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Azobenzene isomerization in polymer co-crystalline phases

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ABSTRACT

Three different co-crystalline phases of syndiotactic polystyrene (s-PS) with azobenzene have been prepared and structurally characterized. The triclinic δ-clathrate phase is characterized by a styrene-monomeric-unit/guest ratio (SU/G) equal to 8/1 while the δ-intercalate phase is characterized by SU/G = 4/1. The orthorhombic ε-clathrate phase allows stacking of a variable number of guest molecules per monomer unit with SU/G $\geq$ 9/1. Isomerization reactions of the azobenzene guest molecules (both photo-induced trans → cis and spontaneous cis → trans) have been studied by UV–Visible and FTIR measurements. Repeated isomerization cycles produce progressive desorption from the polymer film of azobenzene molecules being simply dissolved in s-PS amorphous phases, while poorly affect the content of azobenzene molecules being guest of s-PS co-crystalline phases. Polarized FTIR spectra of axially oriented films indicate that isomerizations occur without expulsion of azobenzene guest molecules from the polymer co-crystalline phases. The whole set of data indicate that films exhibiting co-crystalline phases of azobenzene with s-PS are suitable for producing self-erasing photo-isomerization patterns with molecular size marks.

1. Introduction

Many different types of solid-state chemical reactions [1] that occur in co-crystalline phases [2] have been described. As for polymer co-crystalline phases, i.e. crystalline phases where low-molecular-mass guest molecules are confined by ordered polymer chains, both intramolecular [3] and intermolecular [4] solid-state reactions involving the guest molecules have been reported, although only for syndiotactic polystyrene (s-PS).

In fact, s-PS is able to form co-crystalline phases with a large number of guest molecules [5–7], always assuming the s(2/1)2 helical conformation. Most s-PS co-crystals [5,6] are characterized by the *ac* layers of close-packed alternated enantiomorphous helices, typical of the nanoporous monoclinic δ form [8], and hence have been defined as δ *co-crystals.* These δ co-crystals in most cases are δ *clathrates*, i.e. the guest molecules are imprisoned into isolated cavities (cooperatively generated by two enantiomorphous helices of two adjacent *ac* layers) [5]. A second class of s-PS δ co-crystals, defined as δ *intercalate* (or simply intercalates) [5g,6,9], has been suggested on the basis of qualitative interpretation of X-ray diffraction data since 1996 [9] and proved by crystalline structure resolutions only in recent years [6]. In the intercalates, the guest molecules are not isolated into host cavities but contiguous inside layers intercalated with the polymer layers [5g,6]. A third class of s-PS co-crystals has been more recently obtained by guest sorption in the nanoporous orthorhombic ε phase of s-PS [10]. In these co-crystals, defined as ε *clathrates*, guest molecules are imprisoned into channels passing the unit cells of the ε form from side to side along the *c* direction [5g–h,7].

As for intramolecular reactions, the complete photo-isomerization reaction of norbornadiene to quadricyclane, in its δ-clathrate co-crystalline phase with s-PS, has been demonstrated and suggested as a recording reaction for advanced optical materials [3]. As for intermolecular reactions between guest molecules, the irradiation-induced polymerization of benzylmethacrylate in its intercalate co-crystalline phase with s-PS has been also demonstrated, although the polymerization products are expelled from the crystalline host phase, and the latter, as a consequence of guest exclusion, reorganizes in a lower order helical mesomorphic phase [4].

It is well known that azobenzene represents a very interesting example of molecular switch, and its operating mechanism is based on the trans-cis isomerization of a double bond. The reversible switching of azobenzene is well studied in solution and in the gas phase [11], as well as in amorphous and crystalline phases [12].

In this paper the formation of different co-crystalline phases of azobenzene with s-PS and the isomerization of azobenzene as

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guest of these co-crystalline phases have been studied. In particular, in first part of this contribution, the formation of three different kinds of co-cocrystalline phases (δ-clathrate, intercalate and ε clathrate) of azobenzene with s-PS is described. In the second part of the paper, isomerization reactions (both photo-induced trans → cis and spontaneous cis → trans) of the azobenzene guest molecules have been studied both by UV–Visible and FTIR measurements.

2. Experimental

The s-PS used in this study was manufactured by Dow Chemical Company under the trademark Questra 101. The ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC) in trichlorobenzene at 135 °C was found to be $M_w = 3.2 \times 10^5$ with the polydispersity index, $M_w/M_n = 3.9$.

Azobenzene and solvents were purchased from Aldrich and used without further purification.

Axially oriented films, 10–40 μm thick, were obtained by stretching extruded films at constant deformation rate of 0.1 s^{-1}, in the temperature range 100–105 °C, with a Brükner stretching machine (Labostretcher Karo IV), maintaining fixed the transverse dimension (constant width drawing). The stretched films are mesomorphic [13]and have been crystallized into a δ clathrate form by immersion for 3 h in liquid CH_2Cl_2.

Films presenting the $a_{//}c_{//}$uniplanar orientation, with a thickness of 25–40 μm, were obtained by casting procedure from solution in chloroform at room temperature. Oriented samples, exhibiting the ε clathrate phase [10c], were obtained by immersion in chloroform of γ form samples, in turn obtained by annealing of δ form films at 130 °C for 1 h.

Films exhibiting the nanoporous δ and ε phases were obtained by immersion of the corresponding clathrate films in acetonitrile for 1 h followed by 10–60 min of solvent desorption at room temperature.

s-PS/azobenzene co-crystalline thick films were obtained by immersion of the film exhibiting the nanoporous δ and ε phases in azobenzene solutions in acetone, acetonitrile or chloroform at room temperature, or by casting procedure in presence of azobenzene. Complete solvent desorption was conducted in the temperature range 25–60 °C and verified by Fourier Transform Infrared (FTIR) measurements.

The content of azobenzene molecules in the films was determined by thermogravimetric measurements (TGA), carried out with a Mettler TG50 Thermobalance in a flowing nitrogen atmosphere at a heating rate of 10 °C/min.

Amorphous s-PS films with thickness in the range 0.1–0.2 μm were obtained by spin-coating of s-PS chloroform solution (1 wt %) onto quartz surfaces at a spin-rate of 1600 rpm [14].

The s-PS crystallization was induced by exposition of spin coated films at benzene vapours leading to the δ phase, at tetrahydrofuran vapours followed by slow annealing at 140 °C for 15 min leading to γ phase, or at trichlorobenzene vapours followed by abrupt annealing at 210 °C for 10 min leading to β phase. The s-PS films in γ phase have been exposed to chloroform vapours leading to ε phase. All films have been exposed to solvent vapours at room temperature for 2 h.

2.1. X-ray diffraction

Wide-angle X-ray diffraction patterns with Nickel filtered CuKα radiation were obtained, in reflection, with an automatic Bruker diffractometer as well as, in transmission, by using a cylindrical camera (radius = 57.3 mm). In the latter case photographic patterns were recorded on a BAS-MS Imaging Plate (FUJIFILM) and processed with a digital imaging reader (FUJIBAS 1800).

To recognize the kind of crystalline phase orientation, photographic X-ray diffraction patterns were taken by having the X-ray beam perpendicular to the film surface (THROUGH) or parallel to the transverse direction (EDGE) or parallel to the main draw direction (END) and by placing the film sample parallel to the axis of the cylindrical camera.

2.2. Fourier transform infrared spectroscopy

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 Brucker spectrometer equipped with deuterated triglycine sulphate (DTGS) detector and a KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He–Ne laser. 32 scans were signal averaged to reduce the noise. Polarized infrared spectra were recorded by the use of a SPECAC 12500 polarizer.

As far as infrared spectroscopy is concerned, the axial orientation function is given by [15]:

$$f_{c,IR} = \frac{R-1}{R+2}\frac{2\cot^2\alpha + 2}{2\cot^2\alpha - 1}$$

where $R = A_{//}/A_{\perp}$ is the dichroic ratio, $A_{//}$and $A_{\perp}$ being the measured absorbance for electric vectors parallel and perpendicular to the draw direction respectively, and α being the angle between the chain axis and the dipole moment vector of the vibrational mode.

2.3. UV–Vis spectroscopy

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

2.4. Trans → cis photoisomerization

sPS/azobenzene co-crystalline samples were irradiated by 365 nm light from a 65 W xenon lamp (BLX equipment from BioLink) at room temperature.

3. Result and discussion

3.1. s-PS/Azobenzene co-crystalline phases

s-PS films exhibiting co-crystalline phases with azobenzene can be easily obtained by casting of s-PS solutions, in which different amounts of azobenzene are dissolved. In particular, s-PS films obtained by room temperature casting procedures from chloroform solutions with 1 wt% of s-PS (and with azobenzene content equal to 18%, 26% and 35% of the polymer content) after complete solvent removal, present an azobenzene content (determined by thermogravimetric measurements) close to 16, 22 and 28 wt% and the X-ray diffraction patterns shown in Fig. 1A–C, respectively. The X-ray diffraction patterns of the same cast films, as taken with an automatic powder diffractometer are also shown in Fig. 1D–F, respectively.

The patterns of Fig. 1A and D, obtained for the lowest guest content (16 wt%) show the high intensity of the equatorial peak at $2\theta \approx 8.6°$, clearly indicating the occurrence of the $a_{//}c_{//}$uniplanar orientation, typical of the casting procedure of s-PS with $CHCl_3$ [16] and suggesting the occurrence of a δ clathrate phase. The patterns of Fig. 1C and F, obtained for the highest guest content (28 wt%)