crystalline phases or simply absorbed in PPO amorphous phases were studied at room temperature by both FTIR and UV-Visible measurements.

FTIR measurements were performed on cast PPO films as well as on axially stretched films. FTIR spectra in the wavenumber range 800–500 cm\(^{-1}\) of azobenzene absorbed in CC as well as amorphous films (~50 \( \mu \)m thick) before and after photo-isomerization are reported in Figure 5.

![Figure 5](image-url)

FTIR spectra in the wavenumber range 800–500 cm\(^{-1}\) of azobenzene absorbed in PPO films presenting \( \alpha \) (A), \( \beta \) (B) and amorphous phases (C) before (red, blue and black lines) and after isomerization (green lines). FTIR spectra of starting PPO films presenting \( \alpha \) NC phase, \( \beta \) NC phase as well as amorphous phase are also reported (gray lines).

Peaks associated to trans azobenzene isomer at 524, 545, 690, ~755 cm\(^{-1}\) and at ~775 cm\(^{-1}\) are shown. After photo-isomerization for 1 h, a decrease of trans isomer peaks as well as an increase of cis isomer peaks at ~756 cm\(^{-1}\) and at 701 cm\(^{-1}\) were clearly apparent indicating the occurrence of trans \( \rightarrow \) cis isomerization on PPO thick films.

The degree of isomerization [75], evaluated on the reduction of intensity of trans isomer peak at 524 cm\(^{-1}\) associated to in plane bending \( \delta \) (C-N), \( \delta \) (C-C), and \( \delta \) (N=N) [73] vibrational mode, was close to ~40% for \( \alpha \) and \( \beta \) films and to ~50% for amorphous PPO films.

Additionally informative were polarized FTIR spectra of axially oriented films since, evaluating the linear dichroism of both trans and cis azobenzene isomers before and after isomerization, it was possible to establish if the isomerization, into a confined molecular environment, occurred with or without expelling the cis isomer from the crystalline lattice.

Polarized FTIR spectra of a \( \alpha \) PPO film (150 \( \mu \)m thick) exhibiting CC phase with trans azobenzene showing a degree of orientation \( f_{c,IR} \approx 0.45 \) (evaluated according to ref. [17]), as prepared, after trans \( \rightarrow \) cis photo-isomerization and after spontaneous cis \( \rightarrow \) trans isomerization are reported in Figure 6A–C respectively.
Figure 6. Polarized FTIR spectra in the wavenumber range 800–500 cm\(^{-1}\) taken with polarization plane parallel (thin blue line) and perpendicular (thick red lines) to the draw direction for \(\alpha\) PPO stretched films with \(\approx 3\) wt% of azobenzene before isomerization (A); after 1 h of isomerization (B); after 30 days from isomerization (C).

Dichroic peaks associated to trans azobenzene isomer at 690, and 524 cm\(^{-1}\) with 

\[ S_{\gamma, 690} = -0.05 \quad \text{and} \quad S_{\gamma, 524} = +0.24 \]

respectively, shown in Figure 6A, confirming the inclusion of the trans isomer into the CC phase. After photo-isomerization a peak at 701 cm\(^{-1}\) associated to out of plane bending \(\gamma\) (C-H) vibrational mode of the cis isomer \([73,74]\) was clearly apparent; the presence of dichroism \((S_{\gamma, 701} = +0.03)\) let us suppose the inclusion of cis isomer inside the \(\alpha\) NC crystalline phase of PPO. Moreover, since after 30 days a complete spontaneous return from cis to trans isomer occurred (Figure 6C) without changing the dichroism of peaks at 690 cm\(^{-1}\) and 524 cm\(^{-1}\) mainly due to the trans isomer \([73,74]\), we can conclude that trans \(\rightarrow\) cis \(\rightarrow\) trans isomerization occurred without expulsion of azobenzene guest molecules from PPO co-crystalline lattice.

3.3. Selective Sorption of Azobenzene in PPO Films

In order to evaluate the capability of \(\alpha\) and \(\beta\) NC phases of PPO to include cis azobenzene isomer inside their crystalline lattice, PPO films, presenting NC (\(\alpha\) and \(\beta\)) or amorphous phases, were immersed 30 min in a photo-isomerized 2% azobenzene/methanol solution (irradiated by 365 nm light for 4 h) and analyzed by FTIR measurements.

FTIR spectra reported in Figure 7 indicated that both \(\alpha\) and \(\beta\) NC films absorbed higher amounts of trans and cis azobenzene isomers (see peaks at 690 and 701 cm\(^{-1}\) respectively) with respect to amorphous film, as well as that \(\beta\) NC phase absorbed higher amounts not only of the trans isomer but also of the cis isomer also with respect to \(\alpha\) NC phase.

The amount of cis and of trans azobenzene isomers absorbed in \(\alpha\), \(\beta\) and in amorphous films, evaluated by thermogravimetric measurements, corresponded roughly to \(\approx 1\) wt%, \(\approx 2.5\) wt% and \(\approx 0.5\) wt% for the cis isomer and to \(\approx 4\) wt%, \(\approx 5\) wt% and \(\approx 3\) wt% for the trans isomer, respectively.

This result, indicating a higher selectivity of \(\beta\) NC phase with respect to \(\alpha\) NC phase to absorb cis azobenzene isomer, never observed for other guest molecules so far, can be particularly relevant in order to propose the \(\beta\) NC phase as the PPO nanoporous crystalline phase particularly suitable for absorbing spherically bulky guest molecules.
3.4. Spontaneous Cis $\to$ Trans Isomerization of Azobenzene Molecules

Spontaneous cis$\to$trans isomerization at room temperature of azobenzene molecules, being a guest of co-crystalline phases or dissolved in the amorphous phase have been studied, by FTIR and UV measurements, on PPO thick (~50 $\mu$m) and thin (~100 nm) films.

FTIR spectra, in the wavenumber range 720–670 cm$^{-1}$, of PPO/azobenzene thick films (~50 $\mu$m) presenting $\alpha$, $\beta$ CC as well as amorphous phases, after sorption of trans isomer (black lines), immediately after 1 h of irradiation at 365 nm (green lines) as well as during the time, leading to a spontaneous cis $\to$ trans isomerization, are reported in Figure 8A–C, respectively. The occurrence of trans $\to$ cis isomerization was clearly shown by the reduction of the intensity of peak at 691 cm$^{-1}$ associated to the appearing of a peak at 701 cm$^{-1}$; the spontaneous disappearance of it, during the time, clearly indicated the spontaneous return of cis azobenzene isomers to trans.

The half-time of cis $\to$ trans spontaneous isomerization at room temperature ($\tau_{1/2}$) was evaluated and it was $\sim$48 h for azobenzene molecules included in PPO CC phases while it was five time faster (~10 h) for azobenzene molecules simply absorbed in PPO amorphous film. It is worth noting that the half-life time of cis $\to$ trans spontaneous isomerization of azobenzene dissolved in benzene is $\sim$100 h [61], while in our experiment $\tau_{1/2}$ of cis $\to$ trans isomerization in methanol [76] it was $\sim$240 h (see Figure S1 in supplementary materials).

The obtained $\tau_{1/2}$ values on PPO thick films were comparable to those obtained for azobenzene molecules in molecular structure types AlPO$_4$-5 [65] and ZSM-5 [66] used as host materials. In particular, the half-life time $\tau_{1/2}$ of cis-azobenzene in AlPO$_4$-5 composites was found to be $\sim$100 h, whereas azobenzene in ZSM-5 showed a considerably shorter cis-state lifetime of $\sim$6 h [66]. For host systems, like AlPO$_4$-5 and ZSM-5, difference in channel size, geometry, polarity, and type of acidic sites influenced the relaxation of the cis state. Narrower channels enhanced the guest host interaction lowering the energy of the transition states involved in the cis-trans relaxation and hence having a stabilizing influence on the cis state as occurred for the AlPO$_4$-5 and PPO CC phases. A higher concentration of acidic sites in the host system, as occurred for ZSM-5, may be responsible for the faster cis-relaxation ($\tau_{1/2}$ $\sim$6 h) [66]. For amorphous PPO films the absence of constrained channels or cavities could cause faster cis relaxation leading to a faster half-life time of $\tau_{1/2}$ $\sim$10 h with respect to half-life time occurring if azobenzene molecules were included in CC PPO films ($\tau_{1/2}$ $\sim$48 h).
Narrower channels enhanced the guest-host interaction lowering the energy of the transition states involved in the cis-trans relaxation and hence having a stabilizing influence on the cis state as occurred for the AlPO$_4$-5 and PPO CC phases. A higher concentration of acidic sites in the host system, as occurred for ZSM-5, may be responsible for the faster cis-relaxation ($\tau_{1/2} \sim 6$ h) [66]. For amorphous PPO films the absence of constrained channels or cavities could cause faster cis relaxation leading to a faster half-life time of $\tau_{1/2} \sim 10$ h with respect to half-life time occurring if azobenzene molecules were included in CC PPO films ($\tau_{1/2} \sim 48$ h).

Figure 8. FTIR spectra in the wavenumber range 720–670 cm$^{-1}$ and UV spectra in the range 350–600 nm of $\alpha$ CC (A,A'), $\beta$ CC (B,B') and amorphous PPO films (C,C') as prepared (black line) immediately after irradiation (green line) and collected at different time (colored lines).

Spontaneous cis $\rightarrow$ trans isomerization of azobenzene absorbed in CC and amorphous PPO thick films was also studied by UV measurements and reported in Figure 8A'–C' respectively.

It is well known that trans azobenzene absorption spectrum consists of two well separated bands in the UV visible region. The strong UV band at $\lambda \sim 320$ nm, comes from the allowed $\pi \rightarrow \pi^*$ transition whereas the much weaker band in the visible region at $\lambda \sim 450$ nm corresponds to the forbidden $n \rightarrow \pi^*$ transition [52,77]. As for the cis isomer, $\pi \rightarrow \pi^*$ transitions at $\lambda \sim 250$ nm are weaker, but $n \rightarrow \pi^*$ transition at $\lambda \sim 450$ nm absorbs more strongly than trans azobenzene.

UV-visible spectra in the range 350–600 nm of PPO/azobenzene films (~50 µm) presenting CC and amorphous phases, after sorption of trans isomer (black lines), immediately after 1 h of irradiation at 365 nm (green lines) as well as during the time, leading to a spontaneous cis $\rightarrow$ trans isomerization, are reported in Figure 8A'–C', respectively. After 1 h of ultraviolet light exposure, a decrease in intensity of the 323 nm (out of scale) as well as an increase of the ~446 nm band (green line) was apparent indicating that the photo-induced trans $\rightarrow$ cis isomerization occurred. Moreover, by collecting spectra at different time (colored lines) a decrease of the ~446 nm band was shown indicating the spontaneous return of the cis azobenzene isomer to trans in all PPO films.
The half-times of cis-trans azobenzene spontaneous isomerization, evaluated on \( n \rightarrow \pi^* \) transition band at \( \lambda \sim 446 \) nm, were similar to those obtained by FTIR measurements. Trans \( \rightarrow \) cis photo-isomerization and spontaneous cis \( \rightarrow \) trans isomerization of azobenzene molecules, being guest of PPO co-crystalline phases or dissolved in PPO amorphous phases, were studied at room temperature by UV-Visible measurements also on thin films (0.1–0.2 \( \mu m \)).

UV-Visible spectra in the spectral range between 275 and 500 nm of spin-coated PPO films exhibiting \( \alpha \) phases before (black lines), immediately after photo-isomerization with 365 nm light for 1 min (green lines) and during 20 min (colored lines) a decrease of the \( \sim 446 \) nm band was shown indicating the spontaneous cis \( \rightarrow \) trans isomerization of azobenzene molecules. Moreover, by collecting spectra at different times, \( \tau \rightarrow \) cis isomerization occurred. Moreover, by collecting spectra at different times, \( \tau \rightarrow \) cis band in the UV region close to 3 h for azobenzene included in CC phases and \( \sim 70\% \) for azobenzene absorbed in amorphous phases.

Half-life time of cis \( \rightarrow \) trans spontaneous isomerization as evaluated on the basis of the absorbance at 318 nm \([69,81]\) was approximately \( \approx 55\% \) for \( \alpha \) and \( \beta \) CC phases and \( \sim 70\% \) for azobenzene in amorphous phases.

After only 1 min of UV irradiation a strong reduction of the trans band at 318 nm as well as an increase of the weaker band associated at \( n \rightarrow \pi^* \) (green lines) were apparent, indicating the occurring trans \( \rightarrow \) cis isomerization \([76,80]\). The degree of photoisomerization \([76]\), as evaluated on the basis of the absorbance at 318 nm \([81]\) after 1 min of UV irradiation, was approximately \( \approx 55\% \) for \( \alpha \) and \( \beta \) CC phases and \( \sim 70\% \) for azobenzene absorbed in amorphous phases.

Moreover, it is worth noting that after 1 month of desorption at room temperature (see light blue curves in UV-vis spectra of Figure 9) a desorption of \( \approx 30\% \) of azobenzene molecules being guest of PPO CC phases occurred whereas a much higher desorption of nearly 85\% was apparent if azobenzene molecules were simply absorbed in amorphous PPO films.

Finally, making a comparison with syndiotactic polystyrene (s-PS) the other commercial polymer capable of forming CC phases including azobenzene guest molecules, we can affirm that the main relevant result was the capability of NC PPO phases to absorb higher amounts of azobenzene guest molecules (also for few minutes of exposure time) with respect to NC s-PS phases. For instance, PPO and s-PS films, \( \sim 50 \mu m \) thick, immersed for 30 min into a 2 wt\% azobenzene/methanol solution, showed an azobenzene content close to \( \sim 7.3 \) wt\%, \( \sim 9 \) wt\% and \( \sim 2.8 \) wt\% for PPO films presenting NC \( \alpha \) and \( \beta \) and amorphous phases.
phases, respectively; while only an azobenzene content of ~1 wt% for s-PS films presenting δ NC phase (see supplementary materials).

The obtained results, i.e., the higher amount of azobenzene molecules stably included into CC PPO phases during the time, associated with the availability of PPO films to get different uniplanar orientation of the co-crystalline phases, with the polymer chain prevailing parallel or perpendicular [72] to the film plane, make particularly interesting CC PPO films that could be in principle suitable to develop active materials for the design of stimuli-responsive molecular systems and light-powered molecular machines.

4. Conclusions

Co-crystalline polymeric films of a commercial polymer, as PPO, with azobenzene, i.e., one of the most popular molecular switches, have been prepared and structurally characterized by WAXD, FTIR and UV-Vis measurements.

A comparison with amorphous films revealed a higher solubility as well as a higher stability of azobenzene molecules included as guest in PPO CC phases with respect to azobenzene molecules simply dissolved in amorphous phase.

FTIR linear dichroism measurements on axially oriented PPO films allowed us to establish the inclusion of both trans and cis isomer into α CC phase, as well as the occurrence of trans → cis photo-isomerization and spontaneous cis → trans isomerization without expulsion of azobenzene guest molecules from host co-crystalline lattice.

Sorption studies conducted on photo-isomerized azobenzene methanol solution have shown a higher solubility and selectivity of β NC phase toward cis azobenzene isomer with respect to amorphous and to α NC phase, making the β NC phase particularly promising for absorbing spherically bulky guest molecules and attempting confined photoreactions.

The whole set of data suggests that these films can be suitable for developing active materials for the design of stimuli-responsive molecular systems and light-powered molecular machines.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/chemistry3030078/s1, Figure S1: UV-Visible spectra in the range 350–550 nm of 0.2 wt% azobenzene/methanol solution before (black line), after photoisomerization (green line) and as collected at different times during spontaneous cis-trans isomerization (colored curves). Figure S2: UV-Visible spectra in the range 350–600 nm of α CC PPO (red line), β CC PPO (blue line), amorphous PPO (black line) and δ CC s-PS (green line) films after immersion for 30 min in 2 wt% azobenzene/methanol solution. PPO film spectra (gray line) is also reported for comparison.

Author Contributions: Conceptualization P.R.; methodology, A.C. and N.C.; investigation, N.C. and M.G.; data curation, N.C. and M.G.; writing—original draft preparation, A.C. and P.R.; writing—review and editing, A.C. and P.R.; supervision, A.C., N.C., M.G. and P.R. All authors have read and agreed to the published version of the manuscript.

Funding: This project is Financially supported by Ministero dell’Istruzione, dell’Università e della Ricerca (MIUR), Italy. Nicola Coscia was supported by a research grant from MIUR (PON “R&I” 2014-2020; ARS01_01398 “INPOS—Tecnologia innovativa di rimozione di inquinanti da acquabasati su polimeri cristallini nanoporosi”).

Acknowledgments: Financial support of the “Ministero dell’Istruzione, dell’Università e della Ricerca” is gratefully acknowledged. Gaetano Guerra, Christophe Daniel, Ivano Immediata of University of Salerno are acknowledged for useful discussions.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Kuznicki, S.M.; Bell, V.A.; Nair, S.; Hillhouse, H.W.; Jacubinas, R.M.; Braunbarth, C.M.; Toby, B.H.; Tsapatsis, M. A Titanosilicate Molecular Sieve with Adjustable Pores for Size-Selective Adsorption of Molecules. Nature 2001, 412, 720–724. [CrossRef]
2. Zecchina, A.; Bordiga, S.; Vitillo, J.G.; Ricchiardi, G.; Lamberti, C.; Spoto, G.; Bjørgen, M.; Lillerud, K.P. Liquid Hydrogen in Protonic Chabazite. J. Am. Chem. Soc. 2005, 127, 6361–6366. [CrossRef] [PubMed]
3. Eddaoudi, M.; Li, H.; Yaghi, O.M. Highly Porous and Stable Metal–Organic Frameworks: Structure Design and Sorption Properties. J. Am. Chem. Soc. 2000, 122, 1391–1397. [CrossRef]

4. Pan, L.; Adams, K.M.; Hernandez, H.E.; Wang, X.; Zheng, C.; Hattori, Y.; Kaneko, K. Porous Lanthanide-Organic Frameworks: Synthesis, Characterization, and Unprecedented Gas Adsorption Properties. J. Am. Chem. Soc. 2003, 125, 3062–3067. [CrossRef]

5. Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. Porous Coordination-Polymer Crystals with Gated Channels Specific for Supercritical Gases. Angew. Chem. Int. Ed. 2003, 42, 428–431. [CrossRef]

6. Millward, A.R.; Yaghi, O.M. Metal–Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature. J. Am. Chem. Soc. 2005, 127, 17998–17999. [CrossRef]

7. Soldatov, D.V.; Moudrakovski, I.L.; Ripmeester, J.A. Dipeptides as Microporous Materials. Angew. Chem. Int. Ed. 2004, 43, 6308–6311. [CrossRef]

8. Blau, W.J. Designer Nanotubes by Molecular Self-Assembly. Science 2004, 304, 1457–1458. [CrossRef]

9. Thallapally, P.K.; McGrail, B.P.; Atwood, J.L.; Gaeta, C.; Tedesco, C.; Neri, P. Carbon Dioxide Capture in a Self-Assembled Organic Nanochannel. Chem. Mater. 2007, 19, 3355–3357. [CrossRef]

10. Sozzani, P.; Bracco, S.; Comotti, A.; Ferretti, L.; Simonutti, R. Methane and Carbon Dioxide Storage in a Porous van der Waals Crystal. Angew. Chem. Int. Ed. 2005, 44, 1816–1820. [CrossRef]

11. Reverchon, E.; Guerra, G.; Venditto, V. Regeneration of Nanoporous Crystalline Syndiotactic Polystyrene by Supercritical CO2. J. Appl. Polym. Sci. 1999, 74, 2077–2082. [CrossRef]

12. Daniel, C.; Longo, S.; Fasano, G.; Vitillo, J.G.; Guerra, G. Nanoporous Crystalline Phases of Poly(2,6-Dimethyl-1,4-Phenylene)Oxide. Chem. Mater. 2011, 23, 3195–3200. [CrossRef]

13. De Rosa, C.; Guerra, G.; Petraccone, V.; Pirozzi, B. Crystal Structure of the Emptied Clathrate Form (δe Form) of Syndiotactic Polystyrene. Macromolecules 1997, 30, 4147–4152. [CrossRef]

14. Petraccone, V.; Ruiz de Ballesteros, O.; Tarallo, O.; Rizzo, P.; Guerra, G. Nanoporous Polymer Crystals with Cavities and Channels. Chem. Mater. 2008, 20, 3663–3668. [CrossRef]

15. Nagendra, B.; Cozzolino, A.; Daniel, C.; Rizzo, P.; Guerra, G.; Auriemma, F.; De Rosa, C.; D’Alterio, M.C.; Tarallo, O.; Nuzzo, A. Two Nanoporous Crystalline Forms of Poly(2,6-Dimethyl-1,4-Phenylene)Oxide and Related Co-Crystalline Forms. Macromolecules 2019, 52, 9646–9656. [CrossRef]

16. Nagendra, B.; Cozzolino, A.; Golla, M.; Daniel, C.; Rizzo, P.; Guerra, G. Guest Induced Transition from β to a Nanoporous Crystalline Forms of PPO. Polymer 2020, 187, 122083. [CrossRef]

17. Golla, M.; Nagendra, B.; Fierro, F.; Rizzo, P.; Daniel, C.; Guerra, G. Axially Oriented Nanoporous Crystalline Phases of Poly(2,6-Dimethyl-1,4-Phenylene)Oxide. ACS Appl. Polymer Mater. 2020, 2, 3518–3524. [CrossRef]

18. D’Aniello, C.; Rizzo, P.; Guerra, G. Polymorphism and Mechanical Properties of Syndiotactic Polystyrene Films. Polymer 2004, 45, 11435–11441. [CrossRef]

19. Daniel, C.; Longo, S.; Ricciardi, R.; Reverchon, E.; Guerra, G. Monolithic Nanoporous Crystalline Aerogels. Macromol. Rapid Commun. 2013, 34, 1194–1207. [CrossRef]

20. Mochizuki, J.; Sano, T.; Tokami, T.; Itagaki, H. Decisive Properties of Solvent Able to Form Gels with Syndiotactic Polystyrene. Polymer 2015, 67, 118–127. [CrossRef]

21. Cheng, Y.-W.; Wang, C. Solvent-Induced Crystallization of Electrospun Syndiotactic Polystyrene Nanofibers and Its Reversible Desorption/Sorption of Volatile Organic Vapors. J. Polym. Res. 2016, 23, 234. [CrossRef]

22. Raut, P.; Liang, W.; Chen, Y.-M.; Zhiu, Y.; Jana, S.C. Syndiotactic Polystyrene-Based Ionogel Membranes for High Temperature Electrochemical Applications. ACS Appl. Interfaces 2017, 9, 30933–30942. [CrossRef]

23. Itagaki, H.; Sano, T.; Okabe, T.; Sano, S.; Ebihara, H.; Tomono, F.; Dohra, H. Polymerization of Aniline in Tubular Cavities of the Crystalline Phase of Syndiotactic Polystyrene: Proposal of a Preparation Method of Sophisticated Polymer Composites. ACS Macro Lett. 2017, 6, 1099–1103. [CrossRef]

24. Guerra, G.; Milano, G.; Venditto, V.; Musto, P.; De Rosa, C.; Cavallo, L. Thermoplastic Molecular Sieves. Chem. Mater. 2000, 12, 363–368. [CrossRef]

25. Mahesh, K.P.O.; Sivakumar, M.; Yamamoto, Y.; Tsujita, Y.; Yoshimizu, H.; Okamoto, S. Structure and Properties of the Mesophase of Syndiotactic Polystyrene. J. Membr. Sci. 2005, 262, 11–19. [CrossRef]

26. Tarallo, O.; Auriemma, F.; de Ballesteros, O.R.; Di Girolamo, R.; Diletto, C.; Malafronte, A.; De Rosa, C. The Role of Shape and Size of Guest Molecules in the Formation of Clathrates and Intercalates of Syndiotactic Polystyrene. Macromol. Chem. Phys. 2013, 214, 1901–1911. [CrossRef]

27. Larobina, D.; Sanguigno, L.; Venditto, V.; Guerra, G.; Mensitieri, G. Gas Sorption and Transport in Syndiotactic Polystyrene with Nanoporous Crystalline Phase. Polymer 2004, 45, 429–436. [CrossRef]

28. Uda, Y.; Kaneko, F.; Kawaguchi, T. Selective Guest Uptake from Solvent Mixtures in the Clathrate Phase of Syndiotactic Polystyrene. Macromol. Rapid Commun. 2004, 25, 1900–1904. [CrossRef]

29. Tanigami, K.; Ishii, D.; Nakaoi, T.; Stroeve, P. Characterization of Toluene and 2-Methylnapthalene Transport Separated by Syndiotactic Polystyrene Having Various Crystalline Forms. Polym. J. 2013, 45, 1135–1139. [CrossRef]

30. Kobayashi, H.; Urakawa, O.; Kaneko, F.; Inoue, T. Dynamics of Polar Aromatic Molecules Confined in a Nanocavity of δ-Phase of Syndiotactic Polystyrene as Studied by Dielectric Spectroscopy. Chem. Phys. 2016, 479, 122–128. [CrossRef]
31. Guerra, G.; Daniel, C.; Rizzo, P.; Tarallo, O. Advanced Materials Based on Polymer CocrySTALLine Forms. J. Polym. Sci. B Polym. Phys. 2012, 50, 305–322. [CrossRef]

32. Albunia, A.R.; Minucci, T.; Guerra, G. Ethylene Removal by Sorption from Polymeric Crystalline Frameworks. J. Mater. Chem. 2008, 18, 1046. [CrossRef]

33. Venditto, V.; Pellegrino, M.; Califano, R.; Guerra, G.; Daniel, C.; Ambrosio, L.; Borriello, A. Monolithic Polymeric Aerogels with VOCs Sorbent Nanoporous Crystalline and Water Sorbent Amorphous Phases. ACS Appl. Mater. Interfaces 2015, 7, 1318–1326. [CrossRef]

34. Daniel, C.; Antico, P.; Yamaguchi, H.; Kogure, M.; Guerra, G. Microporous-Crystalline Microfibers by Eco-Friendly Guests: An Efficient Tool for Sorption of Volatile Organic Pollutants. Microporous Mesoporous Mater. 2016, 232, 205–210. [CrossRef]

35. Daniel, C.; Antico, P.; Guerra, G. Etched Fibers of Syndiotactic Polystyrene with Nanoporous-Crystalline Phases. Macromolecules 2018, 51, 6138–6148. [CrossRef]

36. Galizia, M.; Daniel, C.; Fasano, G.; Guerra, G.; Mensitieri, G. Gas Sorption and Diffusion in Amorphous and Semicrystalline Nanoporous Poly(2,6-Dimethyl-1,4-Phenylene) Oxide. Macromolecules 2012, 45, 3604–3615. [CrossRef]

37. Daniel, C.; Zhovner, D.; Guerra, G. Thermal Stability of Nanoporous Crystalline and Amorphous Phases of Poly(2,6-Dimethyl-1,4-Phenylene) Oxide. Macromolecules 2013, 46, 449–454. [CrossRef]

38. Galizia, M.; Daniel, C.; Guerra, G.; Mensitieri, G. 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. 2013, 443, 100–106. [CrossRef]

39. Daniel, C.; Pellegrino, M.; Venditto, V.; Aurucci, S.; Guerra, G. Nanoporous-Crystalline Poly(2,6-Dimethyl-1,4-Phenylene)Oxide (PPO) Aerogels. Polymer 2016, 105, 96–103. [CrossRef]

40. Figueroa-Gerstenmaier, S.; Daniel, C.; Milanò, G.; Guerra, G.; Zavorotynska, O.; Vitillo, J.G.; Zecchina, A.; Spoto, G. Storage of Hydrogen as a Guest of a Nanoporous Polymeric Crystalline Phase. Phys. Chem. Chem. Phys. 2010, 12, 5369. [CrossRef]

41. Mensitieri, G.; Venditto, V.; Guerra, G. Polymeric Sensing Films Absorbing Organic Guests into a Nanoporous Host Crystalline Phase. Sens. Actuators B Chem. 2003, 92, 255–261. [CrossRef]

42. Pilla, P.; Cusano, A.; Cutolo, A.; Giordano, M.; Mensitieri, G.; Rizzo, P.; Sanguigno, L.; Venditto, V.; Guerra, G. Molecular Sensing by Nanoporous Crystalline Polymers. Sensors 2009, 9, 9816–9857. [CrossRef]

43. Erdogan, M.; Özbek, Z.; Çapan, R.; Yagci, Y. Characterization of Polymeric LB Thin Films for Sensor Applications. J. Appl. Polym. Sci. 2012, 123, 2414–2422. [CrossRef]

44. Lova, P.; Bastianini, C.; Giusto, P.; Patrini, M.; Rizzo, P.; Iodice, M.; Soci, C.; Comoretto, D. Label-Free Vapor Selectivity in Poly(p-Phenylene Oxide) Photonic Crystal Sensors. ACS Appl. Mater. Interfaces 2016, 8, 31941–31950. [CrossRef] [PubMed]

45. Marlow, F.; Hoffmann, K.; Caro, J. Photoinduced Switching in Nanocomposites of Azobenzene and Molecular Sieves. Adv. Mater. 1997, 9, 567–570. [CrossRef]

46. Zimmerman, H.E.; Nesterov, E.E. Quantitative Cavities and Reactivity in Stages of Crystal Lattices: Mechanistic and Exploratory Organic Photochemistry. Acc. Chem. Res. 2003, 36, 491–498. [CrossRef] [PubMed]

47. MacGillivray, L.R.; Papaešthathiou, G.S.; Friščič, T.; Hamilton, T.D.; Bučar, D.-K.; Chu, Q.; Varshney, D.-K.; Georgiev, I.G. Supramolecular Control of Reactivity in the Solid State: From Templates to Ladderanes to Metal–Organic Frameworks. Acc. Chem. Res. 2008, 41, 280–291. [CrossRef]

48. Stegmaier, P.; De Girolamo Del Mauro, A.; Venditto, V.; Guerra, G. Optical Recording Materials Based on Photosomerization of Guest Molecules of a Polymeric Crystalline Host Phase. Adv. Mater. 2005, 17, 1166–1168. [CrossRef]

49. Albunia, A.R.; Rizzo, P.; Coppola, M.; De Pascale, M.; Guerra, G. Azobenzene Isomerization in Polymer Co-Crystalline Phases. Polymer 2012, 53, 2727–2735. [CrossRef]

50. D’Aniello, C.; Dondi, D.; Faucitano, A.; Guerra, G. Intercalate Co-Crystals of Syndiotactic Polystyrene with Benzyl Methacrylate and Radiation-Induced Guest Polymerization. Macromolecules 2010, 43, 10560–10567. [CrossRef]

51. Bandara, H.M.D.; Burdette, S.C. Photoisomerization in Different Classes of Azobenzene. Chem. Soc. Rev. 2012, 41, 1809–1825. [CrossRef]

52. Shi, Z.; Peng, P.; Strohecker, D.; Liao, Y. Long-Lived Photoacid Based upon a Photochromic Reaction. J. Am. Chem. Soc. 2011, 133, 14699–14703. [CrossRef]

53. Wang, Y.-T.; Liu, X.-Y.; Cui, G.; Fang, W.-H.; Thiel, W. Photosomerization of Arylazopyrazole Photoswitches: Stereospecific Excited-State Relaxation. Angew. Chem. Int. Ed. 2016, 55, 14009–14013. [CrossRef] [PubMed]

54. Molla, M.R.; Rangadurai, P.; Antony, L.; Swaminathan, S.; de Pablo, J.J.; Thayumanavan, S. Dynamic Actuation of Glassy Polymersomes through Isomerization of a Single Azobenzene Unit at the Block Copolymer Interface. Nat. Chem. 2018, 10, 659–666. [CrossRef]

55. Pianowski, Z.L. Recent Implementations of Molecular Photoswitches into Smart Materials and Biological Systems. Chem. Eur. J. 2019, 25, 5128–5144. [CrossRef] [PubMed]

56. Feringa, B.L. The Art of Building Small: From Molecular Switches to Motors (Nobel Lecture). Angew. Chem. Int. Ed. 2017, 56, 11060–11078. [CrossRef]
58. Kassem, S.; Lee, A.T.L.; Leigh, D.A.; Marcos, V.; Palmer, L.I.; Pisano, S. Stereodivergent Synthesis with a Programmable Molecular Machine. *Nature* 2017, 549, 374–378. [CrossRef]

59. Katsonis, N.; Lubomska, M.; Pollard, M.; Feringa, B.; Rudolf, P. Synthetic Light-Activated Molecular Switches and Motors on Surfaces. *Prog. Surf. Sci.* 2007, 82, 407–434. [CrossRef]

60. Weston, C.E.; Krämer, A.; Colín, F.; Yildiz, O.; Baud, M.G.J.; Meyer-Almes, F.-J.; Fuchter, M.J. Toward Photopharmacological Antimicrobial Chemotherapy Using Photoswitchable Amidohydrolase Inhibitors. *ACS Infect. Dis.* 2017, 3, 152–161. [CrossRef]

61. Asano, T.; Okada, T.; Shinkai, S.; Shigematsu, K.; Kusano, Y.; Manabe, O. Temperature and Pressure Dependences of Thermal Cis-to-Trans Isomerization of Azobenzenes Which Evidence an Inversion Mechanism. *J. Am. Chem. Soc.* 1981, 103, 5161–5165. [CrossRef]

62. Ishikawa, T.; Noro, T.; Shoda, T. Theoretical Study on the Photoisomerization of Azobenzene. *J. Chem. Phys.* 2001, 115, 7503–7512. [CrossRef]

63. Hugel, T. Single-Molecule Optomechanical Cycle. *Science* 2002, 296, 1103–1106. [CrossRef]

64. Alemani, M.; Peters, M.V.; Hecht, S.; Rieder, K.-H.; Moresco, F.; Grill, L. Electric Field-Induced Isomerization of Azobenzene by STM. *J. Am. Chem. Soc.* 2006, 128, 14446–14447. [CrossRef] [PubMed]

65. Kuriyama, Y.; Oishi, S. Mechanism of Thermal Isomerization of Azobenzene in Zeolite Cavities. *Chem. Lett.* 1999, 28, 1045–1046. [CrossRef]

66. Hoffmann, K.; Resch-Genger, U.; Marlow, F. Photoinduced Switching of Nanocomposites Consisting of Azobenzene and Molecula rSieves: Investigation of the Switching States. *Microporous Mesoporous Mater.* 2000, 41, 99–106. [CrossRef]

67. Weh, K.; Noack, M.; Hoffmann, K.; Schröder, K.-P.; Caro, J. Change of Gas Permeation by Photoinduced Switching of Zeolite-Azobenzene Membranes of Type MFI and FAU. *Microporous Mesoporous Mater.* 2002, 54, 15–26. [CrossRef]

68. Wang, L.; Zhang, Y.; Zhan, C.; You, Y.; Zhang, H.; Ma, J.; Xiong, Z.; Liu, X.; Wei, R. Synthesis and Photoinduced Anisotropy of Polymers Containing Nunchaku-Like Unit with an Azobenzene and a Mesogen. *Polymers* 2019, 11, 600. [CrossRef]

69. Al-Bataineh, Q.M.; Ahmad, A.A.; Alsaa d, A.M.; Telfah, A. New Insight on Photoisomerization Kinetics of Photo-Switchable Thin Films Based on Azobenzene/Graphene Hybrid Additives in Polyethylene Oxide. *Polymers* 2020, 12, 2954. [CrossRef]

70. Pesce, L.; Perego, C.; Grommet, A.B.; Klajn, R.; Pavan, G.M. Molecular Factors Controlling the Isomerization of Azobenzenes in the Cavity of a Flexible Coordination Cage. *J. Am. Chem. Soc.* 2020, 142, 9792–9802. [CrossRef]

71. Golla, M.; Nagendra, B.; Rizzo, P.; Daniel, C.; Guerra, G. Axial Orientation of Co-Crystalline Phases of Poly(2,6-Dimethyl-1,4-Phenylene)Oxide Films. *Polymers* 2020, 12, 2394. [CrossRef]

72. Rizzo, P.; Gallo, C.; Vitale, V.; Tarallo, O.; Guerra, G. Nanoporoporous-Crystalline Films of PPO with Parallel and Perpendicular Polymer Chain Orientations. *Polymers* 2019, 11, 193–201. [CrossRef]

73. Biswas, N.; Umapathy, S. Density Functional Calculations of Structures, Vibrational Frequencies, and Normal Modes of Trans- and Cis-Azobenzene. *J. Phys. Chem. A* 1997, 101, 5555–5566. [CrossRef]

74. Flieg l, H.; Köhn, A.; Hättig, C.; Ahrlich s, R. Ab Initio Calculation of the Vibrational and Electronic Spectra of Trans- and Cis-Azobenzene. *J. Am. Chem. Soc.* 2003, 125, 9821–9827. [CrossRef]

75. Fu, L.; Yang, J.; Dong, L.; Yu, H.; Yan, Q.; Zhao, F.; Zhai, F.; Xu, Y.; Dang, Y.; Hu, W.; et al. Solar Thermal Storage and Room-Temperature Fast Release Using a Uniform Flexible Azobenzene-Grafted Polynorborene Film Enhanced by Stretching. *Macromolecules* 2019, 52, 4222–4231. [CrossRef]

76. Ladányi, V.; Dvořák, P.; Al Anshori, J.; Vetráková, L.; Wirz, J.; Heger, D. Azobenzene Photoisomerization Quantum Yields in Methanol Redetermined. *Photochem. Photobiol. Sci.* 2017, 16, 1757–1761. [CrossRef]

77. Forber, C.L.; Kelus ky, E.C.; Bunce, N.J.; Zern er, M.C. Electronic Spectra of Cis- and Trans-Azobenzenes: Consequences of Ortho Substitution. *J. Am. Chem. Soc.* 1985, 107, 5884–5890. [CrossRef]

78. Zimmerman, G.; Chow, L.-Y.; Paik, U.-J. The Photochemical Isomerization of Azobenzene. *J. Am. Chem. Soc.* 1958, 80, 3528–3531. [CrossRef]

79. Rau, H. Photochemistry and Photophysics. In *Progress in Photochemistry and Photophysics*; Rabek, J.F., Ed.; CRC Press: Boca Raton, FL, USA, 1990; Volume 2, pp. 119–141.

80. Lei, Z.; Vaidyalingam, A.; Dutta, P.K. Photochemistry of Azobenzene in Microporous Aluminophosphate AlPO_4-5. *J. Phys. Chem. B* 1998, 102, 8557–8562. [CrossRef]

81. Kazunor i, S.; Masato, K.; Reiko, O.; Teruo, F. Quaternization of Poly(Tertiary Aminostyrene) and Characterization of the Quaternized Polymers. *Polymer* 1997, 38, 5755–5760.