Preprint version: Optical Materials 73 (2017) 595-601 DOI: 10.1016/j.optmat.2017.09.010

Circularly polarized luminescence of syndiotactic polystyrene

Paola Rizzo [a*], -Sergio Abbate [b]-, Giovanna Longhi [b,*] and Gaetano Guerra [a]

[a] Dipartimento di Chimica e Biologia and INSTM Research Unit, Universita` degli Studi di Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy.
[b]Dipartimento di Medicina Molecolare e Traslazionale, Università degli Studi di Brescia, viale Europa 11, 25123, Brescia (Italy)

Abstract: Syndiotactic polystyrene (s-PS) films, when crystallized from the amorphous state by temporary sorption of non-racemic guest molecules (like carvone) not only exhibit unusually high optical activity, both in the UV-Visible and Infrared ranges, but also present circularly polarized luminescence (CPL) with high dissymmetry ratios (g=ΔI/I values in the range 0.02-0.03). Experimental evidences provide support, rather than to the usual molecular circular dichroism, to a *supramolecular* chiral optical response being extrinsic to the site of photon absorption and emission, possibly associated with a helical morphology of s-PS crystallites.

Keywords: Polymers; Luminescence; VCD, FTIR, CD

1. Introduction

Induction of intense chiral optical responses to racemic polymers, by interactions with non-racemic solvents, is a well established phenomenon [1-10]. This phenomenon has been also observed in the solid state [11-24], often associated to co-crystallizations [25] of suitable racemic polymers with non-racemic guests [11,14-24].

Induction of chiral optical behavior generally occurs by a well established *molecular mechanism*, where a non-racemic solvent favors prevalence of a given sense of helicity of polymer chains. In the solid state, the presence of a non-racemic guest leads to formation of a polymer co-crystalline phase that exhibits a non-racemic unit cell, with only one-sense of helicity for the polymer chains. This kind of behavior has been observed for instance for co-crystalline phases of syndiotactic poly(*p*-methylstyrene) [26,27] and poly(2,6-dimethyl-1,4-phenylene)oxide (PPO) (Fig. 1A) [11].

Rather unexpected are, instead, intense circular dichroism phenomena (both in the UV-Visible and Infrared ranges) which have been observed for syndiotactic polystyrene (s-PS) films [14-25]. In fact, in this case, crystallization induced in amorphous films by sorption of non-racemic guest molecules (like carvone or limonene) leads to co-crystals where polymer chains with both senses of helicity are present. The unit cell of the co-crystalline phase of the chiral optical film, obtained by replacement of the non-racemic guest by an achiral chromophore (azulene), is shown in Fig. 1B [18].

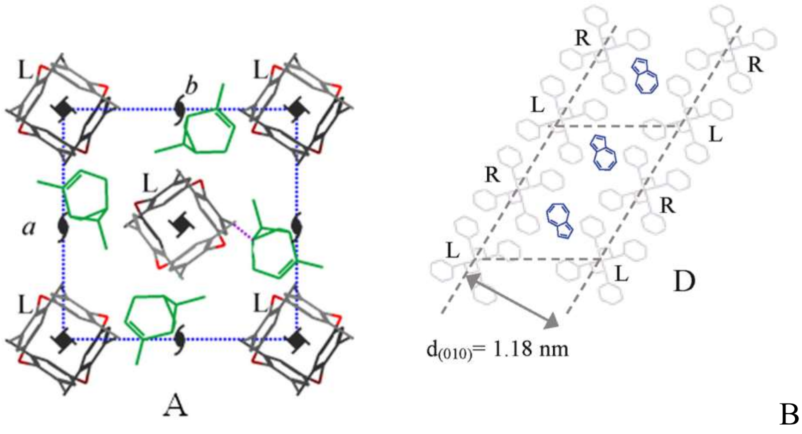

Fig. 1. Projections along the chain axis (*c*) of the unit cell of co-crystalline forms of: (A) of PPO with (1*S*)-(–)-α-pinene, which includes all left handed (L) polymer helices [11]; (B) of s-PS with azulene, monoclinic δ clathrate, which includes the same amount of left handed (L) and right handed (R) polymer helices [18].

All experimental evidences support the idea that s-PS films exhibit chiroptical phenomena, rather than due to the usual molecular mechanism, due to a *supramolecular mechanism* corresponding to the optical chiral response origin being extrinsic to the site of photon absorption [28-32] and connected to effects of the material on the light propagation (birefringence, scattering…). Furthermore, the chiral optical response of s-PS films remains essentially unaltered up to the polymer melting temperature (≈270 °C), not only after the non-racemic guest removal but also after thermal crystal-crystal transitions [16,17], which involve the change in the molecular conformation from chiral helical to achiral trans-planar. The extrinsic character of the phenomenon is confirmed by the extensive nature of the chiral optical response, with large increase of g values (of both host and guest peaks) by increasing the s-PS film thickness [21]. The supramolecular and extrinsic nature of the induced chirality has been further confirmed by a recent study on non-racemic guest molecule, whose chiral response does not depend on their (*R*) or (*S*) molecular chirality but depends essentially only on the polymer host supramolecular chirality [22,23]. This extrinsic nature of the chiral optical response of s-PS films would be associated with the non-racemic helical morphology of crystallites, as induced by the chirality of the co-crystallizing non-racemic guest [18,21].

The supramolecular nature of the chiral response of s-PS is particularly relevant due to the peculiar property of s-PS of forming nanoporous-crystalline phases [25,33-36] and hence to its ability to absorb chromophore molecules in its isolated crystalline cavities. This allows obtaining intense chiral optical absorbance for achiral chromophores, when they replace the non-racemic guest in the crystalline cavities of s-PS co-crystalline phases [18,21,23].

It is well known that s-PS exhibits a well established fluorescence behavior [37-41].

In this paper, the possible occurrence of circularly polarized luminescence (CPL) of s-PS films, whose crystallization has been induced by the temporary sorption of non-racemic guest molecules, is investigated. CPL is indeed a relatively mature technique which has found a recent fortune [42-47]: it allows one to monitor the chiral properties of molecular excited states [48-51] and promises for a wide range of possible applications in advanced optical technologies [52-59].

2. Experimental section

2.1. Materials

The s-PS used in this study was manufactured by Dow Chemical Co. under the trademark Questra 101. ^{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 $M_w/M_n = 3.9$. (-)-(*R*)carvone [enantiomeric excess (ee) 98%], (+)-(*S*)-carvone (ee 96%) and fluorescein were supplied by Aldrich and were used without further purification.

Amorphous s-PS films with thickness of nearly 10 μm were obtained by melt extrusion. s-PS crystallization was induced by liquid (-)-(*R*)carvone or (+)-(*S*)-carvone sorption at room temperature for 1 h.

2.2. Characterization Techniques

IR and VCD measurements were recorded on a commercial Bruker Tensor 27 FT-IR spectrometer coupled to a PMA50 external module (needed to double modulate the infrared radiation) by use of a linear KRS5 polarizer, a ZnSe 50 kHz photoelastic modulator (PEM, by HINDS) with a proper antireflecting coating, an optical filter (transmitting below 2000 cm^{-1}), and a narrow-band MCT (mercury_cadmium_telluride) detector. All VCD spectra were recorded for 5 min of data collection time, at 4 cm^{-1} resolution. According to experimental procedures described in the literature [60,61], films were tested for satisfactory VCD characteristics by comparison with the VCD spectra obtained with the film rotated by 45° around the light beam axis. However, to eliminate any possible linear dichroism influence, the VCD measurements have been conducted by averaging the spectra as collected for several different in-plane rotation angles.

Absorption and CD spectra were measured on a Jasco J-815SE spectropolarimeter. All measurements were performed in the range 650-250 nm, at 200 nm/min scanning speed, 2 nm SBW.

CPL spectra were carried out on a home built instrument [62,63] with depolarized radiation brought to the sample through an optical fiber either from a commercial fluorimeter (Jasco FP8200) or from Jasco-815SE (excluding the PEM). Films were placed perpendicular to the beam and the collected fluorescence was at 0° with respect to the incident beam (forward geometry). Five scans were accumulated for each spectrum, with the following conditions: excitation bandwidth 20 nm, emission bandpass approximately 10 nm, scan speed 2.5 nm/s. Recording the AC component at 100 kHz, information on linear dichroism have been gained both in absorption and in emission. Measurements on fluorescein solution have been obtained with just one scan.

3. Results and Discussion

3.1.Infrared and VCD spectra

FTIR spectra, for the range 1700-400 cm^{-1}, of an extruded s-PS 10 μm thick film, before and after sorption/desorption of carvone are shown in Fig. 2A and B, respectively. The whole spectra indicate that the amorphous extruded sample becomes crystalline after treatment with carvone. This is clearly shown, for instance, by the appearance of intense vibrational peaks at 1352, 1278 cm^{-1} and 571cm^{-1}, (shown by h* in Fig.2B), typical of the crystalline helical phase being associated with a single vibrational mode of the s(2/1)2 polymer helix [64]. Moreover intense carvone absorbance peaks at 1669, 1247 cm^{-1} (labelled as g) are also apparent.

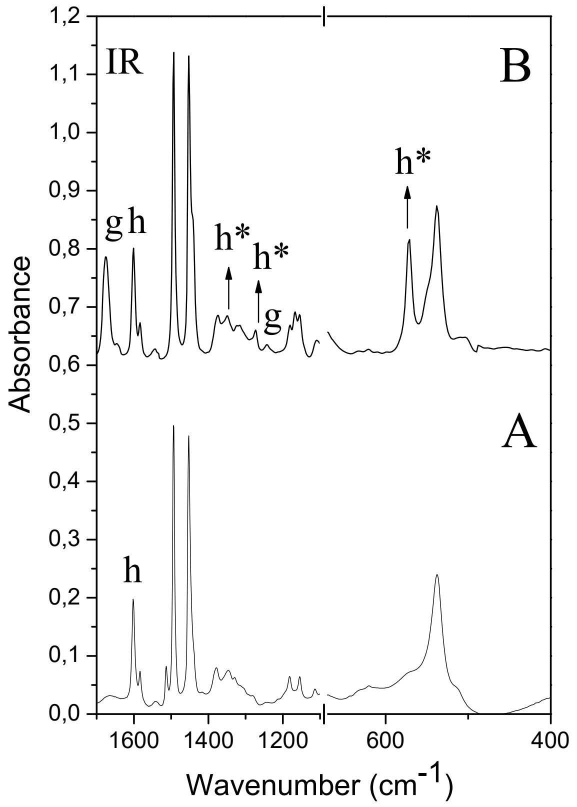

Fig. 2. FTIR spectra, for the range 1700-400 cm^{-1}, of an extruded s-PS film, before (A) and after sorption of carvone (B) . Main vibrational peaks associated with the polymer, with helical s(2/1)2 polymer conformation and with carvone guest are labeled by **h , h*** and **g** respectively.

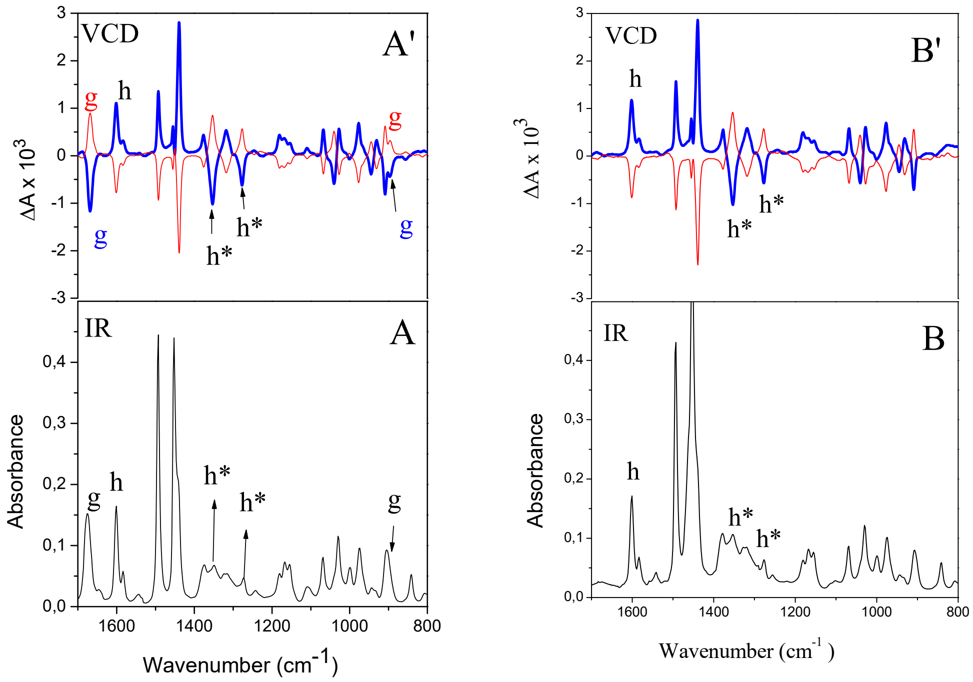

Fig. 3. FTIR and VCD spectra, for the range of 1700-800 cm^{-1}, of sPS film after treatments by (*R*) (red curve) and (*S*) carvone (blue curve) before (A,A') and after guest removal (B,B'). Main vibrational peaks associated with the polymer, with helical s(2/1)2 polymer conformation and with carvone guest are labeled by **h** , **h*** and **g** respectively.

Vibrational Circular Dichroism (VCD) and related IR spectra, for the available range of 1700-800 cm^{-1}, as obtained on samples treated with (*R*) and (*S)* carvone are shown in Figs.3A'-B', as red and blue curves, respectively. In agreement with previous reports [16,17,22-24], the s-PS crystallization induced by carvone sorption leads to an intense chiral response of the polymer host, which remains unaltered even after complete non-racemic guest removal Fig.3B'. Quantitative evaluation of the degree of circular polarization shows that the polymer peaks, when associated with vibrational modes of the s(2/1)2 helices of the s-PS crystalline phases, present ***g*** values even higher than those observed for the non-racemic guest (e.g., for the helical vibrational peak at 1278 cm^{-1}, the dissymmetry ratio is $\boldsymbol{g} \approx 1 \times 10^{-2}$) [21,23].

3.2.Absorption UV-Visible and CD spectra

CD, UV-VIS and LD spectra of the same extruded s-PS film, after crystallization by sorption/desorption of non-racemic carvone, are shown in Fig. 4. s-PS crystallization induced by carvone sorption leads to an intense chiral response of the polymer host, in the spectral range 650-250nm.

Circular dichroism depends only slightly on sample orientation. Linear dichroism components, on the contrary, strongly depend on film orientation, changing sign upon 90° rotation of the sample (as expected**).**

Results of Figs.3 and 4 clearly confirm induction of stable optical activity in the racemic polymer **thick films** , after sorption/desorption of carvone, in agreement with previous results [21-24].

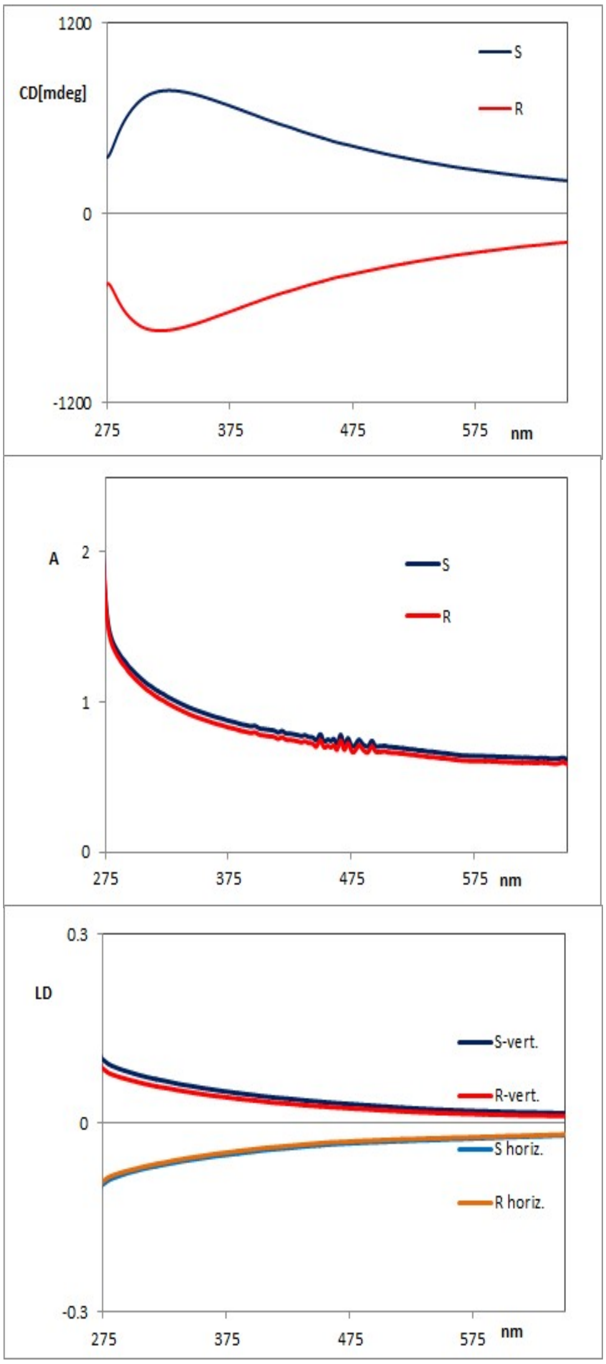

Fig. 4. CD (top) Absorption (middle) and LD (bottom) spectra of extruded s-PS films, after sorption/desorption of (*R*) carvone (red curve) and (*S*) carvone (blue curve). CD spectra are averages over 4 orientations: vertical, horizontal, back and front faces.

The difference in left and right circularly polarized transmission of these films is quite large over a wide spectral range. Due to the anisotropy and semicrystalline nature of the sample it is important to test different orientations, since it has been proven that a surface with non-chiral holes arranged in a plane not exactly perpendicular to the incident beam might give chiral response [65]. The invariance of CD response, with respect to rotation of the sample, is reminiscent of the situation of metamaterials constituted of intrinsically chiral holes, for which CD is observed also for a beam impinging orthogonally to the surface, with amplitude and sign that do not significantly change with rotation [31]. The intrinsically chiral element in the material herein studied could be the helical morphology of s-PS crystallites induced by carvone [15,21]. As explained by Shindo [64], in case of high anisotropy of the sample (evidenced here by intense LD), the superposition of LD and LB contributions may give an intense apparent CD signal that does not depend on rotation. The fact that the signal shows little variations upon changing the front and back faces of the film suggests that the observation is not simply due to cross terms between linear birefringence and linear dichroism [66-68]. Besides all these considerations, one may notice that intense and broad CD bands in absence of a real absorption band strongly suggest the possibility of a circular dichroism phenomenon due to different reflection/scattering of right and left circularly polarized light, as observed for example in ref. [69], and tested on polyfluorene films by Meskers [70] with an ad hoc instrumental set-up. So, the existence of a CD signal does not necessary imply circular dichroism at the molecular level, rather we can state that the material shows different transmission for left and right circularly polarized light.

3.3 Fluorescence and CPL spectra

In order to characterize the optical properties of the material, steady-state emission spectra for excitation at 265 nm of the same semicrystalline s-PS film, as crystallized by sorption/desorption of (*S*)-carvone or of (*R*)-carvone, are shown in Fig. 5. Due to film thickness, the excitation beam is highly absorbed by the sample, but the emitted light can be recorded and analyzed in its components. The polymer host emission spectrum presents a broad band, nearly centered at 320 nm [37-41], analogous to those already described for atactic and isotactic polystyrene films [71-73].

The emission spectra present a remarkable chiral component. Little variations of emission intensities for films crystallized by (*S*)-carvone or by (*R*)-carvone, for four different film orientations have been recorded, the average is presented in Fig. 5. It is clearly apparent a circularly polarized luminescence (CPL) with $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$ value of about 0.03.

In Fig. 5 we show also linear dichroism analysis of the emitted light, which gives a flat response on the same scale of CPL, so we are allowed to conclude that the observed CPL components are not due to instrumental mixing of linear and circular components [74].

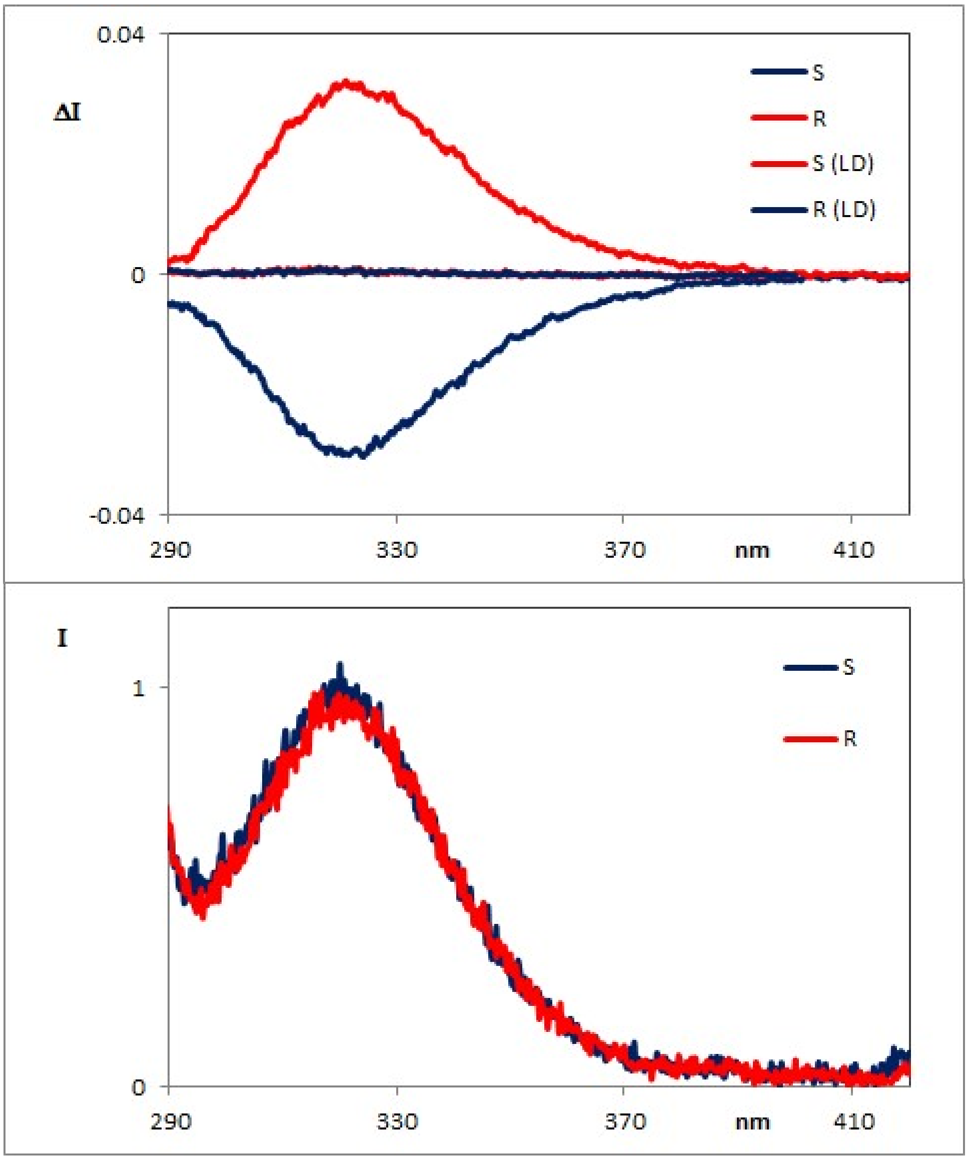

Fig. 5. CPL spectra (top) fluorescence spectra (bottom), spectra of the s-PS film, as crystallized by sorption/desorption of (*S*)-carvone or of (*R*)-carvone: the spectra are averages over 4 orientations: vertical, horizontal, back and front faces. LD spectra give a null trace as compared to CPL component.

It is difficult to analyze the origin of the chiral components of the emitted light, particularly because one should consider the fact that in absorption experiments, transmitted light is highly chiral in the same range of fluorescence emission, as observed in Fig. 4. We only observe that the sign of the CPL band is opposite with respect to CD absorption. This is compatible with the interpretation that fluorescence emission at 320 nm from s-PS exhibits circularly polarized components undergoing different transmission through the sample; note that excitation light has been used at quite lower wavelength than the emission band to avoid superposition.

The observation of chiral components of emitted light (Fig. 5), paralleling the observation of chiral transmission (Fig. 4), suggests a possible use of these films to obtain chiral light from emission by (achiral) fluorophores placed before the s-PS films.

In fact, very simple experiments show how a fluorescent solution, followed by an optically active s-PS film, can be used to obtain emitted light with high chiral components: fluorescence chirally filtered by the dichroic s-PS films. In particular, we measured the circularly polarized components of light emitted by a fluorescein slightly basic water solution and passed through s-PS film sorbed/desorbed with (*R*) and (*S*) carvone (Fig.6). In this case the experiment was conducted with the standard 90° geometry and by polarizing the incident beam parallel to the direction of the output beam.

In this simple experiment, the “CPL” spectrum resulting from fluorescein emission transmitted by a chiral sPS film gives a dissymmetry factor of about one third of the one recorded at about 320 nm (Fig. 5) for s-PS luminescence, the decrease in dissymmetry factor is due to the decrease of CD signal in the fluorescein emission spectroscopic regions.

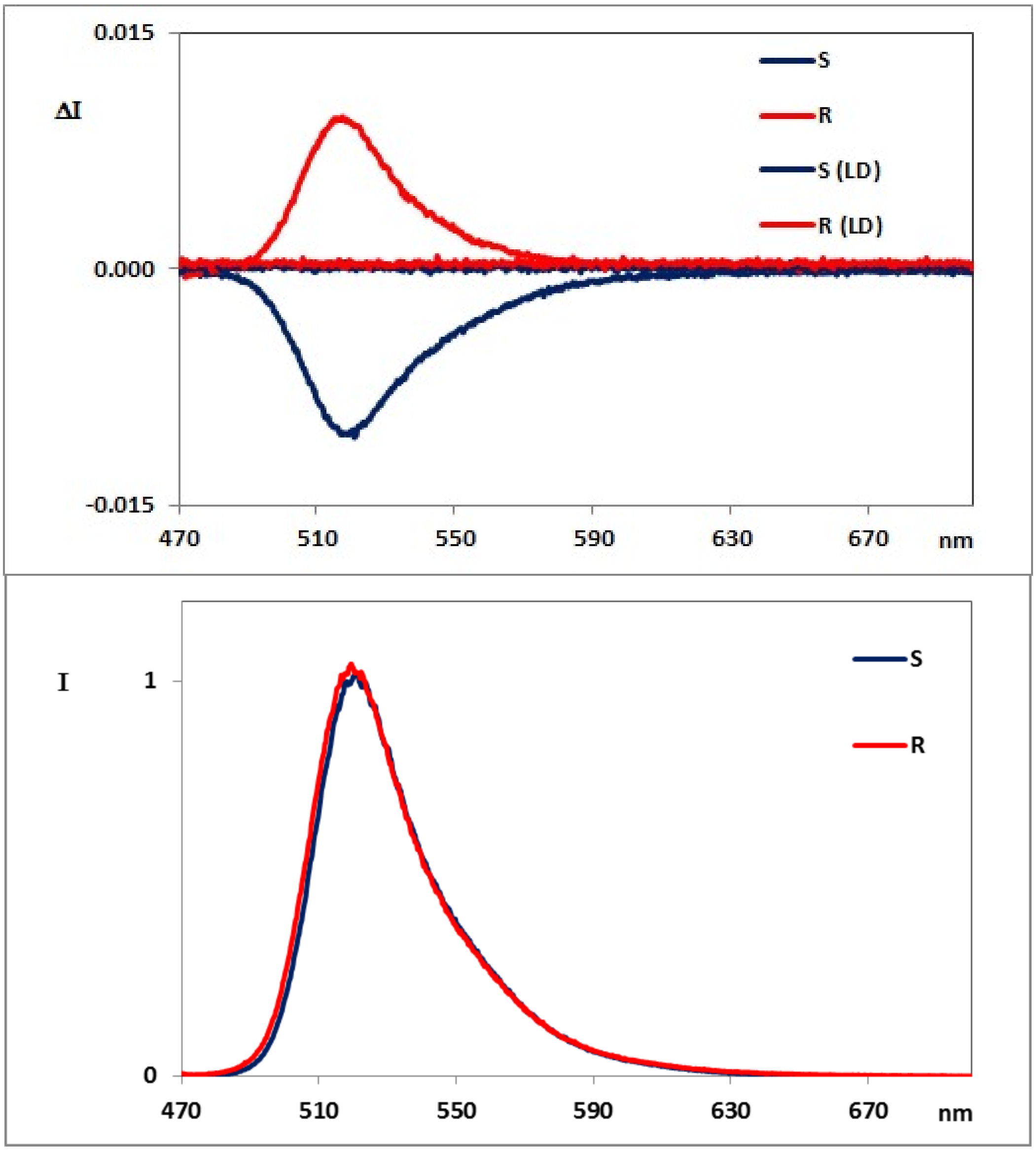

Fig. 6. CPL and fluorescence spectra for excitation at 450 nm of light emitted by a fluorescein solution and passed through s-PS film sorbed/desorbed with (*R*) and (*S*) carvone. Linear dichroism analysis of the emitted light gives a flat response in the same scale of CPL. Only one scan was needed to obtain the signal, the measurement set-up was with a 90° geometry.

Hence, s-PS films with induced chirality, due to sorption/desorption of chiral molecules, have been characterized by considering their emitted light and considering possible applications in case this material is coupled with a previously arranged layer (in our case simply a solution) containing fluorophores. This easily permits obtaining chiral emission in different spectral ranges, depending on the solute compound used.

4. Conclusions

s-PS films with induced chirality, due to sorption/desorption of chiral molecules, exhibit chiral optical properties that resemble those of liquid crystal or polyfluorene film studies (see for example ref. [66]), *i.e.* materials with "macroscopic" chirality. The results obtained recording CD spectra confirm the presence of an extrinsic (not molecular) chiral effect.

These easily processable polymer films provide a few very peculiar optical properties, and one of these, namely the enhancement in VCD response (well documented in several previous papers [14-24]), is somehow similar to what observed in the case of fibrillary systems [75]. To this instance one can think that this polymeric material can be a good model to understand VCD enhancement.

In this work the analysis has been mainly focused on a different manifestation of chiral response enhancement: the high dichroic properties of the material in the UV-VIS range. The different transmission of right and left circularly polarized light, evidenced with CD experiments, appears correlated with the observation of CPL with high g_{lum} when considering fluorescence emitted by the material itself in the UV range. Besides, the extension of CD response on a wide spectroscopic range indicates possible applications of these films coupled with light emitting devices, optical sensors or in general when orthogonal circular polarizers are needed [76]. To this instance the use of a polymeric material presenting optical activity with no need to add chiral units through chemical synthesis is quite advantageous.

Acknowledgments

Financial support of “Ministero dell' Istruzione, dell'Universita' e della Ricerca” is gratefully acknowledged. The authors thank Dr. Antonietta Cozzolino for useful discussions. We wish to gratefully dedicate this paper to Ettore Castiglioni, who passed away in 2016, and participated with competence and enthusiasm to the first part of this work.

References

[1] M. M. Green, C. Khatri , N. C. Peterson, A macromolecular conformational change driven by a minute chiral solvation Energy, J. Am. Chem. Soc. 115, (1993),4941-4942 .

[2] E. Yashima, K. Maeda,Y. Okamoto, Memory of macromolecular helicity assisted by interaction with achiral small molecule, Nature, 399, (1999), 449-451.

[3] M. M. Green, J. W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger, J. Selinger, The macromolecular route to chiral amplification, Angew. Chem., Int. Ed. 38, (1999), 3138- 3154.

[4] H. Goto, Y. Yokochi, E. Yashima, Chirality induction in metal-induced achiral polythiophene aggregates assisted by optically activeamines and polythiophene, Chem. Commun., 48,(2012), 3291-3293.

[5] S. J. George, R. de Bruijn, Z. Tomovic, B. Van Averbeke, D. Beljonne, R. Lazzaroni, A. P. H. J. Schenning, E. W. Meijer, Asymmetric noncovalent synthesis of self-assembled one-dimensional stacks by a chiral supramolecular auxiliary approach, J. Am. Chem. Soc., 134, (2012),17789-17796.

[6] M. Fujiki, Y. Kawagoe, Y. Nakano, A. Nakao, Mirror-symmetry-breaking in poly[(9,9-di-*n*-octylfluorenyl- 2,7-diyl)-*alt*-biphenyl] (PF8P2) is susceptible to terpene chirality, achiral solvents, and mechanical stirring, Molecules, 18, (2013), 7035-7057.

[7] L. Wang, N. Suzuki, J. Liu, T. Matsuda, N.A.A. Rahim, W. Zhang, M. Fujiki, Z. Zhang, N. Zhoua, X. Zhua, Limonene induced chiroptical generation and inversion during aggregation of achiral polyfluorene analogs: structure-dependence and mechanism, Polym. Chem., 5, (2014) 5920-5927.

[8] S. Jiang, Y. Zhao, L. Wang, L. Yin, Z. Zhang, J. Zhu, W. Zhang, X. Zhu, Photocontrollable induction of supramolecular chirality in achiral side chain azo-containing polymers through preferential chiral solvation,Polym. Chem., 6, (2015) 4230-4239.

[9] K. Maeda, T. Miyagawa, A. Furuko, H. Onouchi, E. Yashima, Dual memory of enantiomeric helices in poly(phenylacetylene)s induced by a single enantiomer through helix inversion and dual storage of the enantiomeric helicity memories, Macromolecules 48, (2015), 4281–4293.

[10] B. Zhao, J. Deng, J. Deng, Emulsification-induced homohelicity in racemic helical polymer for preparing optically active helical polymer nanoparticles, Macromol. Rapid Commun. 37, (2016), 568-574 .

[11] O. Tarallo, V. Petraccone, C. Daniel, G. Fasano, P. Rizzo and G. Guerra, A chiral co-crystalline form of poly(2,6-dimethyl-1,4-phenylene)oxide (PPO), J. Mater.Chem. 22, (2012),11672-11680.

[12] K.Shimomura, T. Ikai, S. Kanoh, E. Yashima, K. Maeda, Switchable enantioseparation based on macromolecular memory of a helical polyacetylene in the solid state, Nature Chem. 6,(2014), 429–434.

[13] Y. Zhao, N. A. A. Rahim, Y. Xia, M. Fujiki, B. Song, Z. Zhang, W. Zhang, X. Zhu, Supramolecular chirality in achiral polyfluorene: chiral gelation, memory of chirality, and chiral sensing property, Macromolecules, 49, (2016), 3214–3221.

[14] A. M. Buono, I. Immediata, P. Rizzo, G. Guerra, Detection and memory of nonracemic molecules by a racemic host polymer film, J. Am. Chem. Soc., 129, (2007),10992-10993.

[15] L. Guadagno, M. Raimondo, C. Silvestre, I. Immediata, P. Rizzo, G. Guerra, Processing, thermal stability and morphology of chiral sensing syndiotactic polystyrene films, J. Mater. Chem. 18, (2008), 567-572.

[16] P. Rizzo, C. Daniel, G. Guerra, Chiro-optical materials based on a racemic polymer, Macromolecules, 43, (2010),1882-1887.

[17] P. Rizzo, M. Beltrani, G. Guerra, Induced Vibrational Circular Dichroism and Polymorphism of Syndiotactic Polystyrene, Chirality, 22, (2010), E67-E73.

[18] P. Rizzo, T. Montefusco, G. Guerra, Chiral optical films based on achiral chromophore guests, J. Am. Chem. Soc. 133, (2011),9872-9877.

[19] K. Zheng, R. Liu, H. Kang, X.Gao, D. Shenand, Y. Huang, Chirality amplification of syndiotactic polystyrene induced circular dichroism chiral film in δ form upon annealing, Polymer, 52, (2011),3671-3676.

[20] G. Guerra, P. Rizzo, Racemic synthetic polymers and chirality, Rend. Fis. Acc. Lincei, 24,(2013), 217-226.

[21] P. Rizzo, E. Lepera, G. Ianniello, G. Guerra, Melt-extruded films of a commercial polymer with intense chiral optical response of achiral guests, Macromolecules 47, (2014), 2616-2624.

[22] P. Rizzo, E. Lepera, G. Guerra, Enantiomeric guests with the same signs of chiral optical responses, Chem. Commun. 50, (2014), 8185-8188.

[23] G. Ianniello, E. Lepera , P. Rizzo, Chiral Optical Response of Achiral and Enantiomeric Guests in Syndiotactic Polystyrene Films, *Macromolecular Symposia* , 359, (2016), 9-15.

[24] P. Rizzo, G. Guerra, Intense chiral optical phenomena in racemic polymers by cocrystallization with chiral guest molecules: A brief overview, Chirality 28, (2016),29-38.

[25] G. Guerra, C. Daniel, P. Rizzo, O. Tarallo, Advanced materials based on polymer cocrystalline forms, J. Polym. Sci., Part B: Polym. Phys. 50, (2012),305-322.

[26] D. La Camera, V. Petraccone, S. Artimagnella, O. Ruiz de Ballesteros, Crystal structure of the clathrate form of syndiotactic poly(*p*-methylstyrene) containing benzene, Macromolecules, 34, (2001), 7762-7776.

[27] G. Esposito, O. Tarallo, V. Petraccone, Crystal structures of syndiotactic poly(p-methylstyrene) clathrates with two guest molecules having very similar shape and volume, Eur. Polym. J., 43, (2007), 1278-1287.

[28] F. D. Saeva, P. E. Sharpe, G. R. Oh, Cholesteric liquid crystal induced circular dichroism (LCICD). V. Mechanistic aspects of LCICD, J. Am. Chem. Soc. 95, (1973), 7656-7659.

[29] F. D. Saeva ,G. R. Olin, Extrinsic circular dichroism in twisted nematic mesophases, J. Am. Chem. Soc., 98, (1976),2709-2711.

[30] M. R. Craig, P. Jonkheijm, S. C. J. Meskers, A. P. H. J.Schenning , E. W. Meijer, The chiroptical properties of a thermally annealed film of chiral substituted polyfluorene depend on film thickness, Adv. Mater. 15, (2003),1435-1438.

[31] B. M. Maoz, A. BenMoshe, D. Vestler, O. Bar-Elli, G.Markovich, Chiroptical effects in planar achiral plasmonic oriented nanohole arrays, Nano Lett. 12, (2012), 2357-2361.

[32] A. Yokoyama, M. Yoshida, A. Ishii, Y. K. Kato, Giant circular dichroism in individual carbon nanotubes induced by extrinsic chirality, Phys. Rev. X 4, (2014),011005-1-6.

[33] C. De Rosa, G. Guerra, V. Petraccone, B. Pirozzi, Crystal structure of the emptied clathrate form (δ_e form) of syndiotactic polystyrene, Macromolecules 30, (1997),4147-4152.

[34] V. Petraccone, O. Ruiz de Ballesteros, O. Tarallo, P. Rizzo, G. Guerra, Nanoporous polymer crystals with cavities and channels, Chem. Mater. 20, (2008), 3663-3668.

[35] O. Tarallo, V. Petraccone, A.R. Albunia, C. Daniel, G. Guerra, Monoclinic and triclinic δ - clathrates of syndiotactic polystyrene, Macromolecules 43, (2010), 8549-8558

[36] M.R. Acocella, P. Rizzo, C. Daniel, O. Tarallo, G. Guerra, Nanoporous triclinic δ modification of syndiotactic polystyrene, Polymer 63, (2015),230-236.

[37] V. Venditto, G. Milano, A. De Girolamo Del Mauro, G. Guerra, J. Mochizuki, H. Itagaki, Orientation and microenvironment of naphthalene guest in the host nanoporous phase of syndiotactic polystyrene, Macromolecules 38, (2005), 3696-3702.

[38] A. De Girolamo Del Mauro, M. Carotenuto, V. Venditto, V. Petraccone, M. Scoponi, G. Guerra, Fluorescence of syndiotactic polystyrene/trimethylbenzene clathrate and intercalate co-crystals, Chem. Mater. 19, (2007),6041-6046.

[39] H. Itagaki, T. Sago, M. Uematsu,G. Yoshioka, A. Correa, V. Venditto, G. Guerra, Guest orientation in uniplanar-axial polymer host films and in co-crystal unit-cell, determined by angular distributions of polarized guest fluorescence, Macromolecules 41, (2008),9156-9164.

[40] J. Zhou, J. Yang, K. Yang, B. Zhang, C. Hu, X. Chen, Conformational behaviors of syndiotactic polystyrene in chloroform revealed by intrinsic fluorescence technique, Polymer, 52,(2011), 3503–3511.

[41] T. Sano, A. Uchiyama, T. Sago, H. Itagaki, Fluorescence behavior of syndiotactic polystyrene and its derivative: Formation of a ground-state dimer in the solid state, Eur. Polym. J., 90, (2017), 114–121.

[42] C.A. Emeis, L.J. Oosterhoff, Emission of circularly-polarized radiation by optically-active compounds, Chem. Phys. Lett. 1, (1967), 129-132.

[43] J.P. Riehl, F.G.Muller ,Circularly Polarized Luminescence Spectroscopy and Emission-detected Circular Dichroism, in N.Berova. P.L. Polavarapu, K. Nakanishi, R.W. Woody (Eds.) Comprehensive Chiroptical Spectroscopy. Vol 1., John Wiley & Sons, New York, 2012, pp. 65-90.

[44] E. Sànchez-Carnerero, A.R. Agarrabeitia, F. Moreno, B.L. Maroto, G. Muller, M.J. Ortiz, S. de la Moya, Circularly Polarized Luminescence from Simple Organic Molecules, Chem. Eur. J., 21, (2015), 13488–13500.

[45] G. Longhi, E. Castiglioni, J. Koshoubu, G. Mazzeo, S. Abbate, Circularly Polarized Luminescence: A Review of Experimental and Theoretical Aspects, Chirality, 28,(2016), 696–707.

[46] J. Kumar, T. Nakashima, T. Kawai, Circularly Polarized Luminescence in Chiral Molecules and Supramolecular Assemblies, J. Phys. Chem. Lett. 6, (2015), 3445-3452

[47] M. Fujiki, M. Aggregation-Induced Chirogenesis of Luminescent Polymers. In Aggregation Induced Emission: Materials and Applications; M. Fujiki, B. Liu, B.Z. Tang, Eds.; ACS: Washington, DC, (2016); Vol. 2, Chapter 3, pp 63−92.

[48] G. Longhi, E. Castiglioni, S. Abbate, F. Lebon, D.A. Lightner, Experimental and Calculated CPL Spectra and Related Spectroscopic Data of Camphor and Other Simple Chiral Bicyclic Ketones, Chirality, 25, (2013), 589–599.

[49] S. Abbate, G. Longhi, F. Lebon, E. Castiglioni, S. Superchi, L. Pisani, F. Fontana, F. Torricelli, T Caronna, C Villani, R Sabia, M Tommasini, A Lucotti, D Mendola, A Mele, DA.Lightner, Helical Sense-Responsive and Substituent-Sensitive Features in Vibrational and electronic Circular Dichroism, in Circularly Polarized Luminescence and in Raman Spectra of Some Simple Optically Active Hexahelicenes, J. Phys. Chem. C, 118, (2014),1682-1695.

[50] T. Amako, K. Nakabayashi, T. Mori, Y. Inoue, M. Fujiki, Y. Imai, Sign inversion of circularly polarized luminescence by geometry manipulation of four naphthalene units introduced into a tartaric acid scaffold, Chem. Commun., 50, (2014),12836-12839.

[51] T. Sato, N. Tajima, H. Ueno, T. Harada, M. Fujiki, Y. Imai, Binaphthyl luminophores with triphenylsilyl groups: sign inversion of circularly polarized luminescence and circular dichroism Tetrahedron 72, (2016), 7032–7038.

[52] T. Goto, Y. Okazaki, M. Ueki, Y. Kuwahara, M. Takafuji, R. Oda, H. Ihara, Induction of Strong and Tunable Circularly Polarized Luminescence of Nonchiral, Nonmetal, Low-Molecular-Weight Fluorophores Using Chiral Nanotemplates, Angew. Chem. Int. Ed., 56,(2017), 2989 –2993.

[53] A. Rybicka, G. Longhi, E. Castiglioni, S. Abbate, W. Dzwolak, V. Babenko, M.a Pecul, Thioflavin T: Electronic Circular Dichroism and Circularly Polarized Luminescence Induced by Amyloid Fibrils, ChemPhysChem 17, (2016), 2931 – 2937.

[54] K. Watanabe, I. Osaka, S. Yorozuya, K. Akagi, Helically π-Stacked Thiophene-Based Copolymers with Circularly Polarized Fluorescence: High Dissymmetry Factors Enhanced by Self-Ordering in Chiral Nematic Liquid Crystal Phase, Chem. Mater., 24, (2012), 1011–1024.

[55] T. Amako, K. Nakabayashi, A. Sudo, M. Fujiki, Y. Imai, Solid-state circularly polarised luminescence of atropisomeric fluorophores embedded in achiral myo-inositol-containing polyurethanes, Org. Biomol.Chem. 13, (2015), 2913–2917.

[56] J. Kumar, T. Nakashima, H. Tsutamori, T. Kawai, Circularly Polarized Luminescence in Chiral Aggregates: Dependence of Morphology on Luminescence Dissymmetry, J. Phys. Chem. Lett. 5, (2014), 316-321.

[57]J. Kumar, T. Nakashima, H. Tsutamori, M. Mori, M. Naito, T. Kawai, Circularly polarized luminescence in supramolecular assemblies of chiral bichromophoric perylene bisimides, Chemistry Eur. J. 19, (2013), 14090-14097.

[58] K. Takaishi, T. Yamamoto, S. Hinoide, T. Ema, Helical Oligonaphthodioxepins Showing Intense Circularly Polarized Luminescence (CPL) in Solution and in the Solid State, Chemistry Eur. J. 23, (2017), 9249 – 9252.

[59] M. Gon, R. Sawada, Y. Morisaki, Y. Chujo, Enhancement and Controlling the Signal of Circularly Polarized Luminescence Based on a Planar Chiral Tetrasubstituted [2.2]Paracyclophane Framework in Aggregation System, Macromolecules 50, (2017), 1790–1802.

[60] G. Shanmugam, P.L. Polavarapu, Vibrational circular dichroism of protein films. J. Am. Chem. Soc., 126, (2004), 10292-95.

[61] A.G. Petrovic, P.L. Polavarapu Structural transitions in polyribocytidylic acid induced by changes in pH and temperature: vibrational circular dichroism study in solution and film states, J. Phys. Chem. B 110, (2006), 22826-33.

[62] E. Castiglioni, S. Abbate, G. Longhi, Revisiting with updated hardware an old spectroscopic technique: circularly polarized luminescence, Appl. Spectrosc., 64, (2010), 1416–1419.

[63] E. Castiglioni, S. Abbate, F. Lebon, G. Longhi, Chiroptical spectroscopic techniques based on fluorescence, Methods Appl. Fluoresc., 2, (2014), 024006-024013 .

[64] F. J. Torres, B. Civalleri, A. Meyer, P. Musto, A.R. Albunia, P. Rizzo, G. Guerra, Normal vibrational analysis of the syndiotactic polystyrene s(2/1)2 helix, J. Phys. Chem. B 113, (2009), 5059-5071.

[65] E. Plum, X.-X. Liu, V. A. Fedotov, Y. Chen, D. P. Tsai, N. I. Zheludev, Metamaterials: Optical Activity without Chirality, Phys. Rev. Lett. 102, 2009, 113902-1 113902-4

[66] Y. Shindo, Y. Ohmi, Problems of CD Spectrometers. 3. Critical Comments on Liquid Crystal Induced Circular Dichroism, J. Am. Chem. Snc., 107, (1985), 91-97.

[67] T. Harada, H. Moriyama, Solid-State Circular Dichroism Spectroscopy, in: Encyclopedia of Polymer Science and Technology; John Wiley & Sons Inc.: Hoboken, NJ, 2013, pp.1-29.

[68]R. Kuroda, T. Harada, Y. Shindo A solid-state dedicated circular dichroism spectrophotometer: Development and application, Rev. Sci. Instrum. 72, (2001), 3802−3810.

[69] T. Tachibana, T. Mori, K. Hori, New type of twisted mesophase in jellies and solid films of chiral 12-hydroxyoctadecanoic acid, Nature, 278, (1979), 578-579.

Preprint version: Optical Materials 73 (2017) 595-601 DOI: 10.1016/j.optmat.2017.09.010

[70] G. Lakhwani, S. C. J. Meskers, R. A. J. Janssen, Circular Differential Scattering of Light in Films of Chiral Polyfluorene , J. Phys. Chem. B,111, (2007), 5124-5131.

[71] M.C. Gupta, A. Gupta, J. Horwitz, D. Kliger, Time-resolved fluorescence and emission depolarization studies on polystyrene: photochemical processes in polymeric systems, Macromolecules 15, (1982), 1372-76.

[72] B. Wandelt, Correlation of photophysical parameters with conformational structure of crystalline isotactic polystyrene and comparison with data of atactic polystyrene, Polymer, 32, (1991), 2707-11.

[73] O. B. Svistunova, V.V. Gorbunova, T.B. Boitsova, Fluorescence of polystyrene microspheres during photochemical synthesis of gold nanoparticles, Optics and Spectroscopy 106, (2009), 67-71.

[74] Y. Shindo, M..I Nakagawa, On the Artifacts in Circularly Polarized Emission Spectroscopy, Applied Spectr., 39, (1985), 32-38.

[75] D. Kurouski, X.g Lu, L. Popova, W. Wan, M. Shanmugasundaram, G. Stubbs, R. K. Dukor, I. K. Lednev, L.e A. Nafie, Is Supramolecular Filament Chirality the Underlying Cause of Major Morphology Differences in Amyloid Fibrils? J Am Chem Soc., 136, (2014), 2302–2312.

[76] Al. A. Muravsky, An. A. Murauski, V. E. Agabekov, O. O. Chuvasheva, N. A. Ivanova, A chromatic circular polarizer in the 482-535 nm range based on polypropylene films, Journal of Applied Spectroscopy, 79, (2012), 820-825.