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Green–blue luminescence dichroism of cyano-containing poly[(*m*-phenylene ethynylene)-*alt*-(*p*-phenylene ethynylene)] aggregates dispersed in oriented polyethylene

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Abstract

A new highly luminescent cyano-containing poly[(*m*-phenylene ethynylene)-*alt*-(*p*-phenylene ethynylene)] derivative (CN-PPE) has been prepared and blended in micro/nano-sized dispersions into linear low density polyethylene (LLDPE) films by melt-processing. CN-PPE macromolecules show pronounced tendency to form molecular aggregates in the excited state when dispersed in the polymer matrix with emission characteristics depending on the structural order of the luminescent chromophores. In CN-PPE/LLDPE films, the polymer matrix orientation induces effective anisotropic arrangements of the π–π staking interactions between luminescent guest aggregates, thereby generating a pronounced green–blue dichroic emission. The capability to easily modulate the luminescent properties of polyethylene films (from green to blue reversibly) simply by varying CN-PPE concentration or by stretching the polymer matrix, suggests various technological applications in the field of smart and intelligent films from thermoplastic materials.

Keywords: Luminescent polymeric chromophores; Polyethylene orientation; Smart dichroic materials

1. Introduction

In the past few years many efforts have been devoted to the modification of the optical properties of polyolefins by the dispersion of active dyes [1–6], metal complexes [7,8] and noble metal nano-particles [9–13]. Actually, combining the attractive mechanical properties of the host polymer matrices, i.e. structural order and high degree of chain extension, with the opto-electronic characteristics of organic, inorganic and organo-metallic guest chromophores, highly dichroic polarizing films, photoluminescent devices and efficient optical filters may be prepared.

Particularly, the incorporation of highly luminescent molecules may be advantageously used for the fabrication of anisotropic linear and non-linear optical devices [3–5,14], transistors [15], lasers and molecular strain sensors for polymer films [16–19].

Among very attractive photoluminescent materials are highly π-conjugated semiconducting polymers such as poly(*p*-phenylene vinylene) (PPV) and poly(*p*-phenylene ethynylene) (PPE) derivatives [20,21]. These two classes of polymers, usually employed for the fabrication of organic displays [4,5,22,23], polymer lasers [24,25] and plastic photovoltaic devices [26–29], may be efficiently dispersed into various polyolefins by different preparation routes according to the polymers processability. Interestingly, the photoluminescent emission properties of these conjugated polymers strongly depend on their state of matter and supramolecular architecture. It is well known that luminescent macromolecules of a well defined solid-state ordering tends to have π–π interactions among the planar π-conjugated backbones, which lead to the formation of molecular aggregates and/or excimers and often result in red-shifted emission [30–37]. On the contrary, samples characterized by a low degree of long-range order show an emission behaviour

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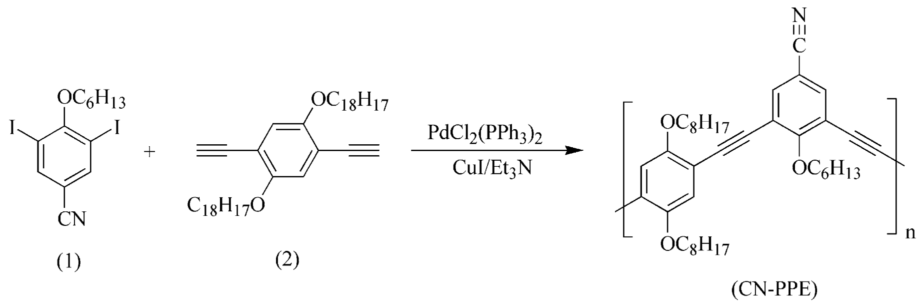

Scheme 1. CN-PPE Synthesis.

that arises from the intrinsic properties of individual luminescent macromolecular chains.

In the blend, the luminescent polymers are surrounded by a host polymer and dispersed in micro/nano-dimension. It is conceivable that the molecular conformation of a luminescent guest molecule can be affected by the morphology or supramolecular structures of the host polymer matrix. It would be a generally interesting issue, therefore, to examine the morphological impact of the polymer matrix on the optical properties of luminescent materials.

The selected luminescent guest is a new cyano-derivative of poly[(*m*-phenylene ethynylene)-*alt*-(*p*-phenylene ethynylene)] (CN-PPE, Scheme 1), which is highly blue–green-emitting in both solution and solid states. Cyano-substituents were suitably introduced on the phenyl ring in order to increase the luminescence efficiency of the conjugated macromolecule. In addition, the presence of *m*-phenylene units reduces the high tendency of conjugated chromophores towards the formation of micro-sized molecular aggregates that often causes phase segregation from polyolefinic host matrices [1,38–42].

The optically inert poly(ethylene) (PE), i.e. linear low density polyethylene (LLDPE), has been used as a dispersing medium. Upon blending by melt-processing, the polymer chromophores of the most probable molecular conformations are confined among PE chains.[1] In addition, any morphological changes of the PE matrix due to elongation by stretching, may induce a corresponding response in the packing and conformation of the nearby guest chromophores. Such induced molecular packing or conformations, which may not be thermodynamically stable, are trapped in the PE matrix and result in attractive optical properties for applications.

2. Experimental part

2.1. Materials

4-Hexyloxy-3,5-diiodobenzenecarbonitrile was purchased from Acros Organics. 1,4-Diethynyl-2,5-dioctyloxybenzene was prepared as reported previously [43]. All the chemicals were used without further purification. Solvents were dried, distilled and stored under nitrogen or argon.

Linear low density polyethylene (LLDPE, Dowlex SC 2107, Melt flow index, 190 °C/2.16 kg = 2.3 g/10 min, d = 0.917 g/cm^3, supplied by Dow Plastics, USA) was used as polymer host matrix.

2.2. Synthesis of cyano-containing poly[(m-phenylene ethynylene)-alt-(p-phenylene ethynylene)] (CN-PPE)

4-Hexyloxy-3,5-diiodobenzenecarbonitrile (0.501 g, 1.1 mmol), 1,4-diethynyl-2,5-dioctyloxybenzene (0.421 g, 1.1 mmol), and triethylamine (5 mL) were dissolved in 15 mL of dry toluene in a 50 mL oven-dried flask, which was equipped with a magnetic stirrer and capped with a rubber septum. The solution was deoxygenated by a freeze-thaw technique, and filled under argon atmosphere. Catalysts PdCl$_2$(PPh$_3$)$_2$ (7 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) were added at room temperature while a slow argon flow was maintained. The reaction mixture was then stirred at room temperature overnight. The polymer was precipitated by dropwise addition of the solution to methanol (200 mL) under vigorous stirring. The crude polymer was dissolved again into 25 mL of THF, and precipitated from methanol (200 mL) as a yellow solid (0.54 g, 84% yield).

^{1}H NMR (400 MHz, CDCl$_3$) (7.71 (2H, Ar-*H*), 6.98 (2H, Ar-*H*), 4.55 (2H, –O*CH*$_2$–), 4.01 (4H, –O*CH*$_2$–), 1.82 (6H, –*CH*$_2$–), 1.0–1.7 (26H, –*CH*$_2$–), 0.83 (9H, –*CH*$_3$). Anal. Calcd for $C_{39}H_{51}NO_2$: C, 80.51%; H, 8.83%; N, 2.41%. Found: C, 80.48%; H, 8.87%; N, 2.39%.

2.3. Apparatus and methods

^{1}H NMR spectra were acquired on a Bruker ARX 400 spectrometer. UV–vis spectra of CN-PPE were acquired either in distilled dry tetrahydrofuran (THF) or from films spin-cast on quartz plates on a Hewlett–Packard 8453 diode array spectrophotometer. Concerning pure CN-PPE, fluorescence spectra were obtained on a PTI steady-state fluorometer. The quantum yield in solution was measured in THF solution by using the literature procedure [44]. Size exclusion chromatography (SEC) was carried out on a Viscotek SEC assembly consisting of a model P1000 pump, a model T60 dual detector, a model LR40 laser refractometer, and three mixed bed columns (10 µm). Polymer solutions for SEC experiments were prepared in a concentration of about 3 mg/mL. The SEC system was calibrated by using narrow and broad polystyrene

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[1] The combination of a low density polymer matrix with the blending in the melt of the components mixture was found to be the best procedure for the preparation of highly compatible polymer blends [2].

standards prior to use. The polystyrene standards were purchased from American Polymer Standards Corp.

LLDPE blends were prepared in a Brabender plastograph mixer (mod. OHG47055, 30 cm^3) under nitrogen atmosphere by introducing about 20 g of the polymer and 0.02–0.3 wt% of CN-PPE in the mixer at 180 °C with a rotor speed of 50 rpm. After 10 min, the mixing was stopped and the recovered materials moulded under compression in a press (Campana PM20/200) at 180 °C for 5 min. After removal from the press, the films were allowed to reach slowly room temperature ($\sim$5 °C min^{-1}). The films were generally analysed after 2–3 days. The thickness of the moulded films was about 80–100 μm. Solid state drawings of the host-guest films were performed on a thermostatically controlled hot stage at 100 °C for LLDPE blend films. The drawing ratio (Dr), defined as the ratio between the final and the initial length of the samples, was determined by measuring the displacement of ink-marks printed onto the films before stretching.

Differential scanning calorimetry (DSC) analyses were performed under nitrogen flux (80 mL/min) with a Mettler-Toledo/DSC 822^e equipped with a cooling system. The calibration was performed with zinc and indium. Heating and cooling thermograms were carried out at a standard rate of 20 °C/min.

Attenuated total reflectance Fourier transform infrared (ATR/FTIR) spectra were recorded on polymer films with the help of a Perkin–Elmer Spectrum One spectrometer fitted with Universal ATR (UATR, DiComp™ crystal) accessories.

The scanning electron microscopy (SEM) analysis was performed with a Jeol 5600-LV microscope, equipped with Oxford X-rays EDS microprobe.

Atomic force microscopy (AFM) images were recorded on a Nanoscope III Multimode microscope operating in Contact Mode.

Digital images were obtained by using a Nikon Coolpix 2000 camera exposing the films under a Camag UV-Cabinet II equipped with Sylvania 8W long-range lamps (366 nm).

UV–vis absorption spectra of PE films were recorded under isotropic conditions with a Perkin–Elmer Lambda 650, and in linearly polarized light by mounting motor-driven Glan–Taylor linear polarizers.

Fluorescence spectra were recorded under isotropic excitation with the help of a Perkin–Elmer Luminescence spectrometer LS50B equipped with motor-driven linear polarizer on the detection side. The position of the sample was adjusted in the direction of the excitation beam in such a way that the optical axis of excitation and emission crossed in the film plane.

The films roughness was diminished, using ultra-pure silicon oil (poly(methylphenylsiloxane), 710® fluid, Aldrich) to reduce surface scattering between the polymeric films and the Suprasil quartz slides used to keep them planar.

Origin 7.5, software by Microcal Origin®, was used in the analysis of the absorption and emission data.

3. Results and discussion

3.1. Polymer synthesis and characterization

The cyano-containing poly[(*m*-phenylene ethynylene)-*alt*-(*p*-phenylene ethynylene)] (CN-PPE) has been synthesized at room temperature by coupling 4-hexyloxy-3,5-diiodobenzene-carbonitrile (1) with 2,5-dialkoxy-1,4-diethynylbenzene (2) (Sonogashira–Hagihara reaction) [45–47] (Scheme 1).

^{1}H NMR spectroscopy shows only two major aromatic protons at 7.0 (on the *p*-phenylene) and 7.7 (on the *m*-phenylene) ppm in about 1:1 ratio as expected. The presence of *m*-phenylene linkages modifies the polymer chain rigidity, to allow polymer solubility in common organic solvents such as THF, chloroform, and toluene [43,48–52].

Size exclusion chromatography (SEC) analysis of the macromolecule shows that the polymer has a $\bar{M}_w$ of 21,200 g/mol (PDI $\approx$ 1.9–2.4).

UV–vis absorption spectrum of CN-PPE in THF exhibits two maxima with $\lambda_{max} \approx 315$ and 399 nm (Fig. 1).

The spin-cast thin film reveals also a high and low energy absorption bands at 328 and 428 nm, respectively. The spectroscopic red-shift ($\sim$30 nm) can be attributed to the formation of inter-chain interaction among the chromophores favoured by the higher packing and more extended chain conformation in the bulk.

Fluorescence of CN-PPE in THF solution shows an emission shoulder at about 423 nm, and a maximum at 443 nm, probably attributed to the 0-0 and 0-1 vibrational transitions, respectively. In addition, the fluorescence quantum efficiency of CN-PPE in THF has been estimated to be about $\phi_{fl} \approx 0.6$.

Its film, however, gives a broad structureless emission with λ_{max} red-shifted to 498 nm (by $\sim$55 nm from its solution fluorescence λ_{max}) suggesting the presence of molecular aggregates also in the excited state.

The broad endotherm of CN-PPE pointed at about 145 °C showed by the differential scanning calorimetry (DSC)

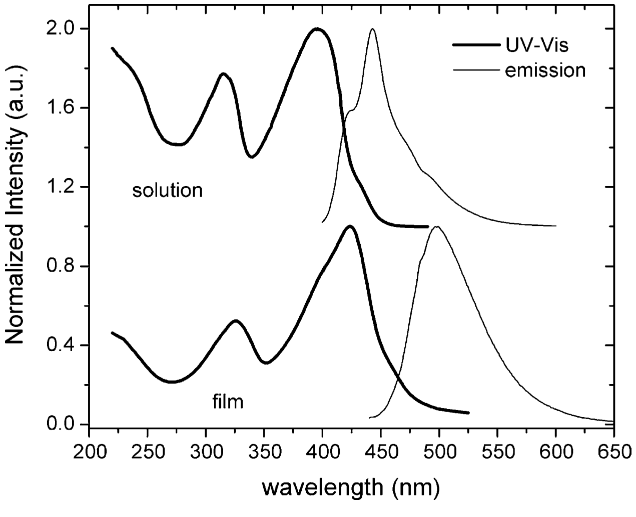

Fig. 1. UV–vis and fluorescent emission ($\lambda_{exc} = 390$ nm) spectra of CN-PPE in THF solution (top) and film (bottom) states.

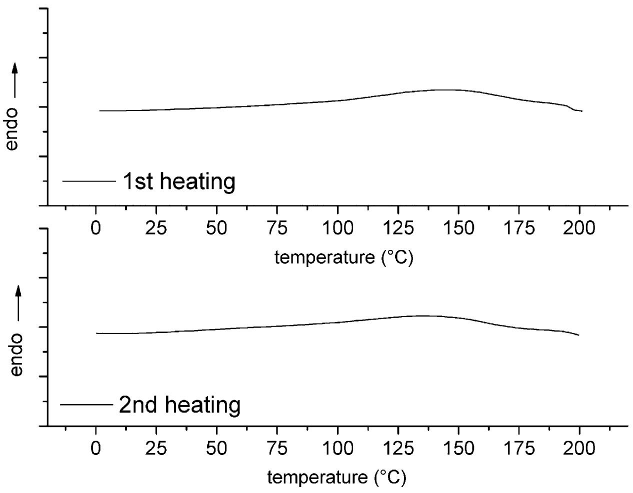

Fig. 2. First and second DSC heating traces of pure CN-PPE.

thermogram (Fig. 2) is attributed to the polymer melting as confirmed by polarized optical microscopy [53]. The broad transition may be probably caused by the contemporary presence in the polymer structure of *m*-phenylene linkages, lateral alkyl groups and by the broad molecular weight distribution that introduce structural defects to the crystalline cell. However, the solid-state structure of the luminescent polymer will be investigated more in detail by small- and wide-angle X-ray measurements in the next future. The similarity between the first and the second heating traces suggests a complete reversible thermal transitions and polymer stability up to 200 °C.

3.2. Films of CN-PPE/polyethylene blends: morphology and guest phase distribution

CN-PPE has been dispersed into LLDPE at different concentrations (from 0.02 to 0.2 wt% with respect to the polymer matrix) by melt-processing in a Brabender type mixer (Table 1).

The scanning electron microscopy (SEM) image of LLPPE5 films (Fig. 3), containing the 0.2 wt% of CN-PPE, reveals no evidence of CN-PPE micro-sized aggregates indicating a good dispersion behaviour of the photoluminescent polymer into the PE matrix.

Accordingly, the first and second heating DSC traces of the polyethylene binary films (data not reported) do not show any detectable endotherm signals for CN-PPE thermal transitions.

Table 1
Composition of the binary polyethylene films prepared

Sample[a]	Polymer matrix	Type of mixing	CN-PPE (wt%)
LLPPE1	LLDPE	Melt-processing	0.02
LLPPE2	LLDPE	Melt-processing	0.05
LLPPE3	LLDPE	Melt-processing	0.10
LLPPE4	LLDPE	Melt-processing	0.15
LLPPE5	LLDPE	Melt-processing	0.20
LLPPE6	LLDPE	Melt-processing	0.30

[a] All the acronyms have to be referred to the pristine films otherwise specified by the drawing extent reported in brackets in the text.

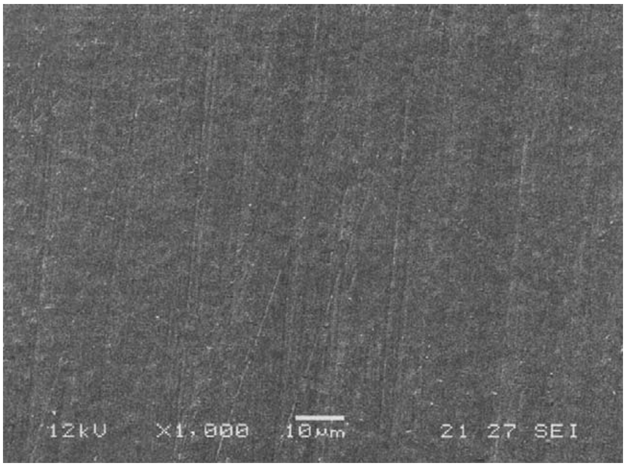

Fig. 3. SEM micrograph of LLPPE5 film. The surface texture of the film is attributed to the compression molding procedure of CN-PPE/LLDPE pellets between polytetrafluoroethylene films.

In addition, Fourier transform infrared (ATR/FTIR) spectroscopy measurements performed on LLPPE5 films (Fig. 4) confirm the good homogeneous distribution of the photoluminescent guest in the low density polyethylene matrix. The CN-PPE macromolecules appear well dispersed under the resolution sensitivity of the ATR/FTIR technique.

Atomic force microscopy (AFM) image of LLPPE5 (Fig. 5) after uniaxial orientation at high temperature (100 °C, drawing ratio = 10), displays irregular rod-shaped structures attributed to the CN-PPE domains, which showed to have a regular height of about 31 ± 1 nm as revealed by the section analysis. Particularly, those nano-sized structures result scarcely oriented along the PE drawing direction.

3.3. Films of CN-PPE/polyethylene blends: optical properties-absorption

The absorption spectra of CN-PPE macromolecules in LLDPE films exhibit a similar profile as observed in tetrahydrofuran (THF) solution. The absorption maximum is

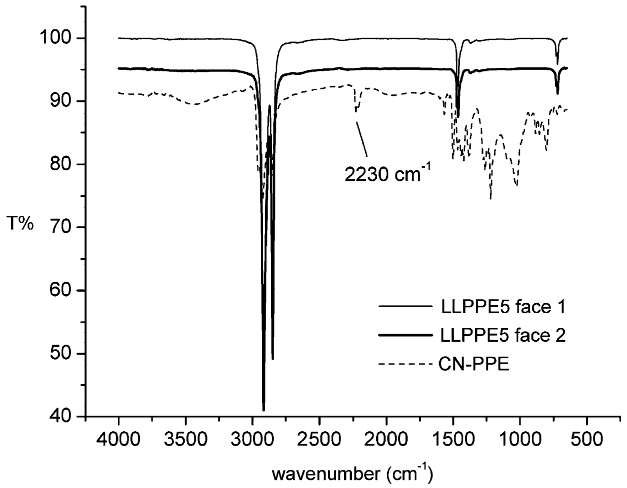

Fig. 4. ATR/FTIR spectra of LLPPE5 film and CN-PPE in KBr dispersion. Face 1 is the lower part of the film; face 2 is the upper one.

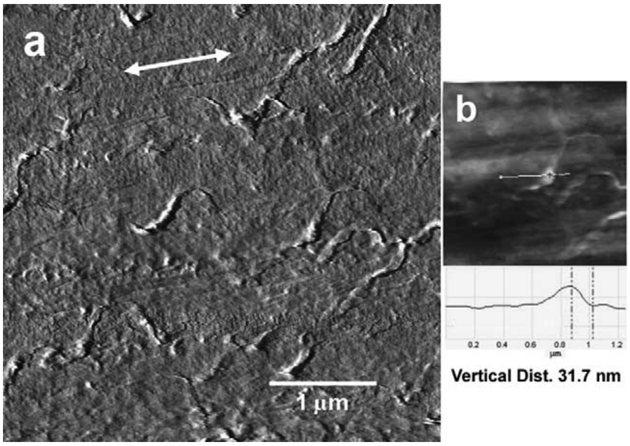

Fig. 5. (a) 8×8 µm^2 AFM deflection images of oriented LLPPE5 (Dr = 10) film showing the dispersion of CN-PPE and (b) cross-sectional analysis of the same film. The white arrows denote the drawing direction of the film.

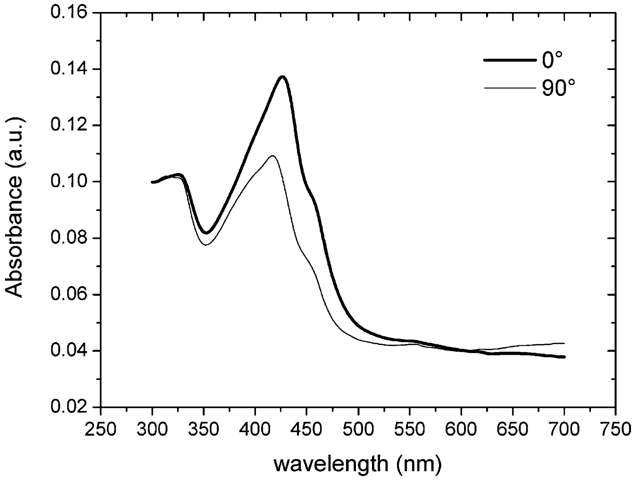

Fig. 7. Polarized light UV–vis spectra LLPPE5 oriented films (Dr = 10), with polarization directions respectively parallel (0°) and perpendicular (90°) to the drawing direction.

red-shifted by ∼30 nm with respect to the solution (Fig. 6), showing a major absorption band ($\lambda_{max} \approx 430$ nm) similar to that of the neat CN-PPE film (Fig. 1).

The spectra of oriented LLPPE5 film (drawing ratio (Dr) = 10, Fig. 7) show a moderate dichroism according to the low overall tendency of the single CN-PPE chromophoric units to align parallel to the PE macromolecular chains. This behaviour is probably due to the poor global linear structure of the photoluminescent macromolecule chains that contain *m*-phenylene linkages.

3.4. Films of CN-PPE/polyethylene blends: optical properties-emission

The emission spectra of CN-PPE in THF solutions and in the LLDPE matrix show remarkable differences (Figs. 8 and 9).

In solution a single band is observed pointed at about 450 nm which shows no concentration dependence (from 4×10^{-6} wt% to 8×10^{-6} wt% the emission bands are superimposable).

Unoriented LLDPE films containing low chromophore concentrations (0.02–0.05 wt%, LLPPE1 and LLPPE2, respectively) show (Fig. 9) luminescent properties very similar to that reported for THF solutions (Fig. 8), with an emission band centred around 450 nm.

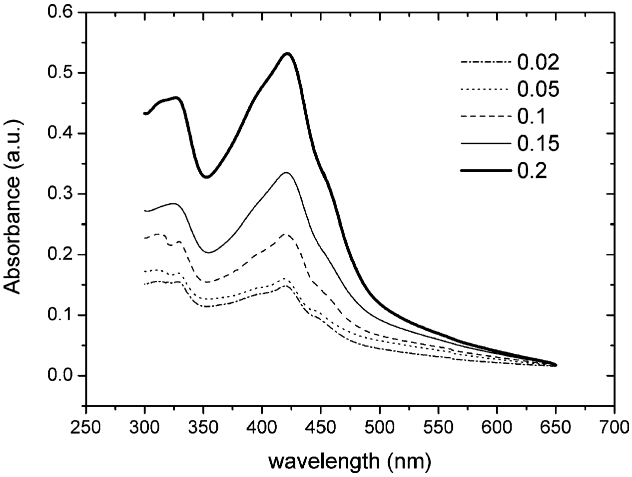

Fig. 6. UV–vis spectra of CN-PPE dispersed in LLDPE films at different concentration (wt%).

LLPPE1 and LLPPE2 films appear, namely, blue under the excitation of a long range UV lamp (366 nm).

In particular, the emission spectra of LLPPE1 and LLPPE2 films display, under the low chromophore loading in the PE blend, a well defined vibronic structure which is absent in either the neat film or THF solution of the CN-PPE.

On the contrary, LLDPE films containing more than 0.1 wt% of CN-PPE show a new strong emission band at about 480 nm, the intensity of which markedly exceeds the emission contribution of the isolated CN-PPE chromophores (450 nm). The films change their emission aspect showing a brilliant green colour under the excitation of the long range lamp at 366 nm.

The occurrence of this broad, unstructured emission, may be attributed to the electronic orbital interactions among different

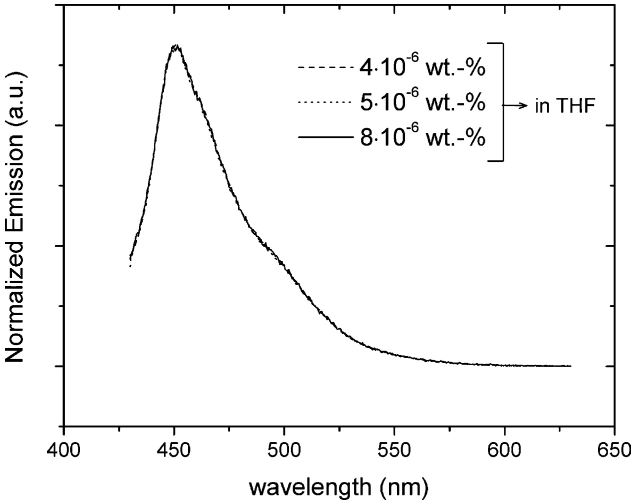

Fig. 8. (a) Fluorescence emission spectra ($\lambda_{exc} = 390$ nm) of CN-PPE dissolved in THF solutions (4×10^{-6}, 5×10^{-6} and 8×10^{-6} wt%). All the spectra are normalized to the intensity of the isolated macromolecule peak (450 nm).

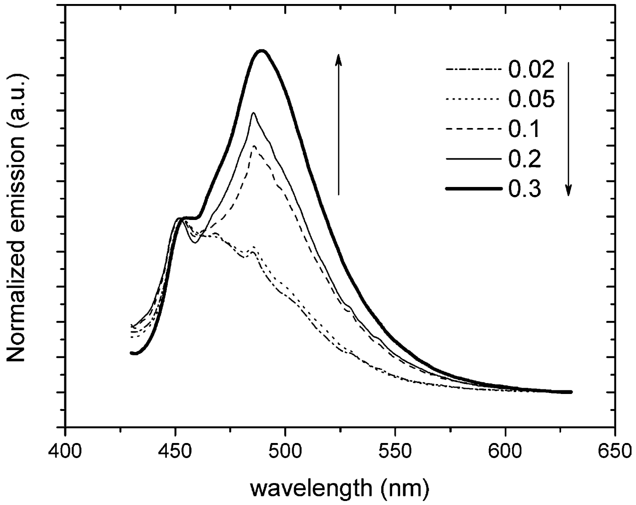

Fig. 9. Fluorescence emission spectra ($\lambda_{exc} = 390$ nm) of CN-PPE dispersed into LLDPE matrix at different concentration (wt%). All the spectra are normalized to the intensity of the isolated macromolecule peak (450 nm). The arrows denote the progressive increasing of the aggregation band as a function of the chromophore load.

chromophoric units of CN-PPE macromolecules (π–π staking, operated by intimate intermolecular or interchain contacts) probably promoted by the more planar chromophore conformation in the solid state [21,50,54].

Accordingly, this phenomenon is clearly absent in the dilute THF solution, where the chromophore diffusion rate is usually high compared to the excited state lifetime [30,55].

In contrast, as CN-PPE concentration is further increased, the relative emission intensity at ~485 nm shows a significant incremental change, to be attributed to the higher aggregate concentration.

The luminescence behaviour of LLPPE films have also been investigated after mechanical stretching at 100 °C. The oriented LLPPE5 film (Dr = 10, Fig. 10) shows an extremely high dichroic behaviour with the complete collapse of the emission band assigned to the chromophore aggregates (485 nm). This interesting behaviour suggests the promotion of well-oriented conformation structures of the chromophores in the excited state after polymer orientation in which the chromophoric long-range π–π interactions result extremely anisotropic.[2]

Despite the low overall tendency of the single CN-PPE macromolecules to align along the oriented polyethylene fibres, the polymer matrix orientation favours the formation of well ordered π–π interactions between the luminescent chromophores, providing composite materials with a smart dichroic behaviour in the emission.

For giving an idea of the anisotropic performance, the dichroic emission ratio is 7, close to the value of 6 that is considered sufficient for linear polarizer in liquid crystal display applications [56].

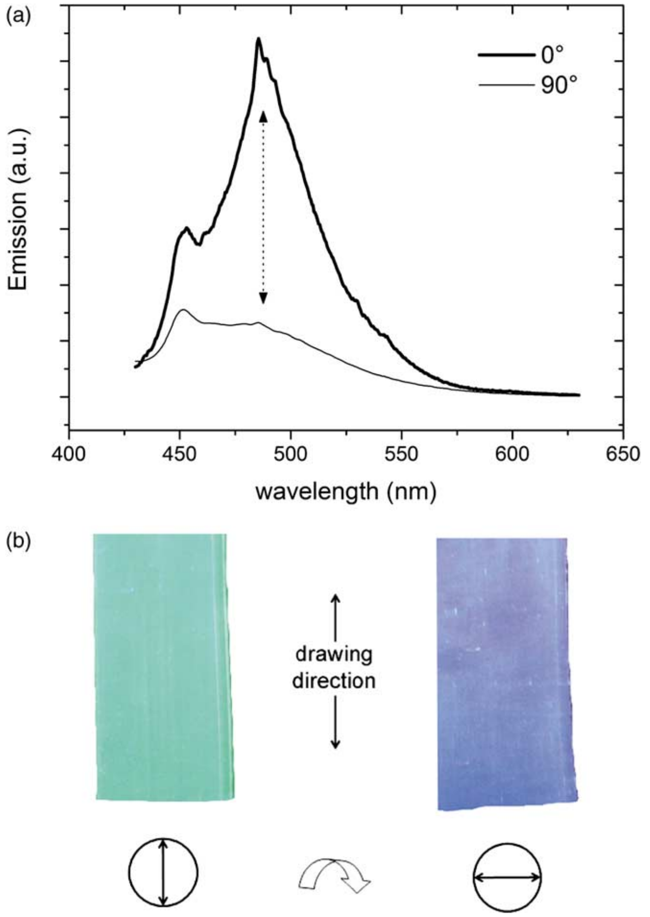

Fig. 10. (a) Fluorescence emission spectra of oriented LLPPE5 film (Dr = 10) recorded with polarization respectively parallel (0°) and perpendicular (90°) to the drawing direction. (b) Digital images of the same film taken under excitation at 366 nm with the camera objective set with a commercial linear polarizer. The arrows denote the orientation of the polarizer transmission axis with respect to the orientation of the film.

The mechanical stretching at high temperature (100 °C) of the polymer composite matrix may induce a temporary disruption of the macromolecular aggregates (favoured by the increased chromophore diffusion rate) that reorganize themselves again in a well ordered conformation after drawing at lower temperature. This fact is supported by tensile drawing experiments performed at 100 °C under irradiation with the UV lamp at 366 nm. The CN-PPE/LLDPE film portion in contact with the hot plate changes its emission quickly from green (the aggregate emission) to blue (the isolated CN-PPE chromophore emission), restoring its original green colour at room temperature just after few seconds. In particular, the de-aggregation phenomenon occurred for LLPPE3-6 films with increasing temperature denotes a particular sensitivity of the CN-PPE aggregates to thermal stress as similarly reported for luminescent oligo(*p*-phenylene vinylene) dispersed into semi-crystalline polyolefin matrices [16–18].

The attractive phenomenon reported by fluorescence dichroism experiments (Fig. 10(a)) results clearly evidenced by exciting the oriented LLPPE5 film with the long range linearly polarized UV source (366 nm, Fig. 10(b)). The suppression of the aggregation band at 485 nm through

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[2] The unoriented film does not show any dichroic emission behaviour.

the rotation of the polarization direction from 0 to 90° modifies the colour of the film from green to blue.

In oriented films, the aggregates emission band results highly dichroic to be easily suppressed by changing the position of a linear polarizer, giving the doped LLDPE films a reversibly tunable appearance under an UV light.

No appreciable influence of the tensile polymer deformation may be detected on the emission properties of CN-PPE/LLDPE based films, differently from polymer matrices doped by low molecular weight luminescent probes [16–19]. The slight decreasing of the emission intensity with the progressive film elongation evidences the resistance of CN-PPE molecular aggregates against polymer deformation. The isolation of the single chromophore units constituent different polymer chains or the same macromolecule results actually much more difficult by LLDPE tensile drawing than chromophores belonging to small molecules.

4. Conclusions

A new cyano-containing poly[(*m*-phenylene ethynylene)-*alt*-(*p*-phenylene ethynylene)] derivative has been prepared and homogeneously dispersed with micro/nano-sized domains in linear low density polyethylene (LLDPE) by melt-processing.

The luminescent polymer exhibits similar absorption and emission behaviour in PE films and THF solutions. An aggregation band is observed at a longer wavelength from the emission spectra of the PE films, attributed to intimate interactions among π-conjugated chromophores. Particularly, the relative emission intensity at ∼485 nm shows a significant rise as CN-PPE concentration is increased in LLDPE. The film remains fluorescent with a green colour, suggesting that the rigid solid environment by PE chains plays a constructive role in the luminescence of the aggregates.

Orientation of the LLDPE films leads to a pronounced change in the film luminescent properties, which exhibit a striking dichroism of the aggregation band and indicate an effective anisotropic arrangement of the CN-PPE aggregates.

In conclusion, highly responsive polyethylene films with modulated luminescent properties may be efficiently prepared by controlled blending of CN-PPE macromolecules adjusting their molecular organization in the polymer matrix simply by changing the chromophores concentration and the anisotropic distribution after film orientation.

These results appear promising for technological applications as high performance optical filters, radiation responsive polymeric objects and as smart and intelligent polymer films in packaging applications. In the future, time-resolved fluorescence spectroscopy will be performed on CN-PPE/PE films before and after solid-state deformation for a deeper and complete understanding of the investigated phenomenon.

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