Fluorescence of Syndiotactic Polystyrene/Trimethylbenzene Clathrate and Intercalate Co-Crystals

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The self-assembling of fluorescent guest molecules, with the δ nanoporous host crystalline phase of syndiotactic polystyrene (s-PS) films, reduces chromophore diffusivity. Moreover, the chromophore fluorescence can be largely perturbed by formation of suitable polymer co-crystals. In particular, by excitation at the absorbance maximum ($\approx$265 nm), s-PS/1,3,5-trimethylbenzene clathrate co-crystals present a broad fluorescence band nearly centered at 300 nm, while the corresponding intercalate co-crystals present a red-shifted fluorescence band with maxima at 330, 340, and 355 nm. This red shifted fluorescence is possibly due to absorption of the primary fluorescence by ground state complexes, formed in the intercalate co-crystal. The enhanced and red-shifted fluorescence could be relevant for optical and optoelectronic applications.

Introduction

Systems composed of solid polymers and of low molecular mass chromophore compounds find several practical applications, including advanced optoelectronic applications.[1] In several cases, chromophore molecules are simply absorbed in polymeric amorphous phases, although frequently to reduce their diffusivity the chromophores are covalently attached to the polymer backbone, either by polymerization of chromophore monomeric units or by grafting the active species onto preformed polymers.[1] The polymerization technique has been often limited by the difficulties in synthesizing and polymerizing highly functionalized monomers. The grafting technique has been limited by the often poor stability toward oxygen or water of the reactive polymeric substrates as well as by the need of several synthetic steps generally leading to low chromophore concentrations.

In recent years, to reduce diffusivity of dye molecules in the solid state and to prevent their self-aggregation, dendrimers have been used.[2] In fact, it has been shown that encapsulating individual chromophores greatly enhances their optical properties due to the reduced self-quenching.[2] The encapsulation of individual chromophores has been also studied in solutions, by using as host molecules not only dendrimers[3] but also large cyclic compounds, like cyclodextrins, cyclophanes, and crown ethers containing many 1:1 supramolecular optical sensing complexes.[4] For these artificial optical sensor materials, based on the inclusion of the guest into the host cavity, the host fluorescence can be bleached or new fluorescent signals can be generated for host–guest binding affinity.

A more simple alternative method to reduce diffusivity of dye molecules in the solid state and to prevent their self-aggregation consists of the formation of co-crystals

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with suitable polymer hosts. Particularly efficient and versatile appears to be the encapsulation of chromophore molecules as the guest of a host nanoporous crystalline phase (the so-called δ phase) of syndiotactic polystyrene (s-PS).[5]

This nanoporous s-PS crystalline phase, which presents eight styrene monomeric units per unit cell and two identical cavities generated between two enantiomorphous s(2/1)2 helices,[6] is promising for applications in chemical separations and air/water purification[7] as well as in sensorics.[8] In fact, it rapidly and selectively absorbs (both from gas phase and from aqueous solutions) suitable guest molecules even at very low activities, while polymer chains maintain their helical conformation. In most cases, *clathrate* phases including isolated guest molecules (generally one per cavity, corresponding to a maximum molar ratio guest/host-monomer-unit of 1/4),[9] are formed while, in few cases, *intercalate* phases including layers of guest molecules intercalated with layers of polymer helices (corresponding to maximum molar ratio guest/host-monomer-unit of 1/2)[10] are instead obtained.

Studies of guest desorption kinetics[11] and of gas transport[12] on s-PS films have shown that the guest solubility can be much higher in the crystalline δ phase (mainly for low solute activities) while the solute diffusivity is generally much higher in the amorphous phase. This offers the opportunity to prepare and characterize samples including low-molecular-mass molecules essentially only as guests of the host crystalline phase. X-ray diffraction[9,10] and linear dichroism infrared[13] studies have clearly shown that the guest molecules present well defined average locations and orientations into co-crystalline phases. Moreover, solid-state ^{2}H NMR studies have shown that the mobility of the solute molecules is heavily reduced when they are guests of the crystalline host phase, rather than simply absorbed in the amorphous phase.[14]

In recent papers, it has been shown that with s-PS some fluorescent molecules (e.g., naphthalene) form clathrate co-crystals while other fluorescent molecules (e.g., 1,4-dimethyl-naphthalene and 1,3,5-trimethyl-benzene (TMB)) form intercalate co-crystals. In this paper we report that TMB can form both clathrate and intercalate co-crystals and that these co-crystals show different fluorescence behavior. In particular, the fluorescence spectra of the intercalate co-crystals show a large red shift, sufficiently far from the host absorption that self-absorption by the host becomes negligible.

Experimental Section

Materials. TMB was purchased from Aldrich and used without further purification.

s-PS was supplied by Dow Chemical under the trademark Questra 101. ^{13}C nuclear magnetic resonance characterization showed that the content of s-PS 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 $M_w/M_n = 3.9$.

δ form films, with thicknesses in the range 25–30 μm, were obtained by casting from 0.5 wt % polymer solution in chloroform, followed by extraction by carbon dioxide in supercritical conditions.[6b] This procedure, as described in detail in ref 15, produces a (010) uniplanar orientation of the crystalline phase, with an orientation factor $f_{010} \approx 0.7$.

s-PS/TMB intercalate and clathrate co-crystals have been obtained by absorption in δ form films of TMB, liquid (for the temperature range 20–50 °C), or in acetone solution, respectively. To allow acetone desorption, our measurements have been effected on polymer films left at room temperature in air at least for 1 day, after their preparation.

The content of chromophore molecules was determined by thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) measurements.

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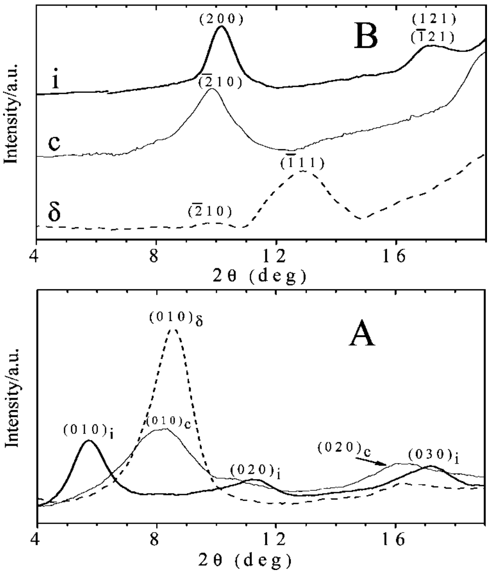

Figure 1. X-ray diffraction patterns (Cu Kα radiation) for the 2θ range 4−19° for s-PS films, presenting orientation of the (010) crystalline plane preferentially parallel to the film plane:[15] (A) as collected by an automatic powder diffractometer; (B) as obtained with X-ray beam perpendicular to the film plane and by using a photographic cylindrical camera. δ form film (dashed line); s-PS/TMB clathrate film (thin line); s-PS/TMB intercalate film (thick line).

Characterization Techniques. Wide-angle X-ray diffraction patterns with nickel-filtered Cu Kα radiation were obtained, in reflection, with an automatic Bruker D8 Advance diffractometer as well as in transmission by using a cylindrical camera (radius = 57.3 mm). In the latter case the patterns were recorded on a BAS-MS imaging plate (FUJIFILM) and processed with a digital imaging reader (FUJIBAS 1800). In particular, to recognize the kind of crystalline orientation present in the samples, photographic X-ray diffraction patterns were taken with X-ray beam both perpendicular and parallel to the film surface.

The degree of uniplanar orientation (parallelism of (010) crystal planes with respect to the film plane) has been formalized on a quantitative numerical basis using Hermans' orientation function, f_{010}

$$f_{010} = (3\cos^2 x - 1)/2$$

by assuming $\cos^2 x$ as the squared average cosine value of the angle, x, between the normal to the film surface and the normal to the (010) crystallographic plane.[15b]

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 Bruker spectrometer equipped with deuterated triglycine sulphate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He–Ne laser. Thirty-two scans were signal averaged to reduce the noise. The degree of crystallinity has been evaluated by the FTIR spectral subtraction procedure described in ref 16.

The fluorescence measurements were obtained by a modular spectrofluorimeter equipped with a 75 W Osram high pressure xenon lamp as the excitation source. The excitation light (265 nm) was isolated by an Acton Research SpectraPro 150 mm focal length grating monochromator and focused onto the face of the s-PS film placed between two microscope slides and rotated with respect to the incident beam of 45°. The fluorescence from the front face was focused on the entrance slit of a Acton Research SpectraPro 300 mm focal length grating monochromator and the fluorescence light was gathered by an HAMAMATSU R928 photomultiplier as detector. To control the spectrofluorimeter and acquire data from the detector, an Acton Research NCL acquisition package and SpectraSense software were utilized.

Fluorescence emission lifetimes of polymers films containing guest molecules were measured with a PRA system 3000 time correlated single-photon-counting apparatus (1–800 ns), equipped with a Norland model 5000 MCA cardboard and a hydrogen discharge pulsing lamp (pulse half-width of 2 ns). Emission decays, observed with an incident light beam at 45°, having an excitation wavelength of 265 nm, were analyzed by means of Edinburgh FLA900 iterative software using a bi-exponential decay.

Results and Discussion

s-PS/TMB Intercalate and Clathrate Host/Guest Co-Crystals. The X-ray diffraction pattern of a s-PS δ form film, presenting orientation of the (010) crystalline plane preferentially parallel to the film plane ($f_{010} \approx 0.7$),[15] as collected by an automatic powder diffractometer for the 2θ range 4–19°, is shown by a dashed line in Figure 1A. The X-ray diffraction pattern of the s-PS δ form film, after equilibrium absorption at 50 °C of liquid TMB, followed by 1 day of room temperature desorption in air (TMB uptake of nearly 16 wt%), is shown as the thick line in Figure 1A. The film maintains essentially the same X-ray diffraction pattern after several months of desorption, when its TMB content reduced to 13 wt %. The observed diffraction peaks at $2\theta_{\mathrm{CuK\alpha}} = 5.7°$, 11.2°, and 17.2°, corresponding to Bragg spacings $d = 1.55$, 0.79, and 0.51 nm, can be immediately attributed to the (010), (020), and (030) reflections (because their intensity is largely increased, as a result of the (010) uniplanar orientation of the crystalline phase) of the s-PS/TMB intercalate phase, which has been recently described in detail by some of us (Figure 2A).[10b] It is worth adding that, because the molar ratio guest/host-monomer-unit is equal to 1/2 and because the degree of crystallinity of the films is not far from 35%, it is possible to infer that in the examined sample most TMB molecules are enclosed as guests of the co-crystalline phase.

The X-ray diffraction pattern of the s-PS δ form film after equilibrium absorption at room temperature from acetone/TMB solutions (20 wt%) and after complete acetone desorption (as pointed out by the disappearance of the FTIR peak at 1219 cm^{-1}, after only a few minutes), corresponding to a TMB uptake of 9 wt %, is shown as a thin line in Figure 1A. The reduction of the intensity and the shift from $2\theta = 8.4°$ down to 8.1°, of the (010) reflection of the δ form, is typical of s-PS clathrate phase formation.[6a,c] In fact, the diffraction pattern presents (010) and (020) reflections corresponding to a spacing perpendicular to the *ac* plane, $d_{010} = 1.09$ nm, typical of a clathrate phase (see, e.g., Figure 4 in ref 10b).

X-ray diffraction patterns of the same films of Figure 1A obtained with the X-ray beam perpendicular to the film plane, by using a photographic cylindrical camera, recorded on an imaging plate and processed with a digital imaging reader,

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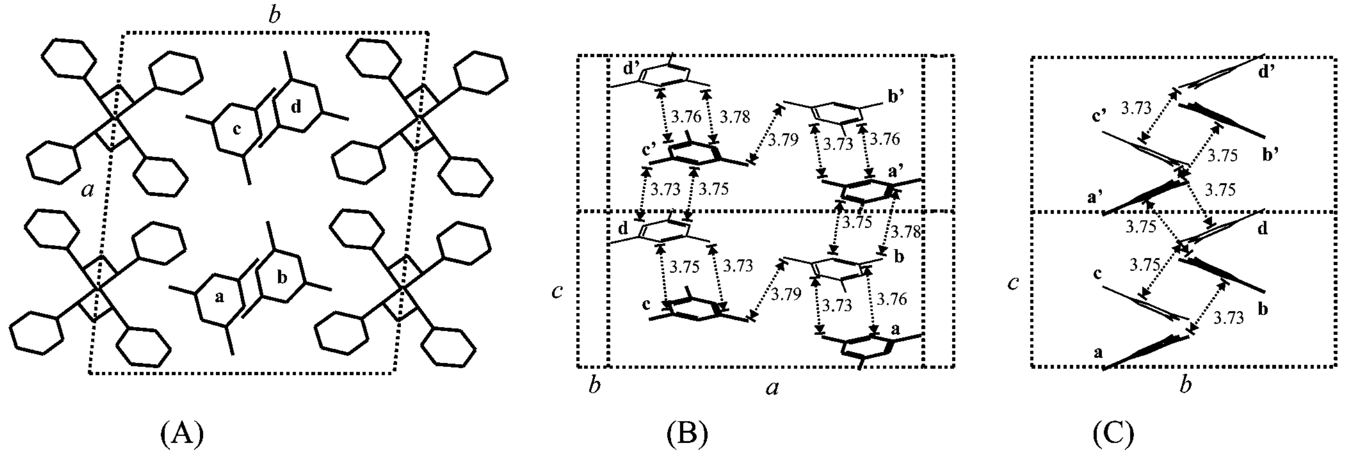

Figure 2. Structure of the intercalate form of s-PS containing TMB, as determined in ref 10b: (A) projection along the *c* axis. (B, C) Two different views of the guest layer, obtained by making projections of the guest molecules contained in two unit cells: (B) perpendicular to the *ac* plane; (C) along the *a* axis. Guest molecules near to the reader are represented with bold lines. The shortest distances (expressed in Å) between neighboring guest atoms are also indicated.

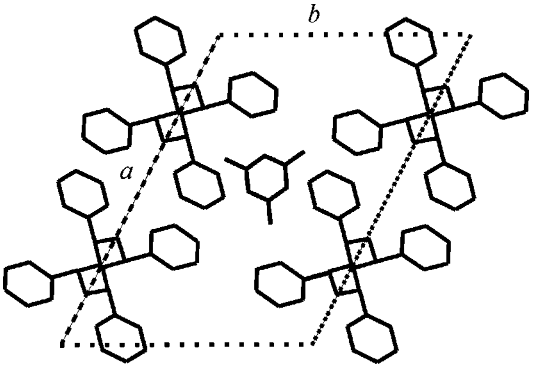

Figure 3. Schematic model of the projection along the *c* axis of the clathrate form of s-PS containing TMB, as roughly anticipated by analogy with structures of other s-PS clathrate co-crystals.[9]

are shown in Figure 1B. For both s-PS/TMB systems, a large decrease of the intensity of the $(\bar{1}11)$ peak, typical of the δ form, associated with an increase of intensity of the peak located at $2\theta_{\mathrm{CuK}\alpha} \approx 10.2°$ (which is indexed as $(\bar{2}10)$ for the δ-form[6a] and for all known s-PS clathrate phases[9] while indexed as (200) for the s-PS/TMB intercalate phase[10b]) is clearly observed, as a consequence of TMB absorption. This confirms that both s-PS/TMB films of Figure 1 present co-crystalline phases. The overall information from Figure 1 clearly indicates that δ form s-PS films, after treatments by acetone/TMB solutions, present a clathrate rather than an intercalate phase.

The crystalline structure of the s-PS/TMB clathrate co-crystals is not known and is presently studied in our laboratories. However, on the basis of analogy with other s-PS clathrate co-crystals,[9] its approximate model can be easily anticipated, as schematically shown in Figure 3.

Because the clathrate guest/host-monomer-unit molar ratio is 1/4 and the degree of crystallinity of the films is not far from 35%, it is reasonable to assume that, also for the clathrate film, most TMB molecules are enclosed as guest of the co-crystalline phase. This conclusion has been confirmed by the method described in Figure 4 of ref 10a, that is, by combining TGA and infrared dichroism measurements on uniaxially oriented films presenting the s-PS/TMB clathrate phase.

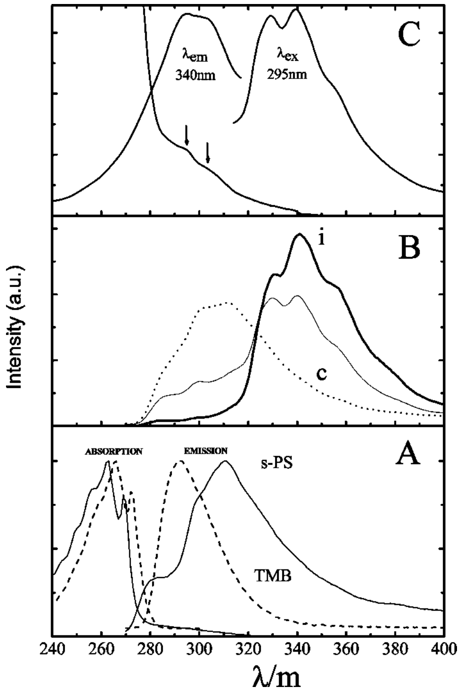

Figure 4. Fluorescence of s-PS films: (A) Absorption and emission spectra (excitation at 265 nm) of a semicrystalline δ form s-PS film (thin lines) and of a TMB solution in cyclohexane (dashed lines). (B) Emission spectra (excitation at 265 nm) of s-PS films presenting clathrate co-crystals (guest content 9 wt %, dotted line) and intercalate co-crystals: freshly prepared (guest content 16 wt %, thin line) and aged (guest content 13 wt %, thick line). (C) Absorption, fluorescence excitation ($\lambda_{\mathrm{em}} = 340$ nm) and emission spectra ($\lambda_{\mathrm{ex}} = 295$ nm) of a s-PS/TMB intercalate co-crystalline film.

In summary, by absorbing TMB, pure or as acetone solution, in δ form s-PS films it is possible to obtain two different kinds of s-PS/TMB molecular-complex phases, being intercalate (with layers of guest molecules, Figure 2) or clathrate (with isolated guest molecules, Figure 3), respectively. The formation of both intercalate and clathrate phases with s-PS by the same guest has been already pointed out for benzene,[10b] although one of the two phases (intercalate) has been observed only in the gel state.[17] TMB is

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the first s-PS guest for which the occurrence of both clathrate and intercalate co-crystalline phases has been found to be stable in the solid state.

Fluorescence of the s-PS/TMB Host/Guest Co-Crystals. Steady-state absorption and emission spectra for excitation at 265 nm of a semicrystalline δ form film (thin lines) and of TMB dissolved in cyclohexane (0.5 wt%, dashed lines) are compared in Figure 4A. It is apparent that absorption spectra are similar for the polymer host and for the TMB guest, while the polymer host emission spectrum presents a broad excimer component, nearly centered at 315 nm. Hence, s-PS films can generate excimers, analogous to those already described for atactic and isotactic polystyrene films.[18]

Steady-state emission spectra for excitation at 265 nm of clathrate and intercalate s-PS/TMB films are compared in Figure 4B. The fluorescence of an s-PS/TMB film (9 wt % of TMB) containing the clathrate phase is shown as a dashed line in Figure 4B and is strictly similar to those of films presenting dense polymeric crystalline phases (α, β, or γ) with TMB simply dissolved in their amorphous phases, as well as rather similar to those of fully amorphous films with TMB dissolved in atactic PS (not reported). For these PS/TMB systems the fluorescence presents a broad maximum nearly centered at 300 nm, which is essentially additive with respect to the host (nearly at 315 nm, Figure 4A) and the guest (nearly at 290 nm, Figure 4A) fluorescence.

The fluorescence of an s-PS/TMB film (13 wt % of TMB) containing the intercalate phase, which is shown as a thick line in Figure 4B, presents instead a nearly negligible emission band in the range 270–310 nm and an intense fluorescence band with three clearly apparent maxima at 330, 340, and 355 nm. The same sample, when freshly prepared (TMB content of 16 wt %, thin line in Figure 4B), presented, beside this fluorescence band, also a minor band in the usual fluorescence range of s-PS/TMB systems. These results can be rationalized by assuming that the emission below 310 nm is due to TMB molecules simply dissolved in the amorphous phase, which are more easily released by the film than TMB guest molecules of the co-crystalline phase.[11,12]

The observed red-shifted fluorescence phenomenon cannot be attributed to excited-state complexes, which generally produce unstructured emissions. It is worth noting that for TMB a broad unstructured excimer emission, centered nearly at 315 nm, has been observed at low temperatures (−78 °C) while no excimer emission at room temperature has been found, even in the pure liquid state.[19]

The high wavelength fluorescence maxima of the intercalate host-guest system have been studied in more detail by collecting fluorescence emission spectra for excitation at 295 nm (Figure 4C). The excitation spectrum, obtained for the emission at 340 nm, follows the usual mirror image rule and two maxima nearly at 295 and 305 nm are observed (Figure 4C). The absorption spectrum of the intercalate host-guest system (also shown in Figure 4C) also shows two minor high wavelength shoulders, located at 295 and 305 nm. It is worth noting that the large difference between absorption and excitation spectra of Figure 4C gives a clear indication of specific complex formation, which is energetically favored in the ground state.

Table 1. Fluorescence Emission Lifetimes of δ-s-PS and s-PS/TMB Co-Crystalline Films

crystalline phase	TMB content wt %	λ_{ex}, λ_{em}[a]	τ_1 (nsec)[b]	τ_2 (nsec)[b]	$B = B_1/B_2$[c]	χ^2
δ	none	260, 330	4.8	14.6	1.81	1.189
clathrate	1.5	260, 360	6.0	40.7	0.21	1.170
intercalate	13	260, 360	5.7	42.9	0.08	1.114

[a] Excitation (ex) and emission (em) wavelengths expressed in nm. [b] Fluorescence lifetimes having an uncertainty of ±0.8 ns. [c] Pre-exponential factor ratios of biexponential decays. [d] χ^2 squared best fitting parameter.

Hence, an unexpected strong fluorescence bleaching is observed in s-PS/TMB intercalate co-crystals, inducing a red shift (i.e., 35–45 nm) of the corresponding steady state fluorescence spectra. This effect is not simply due to the high TMB guest concentration, but it is related to the three-dimensionally ordered organization of TMB in its intercalate co-crystals with s-PS. As a consequence, the ground state complexes, which are responsible for the new fluorescence phenomena, are expected to present geometry not far from those observed in the TMB layers of the s-PS/TMB intercalate phase,[10b] which are shown for two different views in Figure 2B,C.

Additional information on the photophysical properties was achieved by the fluorescence lifetime measurements, by using a time correlated single photon counting technique, as reported in Table 1. All fluorescence lifetime measurements at room temperature on s-PS films provide, by iterative deconvolution analysis, biexponential decays, in which the short-lived and long-lived emission lifetimes are found at 4.8 ns and 14.6 ns, respectively. The long-lived fluorescence emission can be reasonably ascribed to excimer, while that of the short-lived component is due to the s-PS singlet excited states. When TMB guest is present in the s-PS host films, the long-lived fluorescence emission reaches about 41–43 ns, while the short-lived emission component remains quite unchanged. The TMB guest content has a dominant effect both in the pre-exponential factor ratio and in the long-lived fluorescence emission intensities of host/guest fluorescence decays (see Table 1). The previous measured fluorescence lifetimes, ranging from 36 to 39 ns in *n*-hexane TMB solution,[19] are in good agreement with the results found for TMB/s-PS complexes. The time resolved fluorescence intensities of the s-PS/TMB co-crystal complexes and those due to s-PS excimers guest films cannot be separated under the above described experimental conditions.

The lifetime data of Table 1 are very similar for the film containing only 1.5 wt % of TMB (presenting a clathrate phase, being prevailingly empty) and for the film containing 13 wt % of TMB (a typical intercalate co-crystal). Hence, the long-lived fluorescence lifetimes attributed to TMB are essentially independent on the structural organization of the s-PS co-crystals.

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Conclusions

New transparent polymer/chromophore systems have been prepared by simple procedures on s-PS, a robust and cheap hydrocarbon polymer. The formation of these host/guest complexes is highly beneficial to the stability of the polymer/chromophore systems because it strongly reduces the chromophore diffusivity.

For the s-PS/TMB system, X-ray diffraction measurements have proved the formation of two different kinds of polymer/chromophore host/guest co-crystals: *intercalate*, including layers of guest molecules intercalated with layers of polymer helices (corresponding to molar ratio guest/host-monomer-unit of 1/2) as well as *clathrate*, including isolated guest molecules into the cavities (corresponding to a molar ratio guest/host-monomer-unit of 1/4).

UV absorption and emission studies on s-PS films have shown that fluorescence phenomena are essentially additive when the chromophore is simply absorbed in the polymeric amorphous phase or isolated guest of the clathrate co-crystal. On the other hand, the fluorescence of the intercalate s-PS/TMB co-crystal, when excited at its absorbance maximum, is red-shifted with respect to both host and guest emissions. This phenomenon has been attributed to a fluorescence bleaching, which is related to the three-dimensional order of the intercalate s-PS/TMB co-crystals.

The achieved fluorescence enhancement and red-shift could be relevant for optical and optoelectronic applications. Particularly relevant is the ability to emit at longer wavelengths, which could bring the benefit of minimum losses due to re-absorption of the host phase.

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