Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 76 (2008) 386−393

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Photochromic behavior of spiropyran in polystyrene and polycaprolactone thin films − Effect of UV absorber and antioxidant compound

A. Samoladas [a], D. Bikiaris [b], T. Zorba [c], K.M. Paraskevopoulos [c], A. Jannakoudakis [a,*]

[a] *Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Macedonia, Greece*
[b] *Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Macedonia, Greece*
[c] *Physics Department, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Macedonia, Greece*

Received 18 January 2006; received in revised form 17 September 2006; accepted 17 September 2006
Available online 5 February 2007

Abstract

The photochromic spiropyran 1′,3′-dihydro-8-methoxy-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] has been dispersed into polystyrene (PS) and polycaprolactone (PCL) matrices in the form of thin films. These photochromic films were illuminated with ultraviolet irradiation (365 nm) at room temperature and for different time periods in the absence and in the presence of a UV absorber and an antioxidant compound, at specific proportions. The polarity of the polymer matrix can induce the maximum absorbance of the photochromic compound. In pure polymers the most intense peaks occur at 608 nm in PS and at 589 nm in PCL. It is shown that the decoloration rate was faster in the case of polycaprolactone in comparison with that of polystyrene. This is due to the interactions that take place between carboxyl and hydroxyl end groups of PCL and merocyanine, which is the open form of spiropyran produced after UV irradiation. The addition of a UV absorber and an antioxidant has almost the same accelerating effect. Due to the presence of polar groups in both compounds coloration and decoloration rates are faster. Furthermore, the successive increase of the UV absorber percentage in the polymeric film in both cases results in a significant decrease in the maximum absorbance intensity.

Keywords: Photochromic behavior; Spiropyran; Polystyrene; Polycaprolactone

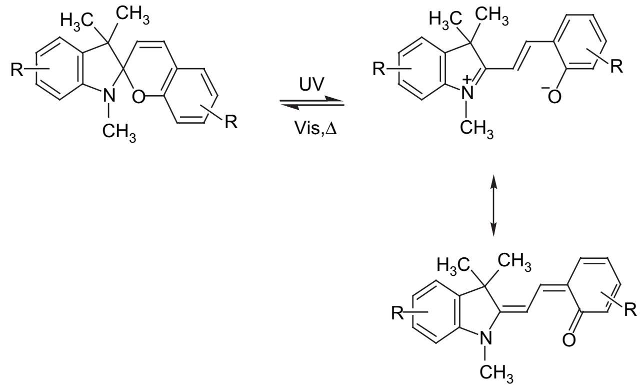
1. Introduction

The photochromism of spiropyrans (SP) was reported by Fischer and Hirshberg [1] in 1952 and since then these organic compounds have been extensively studied due to their possible application in many fields. Spiropyrans being a class of photochromic compounds are potentially applicable as chemical-UV-dosimeters for personal protection [2] or they can be incorporated into the materials used for packaging applications in the case of UV sensitive products like food products. Generally, there is a great interest for the properties of photochromic compounds inserted into polymer films due to their possible use in practical applications. Spiropyrans are composed of an indoline and a chromene moiety that are linked by a spirocarbon atom. Irradiation of spiropyrans with UV light induces heterolytic cleavage of the spiro carbon−oxygen bond, thus, producing the ring opened form, the intensively coloured merocyanine (MC). Merocyanine returns to the initial spiropyran form in the dark or by visible light irradiation [3,4]. The time to resume the initial colour depends on temperature and on the nature of the compound. The equilibrium between the SP and the MC is depicted schematically below.

---

* Corresponding author. Tel.: +30 2310 997683; fax: +30 2310 997769.
E-mail address: andreasj@chem.auth.gr (A. Jannakoudakis).

doi:10.1016/j.dyepig.2006.09.012



The open ring compound is represented in two resonance forms, one merocyanine like and the other quinoidal. The presence of the $-NO_2$ group in the spiropyran enhances its photochromic activity [2,5]. The effect of the substituents on the rate of the ring closure of the merocyanine has been reported [6]. Also, it has been found that the kinetics and spectral properties of the merocyanine depend on the spiropyran concentration [7]. The photochromic behavior of spiropyran in polymer matrices has been studied by several workers [8,9]. It is known that the colour reversibility between the two forms is satisfactory only for a limited number of repetitive coloring and decoloring changes. Furthermore, the insertion of spiropyrans into polymer films decreases their photocoloration rate in comparison to that in liquid solutions [10]. As this decrease could be due to the oxidation, in this work we have examined the presence of an antioxidant compound [Irganox 1098: (*N*,*N*′-hexamethylene bis(3,5-di-*t*-butyl-4-hydroxyhydrocinnamide)] and a UV absorber [UVASORB S5: (2-hydroxy-4-methoxy-benzophenone-5-sulfonic acid)]. The UVASORB S5 is a water soluble pale yellow powder with a broad absorbance spectrum, which finds application in many fields.

The main problem of spiropyrans is their low stability and for this reason several attempts have been performed in order to graft them in the backbone of a macromolecular chain or to incorporate them into a polymer matrix [9,11–14].

In the present work, two different polymers namely polycaprolactone and polystyrene were used in order to examine the photochromic behavior of spiropyran. PCL is a crystalline aliphatic polyester and has received much attention because of its high flexibility and its possible application as both a biocompatible and a biodegradable material [11–15]. PCL has a glass transition temperature at about −60 °C, a melting temperature point at about 60–70 °C and presents a slower biodegradation rate than other biodegradable polymers (BDP) while it is interesting due to its property to form compatible blends with a variety of polymers [16,17]. Also, it is currently regarded as nontoxic and is one of the most hydrophobic, commercially available biodegradable polymers. Polystyrene is an inexpensive vinyl polymer, which is extensively used in many applications. It is produced by free radical vinyl polymerization from the monomer styrene. PS is a colorless, transparent thermoplastic that softens in a temperature close to 100 °C and turns to a viscous liquid at around 185 °C. It is resistant to acids, alkalies, oils, and alcohols and is produced either as a solid or as a foamed plastic, marketed under the trade name Styrofoam. Both polymers (PS and PCL) are used for packaging applications.

The aim of the present work is to study, comparatively, the influence of two different polymers, one polar-like, PCL, containing besides the backbone polar groups, such as ester groups and reactive hydroxyl and carboxyl end groups, one nonpolar-like, PS, on the photochromic behavior of 1′,3′-dihydro-8-methoxy-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] spiropyran. In this direction photochromic polymeric films were prepared, and furthermore, the spectroscopic behavior of these films when a UV absorber and an antioxidant compound were simultaneously added has been examined. Such compounds are extensively used as additives in many polymers, including PCL and PS, in order to prevent their deterioration during their lifetime usage.

2. Experimental

The 1′,3′-dihydro-8-methoxy-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (Sigma–Aldrich) was used as received. Polystyrene and polycaprolactone pellets with molar mass of M_n 170 000 g/mol and 65 000 g/mol, respectively, were purchased from Aldrich. The antioxidant compound (Irganox 1098) was purchased from Ciba–Geigy and the UV absorber (UVASORB S5) was from Sigma–Aldrich. Both chloroform and carbon tetrachloride used as solvents (Fluka) were p.a. grade.

2.1. Film preparation

The thin polymeric films were fabricated according to the following procedure: 2 g of polycaprolactone and 2 g of polystyrene were dissolved in chloroform and carbon tetrachloride, respectively. Into the polymer solution a 0.5 wt% of a photochromic spiropyran was added and stirred well to mix. Then, the solution was kept at room temperature for several hours to remove all traces of solvent. The prepared photochromic films were heat pressed to form thinner films of uniform thickness of approximately 40 μm. The temperature of the heating press was maintained at 120 °C. The resulting films were kept in the dark to prevent their degradation by direct sunlight prior to the spectroscopic measurements. The antioxidant compound was added to the polymer solution in the beginning of the film formation in a 1 wt% of the polymer weight. The UV absorber was admixed in a 0.25, 0.5 and 1 wt% of the polymer.

2.2. Thermal analysis

Thermal analysis of the samples was carried out using a Perkin–Elmer, Pyris 1 Differential Scanning Calorimeter (DSC). The calorimeter was calibrated with Indium and Zinc standards. For each measurement a sample of approximately 6 mg was used, placed in aluminum seal and heated at the rate of 20 °C/min. From recorded thermograms the temperatures of glass transition (T_g) and melting point (T_m) were determined.

2.3. Mechanical properties

Measurements of the mechanical properties, such as tensile strength and elongation at break, were performed on an Instron 1122 dynamometer, in accordance with ASTM D638, using a crosshead speed of 5 and 50 mm/min for PS and PCL, respectively. Prior to measurements the samples were conditioned at $50 \pm 5\%$ relative humidity for 36 h by placing them in a closed chamber containing a saturated $Ca(NO_3)_2 \cdot 4H_2O$ solution in distilled water (ASTM E-104). Five measurements were conducted for each sample, and the results were averaged to obtain a mean value.

2.4. Photochromic experiment

The spectroscopic measurements were performed with a UV–vis absorption spectrophotometer (Perkin–Elmer, Lambda 18). The ultraviolet source of irradiation was a 20 W Hg lamp obtained from Philips with a maximum at 365 nm. First, the polymer films were irradiated with the Hg lamp for 2 min, the absorbance spectra were recorded until the maximum absorbance decreased to that of the nonirradiated films, and the variation of maximum absorbance was plotted against time. Then the polymer films were irradiated for subsequent times until no change in the photochromic properties of the polymer films was recorded. The ultraviolet light excitation was performed for 2 min. Again the plots of maximum absorbance with time were reported. These two series of experiments were performed for all the films without the UV absorber and the antioxidant compound, and with their addition. The spectral region for all the examined photochromic films was between 200 and 900 nm in order to follow the phototransformations between spiropyran and merocyanine.

3. Results and discussion

3.1. Polymer–spiropyran characterization

All prepared samples in the form of thin films were studied with a Differential Scanning Calorimetry in order to evaluate the spiropyran effect on polymer thermal properties. PS has a glass transition at the temperature of 81 °C, while after SP addition this shifts to lower temperature, 76 °C (Fig. 1a). It seems that SP has a plasticizing effect on PS matrix. The same behavior is also observed in PCL, which is semicrystalline polyester. Initially PCL presents a melting temperature at 69.5 °C, which shifts to 65 °C, after the addition of SP (Fig. 1b). Consequently, it is found that spiropyran has a small plasticizing effect on both polymers. For this reason, in order to verify this finding, mechanical properties were also, studied.

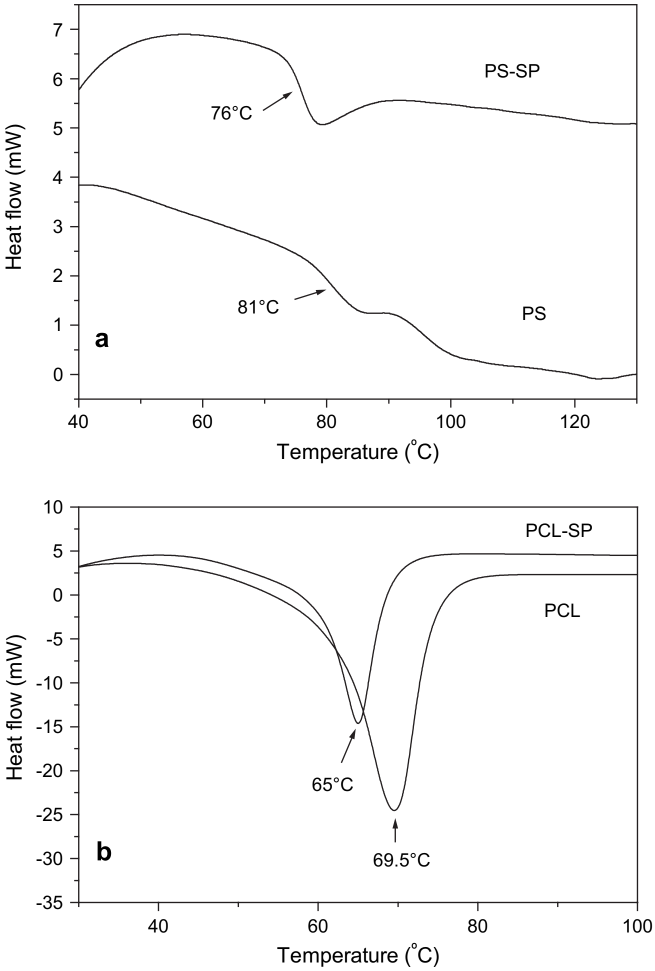


Fig. 1. DSC thermograms of PS and PCL before and after SP addition.

Tensile strength and elongation at break of the polystyrene and polycaprolactone films, with and without the spiropyran, are summarized in Table 1. As it can be seen, PS is a brittle polymer with tensile strength 21 MPa and elongation at break only 4%. This means that it fractures immediately during extension before yielding. On the contrary, PCL is a typical thermoplastic polyester with satisfactory tensile strength 22.9 MPa and very high elongation comparable to that of polyolefines. The addition of spiropyran in both polymer matrices results in a slight variation of mechanical properties. This is rather unexpected since the amount of spiropyran is very small (<1 wt%). In PS, which is very brittle polymer, this effect has less intensity compared to that in PCL. Tensile strength

Table 1
Mechanical properties of the PS and PCL films before and after the spiropyran addition and UV irradiation

Polymer	Tensile strength (MPa)	Elongation at brake (%)
Polystyrene	21	4
Polystyrene + spiropyran	20	6.5
Polystyrene + spiropyran + UV	20	6.5
Polycaprolactone	22.9	1000
Polycaprolactone + spiropyran	18	820
Polycaprolactone + spiropyran + UV	17.2	820

was reduced only by 1 Mpa, which is in the confines of experimental error, while elongation at break was increased from 4 to 6.5%, which is a negligible increase. In PCL the spiropyran addition seems to have a higher plasticizing effect, since both tensile strength and elongation at break are reduced in a more pronounced way. Such a plastisizing effect after the addition of spiropyrans in polymer matrices is in agreement with DSC measurements and has also been reported previously [18].

It is well known that polymers are strongly affected by UV exposure for a long time and molecular weight as well as mechanical properties deteriorate. In order to evaluate the effect of UV irradiation on polymer matrices SP–PCL and SP–PS films were irradiated for 40 min. As can be seen in Table 1, mechanical properties of both polymers remain unaffected after irradiation and only spiropyran is destroyed. The above study is an indication that the addition of spiropyran has negligible plasticizing effect on polymer matrices, while UV irradiation does not create any alteration on polymers. Thus, the recorded differentiation on film absorbancies after UV irradiation shall be attributed only to the spiropyran changes.

3.2. Matrix effect on spiropyran photochromism

After the insertion of 1′,3′-dihydro-8-methoxy-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] into polystyrene and polycaprolactone the photochromic films were excited by ultraviolet light (λ_{max} 365 nm) for various time periods in order to follow the coloration. The result of ultraviolet radiation is the cleavage of the spiro carbon–oxygen bond. Then, the molecule becomes a metastable amphoteric ion, the merocyanine and the coloration of the films is due to the formation of this metastable ion. The latter may exist in different geometrical isomers, *cis* or *trans*, the *cis* isomer being unstable and transforming into the *trans* isomer. The spiropyran–polymer films were colorless before the ultraviolet excitation and turned to deep blue under 365 nm irradiation and then the film colour is changed to yellow upon fading. In Figs. 2 and 3 the absorbance spectra of the SP–PS and SP–PCL films are, respectively, depicted after the ultraviolet irradiation for 2, 4, 6 and 8 min. Each spectrum was taken after the decoloration of the polymer film in the dark.

The spectra of the films reveal that no absorption peak is observed in the range of 580–610 nm before irradiation. On the contrary, a well-formed peak is obtained under 365 nm irradiation. A smooth absorption peak between 598 and 609 nm for SP–PS and between 585 and 592 nm for SP–PCL films, can be observed and the maxima occur at 608 and 589 nm, respectively. The peaks between 200 and 400 nm are attributed to the polymer and the initial spiropyran compound as these were observed, also without the ultraviolet excitation. The polarity of the polymer matrix can induce the maximum absorbance of the photochromic compound. In the case that the polymer is more polar, the frequency of the absorption band, λ_{max}, shifts to the short wavelength region due to the stabilization of the ground state relative to that of the excited state. Thus as shown, the more polar the polymer the more the absorption – of the coloured species that are formed – shifts to the shorter wavelength region. Similar behavior was also observed in the case of poly(methyl methacrylate) (PMMA) and styrene–butadiene–styrene copolymer (SBS) [9]. When spiropyran was dispersed in PMMA, which is polar compared to the nonpolar SBS, the strongest absorption peak was shifted from 575 to 603 nm in SBS. Furthermore, for SBS a slightly lower value in the intensity of the maximum absorbance at 595 nm was also, mentioned.

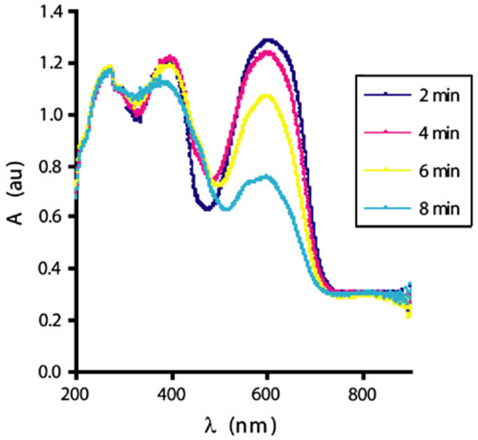


Fig. 2. Changes in the absorbance spectra of spiropyran–polystyrene film after irradiation at 365 nm for 2, 4, 6 and 8 min.

The increase in the time of ultraviolet irradiation causes the reduction of the intensity of the initial blue colour and results in increase in the decoloration rate. This rate for the SP–PS film is much smaller than that of the SP–PCL indicating that the latter is unstable and its absorbance maximum changes in a shorter period of time. After 20 min of total irradiation time the films become faintly yellow coloured and their photochromic properties are then, ceased significantly. Polycaprolactone is a polyester containing polar ester groups in its

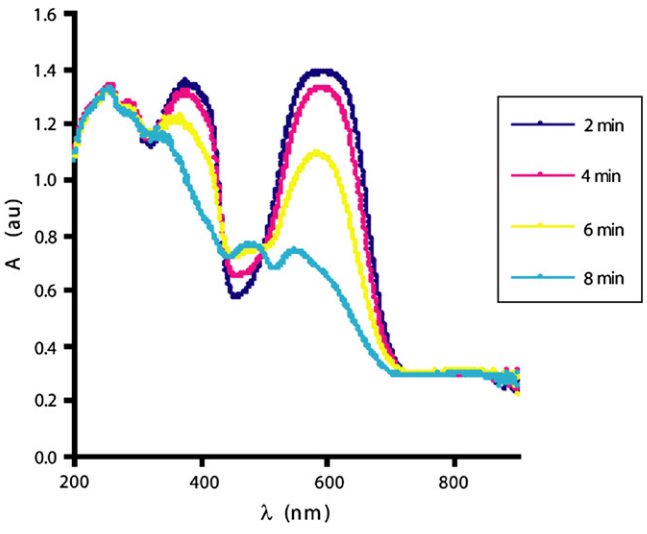


Fig. 3. Changes in the absorbance spectra of spiropyran–polycaprolactone film after irradiation at 365 nm for 2, 4, 6 and 8 min.

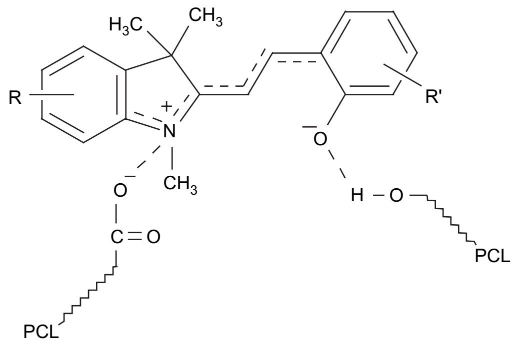
macromolecular chains, as well as carboxyl and hydroxyl end groups, which may interact with the merocyanine after the cleavage of the spiro carbon–oxygen bond. These interactions are depicted in Scheme 1. Similar interactions were mentioned in the case that PMMA and SBS were used as matrix [11]. The ester groups of PMMA can evolve dipole–dipole interactions with merocyanine, and thus, the coloration as well as decoloration rate is faster in PMMA than in SBS which does not contain available polar groups to interact with merocyanine. In our case the most possible interactions are those taking place between carboxyl and hydroxyl end groups of PCL, rather than the ester groups of backbone (Scheme 1).

Besides the changes caused in the absorbance spectra of spiropyran–polymer films by UV irradiation after different times, the decoloration rate of these films was also studied after the initial irradiation with ultraviolet light for 2 min. In order to follow the decoloration rate the spectra were taken after each 60 s from the sweep ending for the SP–PS films and after 30 s for the SP–PCL films (Figs. 4 and 5).

As it is indicated, the decoloration rate in the case of SP–PS film is much slower and the total decororation time, after 2 min of initial irradiation, is almost double than that of SP–PCL film, as noticed by the maximum absorbance intensity decrease. This can be clearly followed from the dependence of the maximum absorbance intensity on time. Considering the decoloration rate of the spiropyran–polymer film as a first order reaction, then in the plot of the log of the maximum absorbance against time a linear dependence must be observed. Indeed, Fig. 6 shows a near linear dependence between $\log A$ and time (t) for SP–PS film as well as for SP–PCL film. This linearity in the dependence of the logarithmic of maximum absorbance intensity against time (Fig. 6) favors the consideration of the decoloration mechanism of spiropyran–polymer film as a first order reaction.

The absorbance spectra of SP–PS and SP–PCL films were recorded every 2 min of UV irradiation (spectra are not shown) in order to measure the first order rate constant k of the polymeric film decoloration. The whole irradiation time was close to 30 min and the constant rate k can be determined by the following equation [19,20]:

$$k = (2.303/t)\log(A_0/A)$$



Scheme 1. Possible interactions between PCL end groups and merocyanine, which is the open form of spiropyran.

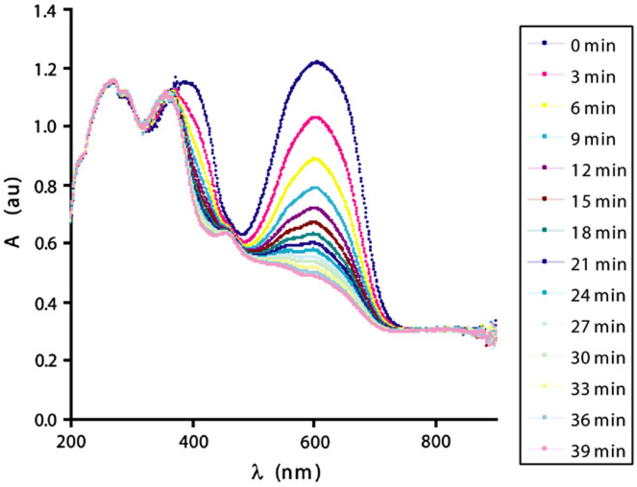


Fig. 4. Changes in the absorbance spectra (decoloration) of spiropyran–polystyrene film after 2 min of irradiation at 365 nm.

where A_0 and A are the absorbance intensities before and during irradiation, respectively, and t is the irradiation time. The results are summarized in Table 2. It is clear that the rate constant k decreases with increase in the irradiation time. As it is mentioned the successive ultraviolet irradiation on the surface of the spiropyran–polymer films results in the formation of inactive to excitation regions. The photodegradation of the films and the cease of their photochromic properties are accelerated by increasing the time and hence, indirectly the amount of irradiated ultraviolet light. The decay of colour, associated with the photochromic isomerism of spiropyrans incorporated into the polymer matrices, can be possibly attributed to the thermally irreversible decomposition of both the spiropyran–merocyanine forms. Despite the fact that the decoloration constant of the SP–PS film presents significant variation for the first 4 min, the rate of decrease is slower in comparison with that of the SP–PCL film

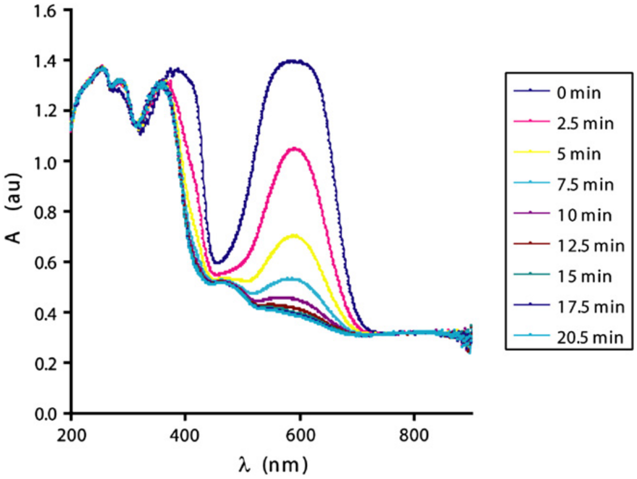


Fig. 5. Changes in the absorbance spectra (decoloration) of spiropyran–polycaprolactone film after 2 min of irradiation at 365 nm.

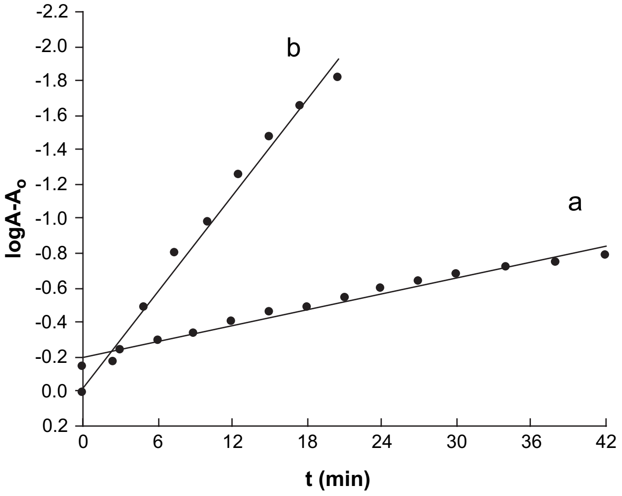


Fig. 6. Logarithmic dependence of maximum absorbance on decoloration time after 2 min of irradiation at 365 nm of (a) spiropyran–polystyrene and (b) spiropyran–polycaprolactone films.

(Fig. 7). This is also obvious from the slopes of the log of the maximum absorbance against time. The slope of the SP–PCL film is slightly greater indicating the faster photodecomposition of this film. It is interesting to notice that for both polymer films the relationship between the maximum absorbance and time presents deviation from linearity at the beginning of the decoloration process indicating a more complex behavior than that of first order kinetics.

3.3. Addition of UV absorber and antioxidant compounds

In order to investigate the spectroscopic changes of the spiropyran–polymer films in blends with a compound that absorbs the ultraviolet radiation, we prepared polymer films containing settled amounts of UVASORB S5. The UVASORB S5 has the following chemical formula:

Table 2
Photochromic behavior of spiropyran–polycaprolactone and spiropyran–polystyrene films

SP–PLC			SP–PS		
Irradiation time (s)	Absorbance ratio	$k \times 10^{-3}$ (s^{-1})	Irradiation time (s)	Absorbance ratio	$k \times 10^{-3}$ (s^{-1})
120	0.271	10.85	60	0.259	22.4
240	0.274	5.39	240	0.260	5.60
360	0.286	3.47	480	0.281	2.64
480	0.301	2.50	720	0.332	1.52
600	0.328	1.85	960	0.390	0.98
720	0.363	1.40	1200	0.449	0.66
840	0.404	1.07	1440	0.509	0.46
960	0.435	0.86	1680	0.547	0.32
1080	0.488	0.66	2040	0.667	0.19
1200	0.555	0.49			
1320	0.624	0.35			
1440	0.715	0.23			

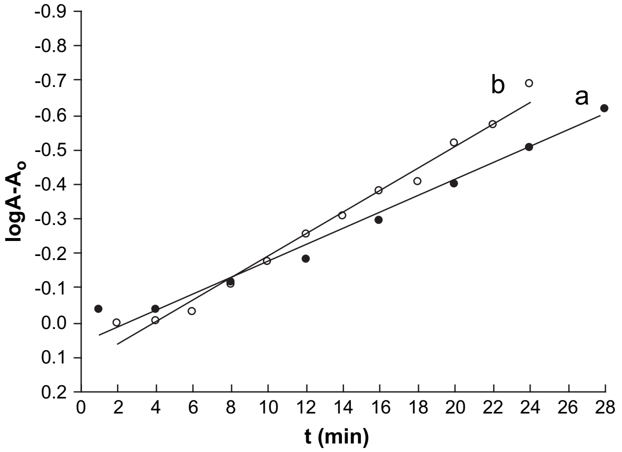
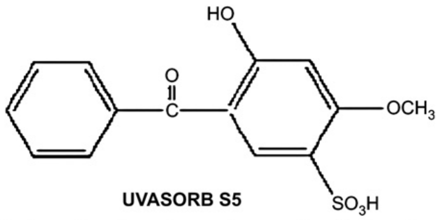


Fig. 7. Dependence of maximum absorbance on time (every 2 min of irradiation at 365 nm) for (a) spiropyran–polystyrene and (b) spiropyran–polycaprolactone films.



UVASORB S5
2-Hydroxy-4-methoxy-benzophenone-5-sulfonic acid

The variation of maximum absorbance intensity during time for the decoloration of the SP–PS and SP–PCL films containing different amounts of UVASORB S5 is presented in Figs. 8 and 9. Initial time of film irradiation was 2 min.

As can be followed from these figures the addition of the UV absorber as well as the amount added has an important effect on the spectroscopic properties of the spiropyran–polymer films. When the UV absorber was added to the SP–PCL at 1 wt% of the polymer weight, no remarkable change in the film colour upon UV excitation was observed. Due to the excessive amount of the UV absorber, the formed film under these conditions was

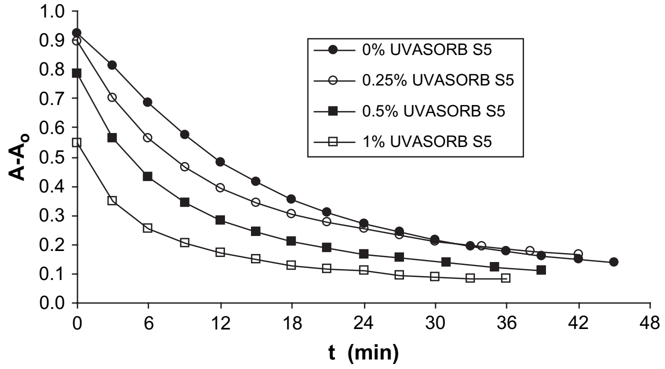


Fig. 8. Dependence of maximum absorbance on time for the spiropyran–polystyrene film after the addition of UVASORB S5.

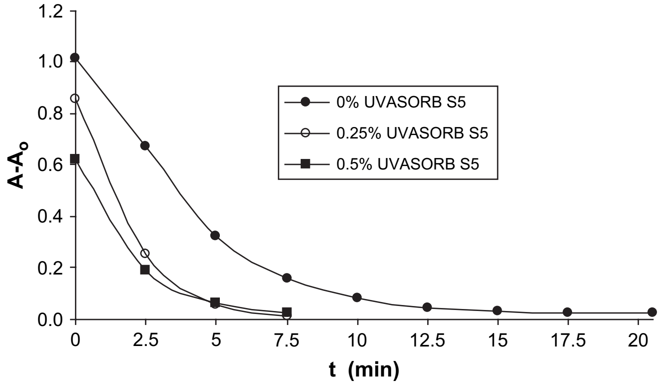


Fig. 9. Dependence of maximum absorbance on time in the case of spiropyran–polycaprolactone film after the addition of UVASORB S5.

strongly yellow coloured, which is an indication that spiropyran was destroyed. Furthermore, with the addition of other concentration of UV absorber, it is observed, in most of the polymeric films, a remarkable reduction of the maximum absorbance intensity depending on the absorber percentage in the film. This decrease is especially intense in the case of SP–PCL film (from approximately 1 to 0.6 absorbance units, Table 3). Similar behavior was observed also for the SP–PS films. This accelerating effect of UV absorber to films decoloration can be seen more clearly in the above mentioned Figs. 8 and 9.

The initial maximum absorbance was decreased with the increasing amount of the absorber from 0.5 to 1% (Fig. 8). This decrease in the maximum absorbance for both the photochromic films can be attributed in principle to the absorption of the absorber in the wavelength region where the spiropyran after excitation isomerized into the merocyanine and secondly to the possible interactions between the polar groups of the ultraviolet absorber with the photosensitive compound. The accelerating effect of UV absorber to film decoloration could be attributed to the existence of $-SO_3H$ and $-OH$ polar groups in the molecule of UV absorber. These groups can also cause interactions with merocyanine similar to that mentioned before for PCL end groups.

Besides the UV absorber, an antioxidant was also used to study its effect on matrices photochromism. The antioxidant compound which was used in this work was the Irganox 1098 [21,22]. From a previous study it was found that this antioxidant is very effective in polyesters such as poly(ethylene terephthalate), by using 1 wt% [23].

Table 3
Relation between the weight percentage (wt%) of the UV absorber and the maximum absorbancies of the photochromic films

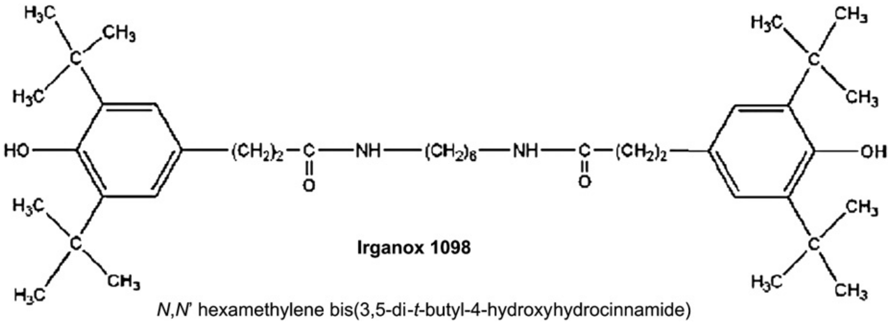
UVASORB S5 (wt%)	*A* (au) of SP–PS films	*A* (au) of SP–PCL films
0	0.926505	1.011735
0.25	0.947113	0.770685
0.5	0.824538	0.663955
1	0.591072	

The spectroscopic behavior of the SP–PS and SP–PCL films with the addition (1 wt%) of Irganox 1098 in the case of successive irradiation is presented in Fig. 10a and b. It is also important to be mentioned that the dependence between the log of the maximum absorbance intensity versus time of decoloration and photodecomposition of the photochromic films containing UV absorber and antioxidant is linear in all the investigated films with slight variations from linearity only in the case of SP–PCL film for the experiment with successive irradiation. However, this was observed only at the beginning of excitation. As is illustrated in Fig. 10a and b the decoloration rate of the spiropyran–polymer films is influenced by the antioxidant addition. Also a remarkable decrease in the maximum absorbance of the polymeric films was observed in both polymers. For the SP–PCL film the decay was realized to be faster with a significant decrease in the absorption after the 16th minute. The effect is also, similar to that already discussed before, due to the addition of UV absorber and the presence of polar groups. Irganox 1098 contains secondary amine, as well as hydroxyl groups, which could accelerate the decoloration rate of both film matrices.

4. Conclusions

The photochromic behavior of a spiropyran incorporated into polystyrene and polycaprolactone thin films with and without the addition of an ultraviolet absorber and an antioxidant compound has been investigated. Under the mentioned experimental conditions both the decoloration and photodegradation processes followed the law of first order reactions. The same spectroscopic behavior was also observed in the cases of the admixture into the polymer matrix 0.25, 0.5 and 1% of the UVASORB S5 as well for 1% of the Irganox 1098.

The fast decoloration rate of the spiropyran–polycaprolactone film relative to that of the polystyrene was attributed to



Irganox 1098

N,N' hexamethylene bis(3,5-di-*t*-butyl-4-hydroxyhydrocinnamide)

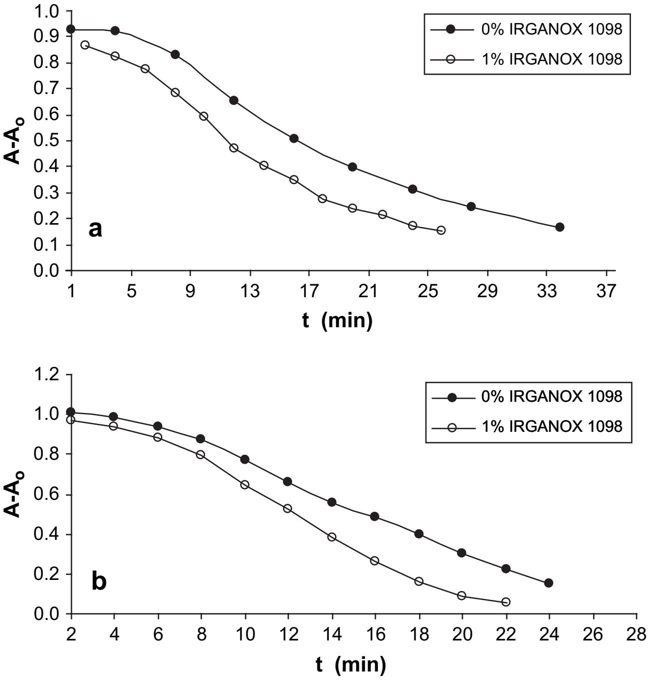


Fig. 10. Variation of maximum absorbance with time of (a) spiropyran–polystyrene and (b) spiropyran–polycaprolactone films.

the possible interactions between the polar groups of the matrix with the coloured species of the spiropyran after the ultraviolet excitation. It is also reported that no significant resistance to photocoloration fatigue with successive ultraviolet irradiation after the addition of the absorber and the antioxidant compound was observed.

The addition of a UV absorber and an antioxidant accelerates the decoloration rate of studied films. Both compounds include reactive groups, which can cause interactions with merocyanine.

References

[1] Fischer E, Hirshberg Y. Formation of coloured forms of spirans by low-temperature irradiation. J Chem Soc 1952;4522–4.

[2] Bertelson RC. In: Brown GH, editor. Photochromism, vol. III. Wiley Interscience Inc; 1971.

[3] Heiligman-Rim R, Hirshberg Y, Fisher E. Photochromism in spiropyrans. Part IV. Evidence for the existence of several forms of the colored modification. J Phys Chem 1962;66(2):2465–70.

[4] Heiligman-Rim R, Hirshberg Y, Fisher E. Photochromism in spiropyrans. Part V. On the mechanism of phototransformation. J Phys Chem 1962;66(2):2470–7.

[5] Krysanov SA, Alfimov MV. Ultrafast formation of transients in spiropyran photochromism. Chem Phys Lett 1982;91(1):77–80.

[6] Samat A, Dekeukeleire D, Guqlielmetti R. Synthesis and spectrokinetic properties of photochromic spiropyrans. Bull Soc Chim Belg 1991; 100(9):679.

[7] Berman E, Fox RE, Thomson FD. Photochromic spiropyrans. I. The effect of substituents on the rate of ring closure. J Am Chem Soc 1959;81:5605–8.

[8] Eckhardt H, Bose A, Krongauz VA. Formation of molecular H-stacks and J-stacks by the spiropyran merocyanine transformation in polymer matrix. Polymer 1987;28(11):1959–64.

[9] Lin JS, Chiu HT. Photochromic behavior of spiropyran and fulgide in thin films of blends of PMMA and SBS. J Polym Res 2003;10(2): 105–10.

[10] Smets G. Photochromic phenomena in the solid phase. Adv Polym Sci 1983;50:17–44.

[11] Lin JS. Interaction between dispersed photochromic compound and polymer matrix. Eur Polym J 2003;39(8):1693–700.

[12] Kim SH, Lee SJ, Park SY, Suh SJ, Jin SH, Gal YS. Synthesis and properties of ionic conjugated polymer with spiroxazine moiety. Dyes Pigments 2006;68(1):61–7.

[13] Lee BH, Kim JH, Cho MJ, Lee SH, Choi DH. Photochromic behavior of spiropyran in the photoreactive polymer containing chalcone moieties. Dyes Pigments 2004;61(3):235–42.

[14] Choi DH, Ban SY, Kim JH. Stability of photochromism in new bifunctional copolymers containing spiropyran and chalcone moiety in the side chain. Bull Korean Chem Soc 2003;24(4):441–5.

[15] Tsuji H, Suzuyoshi K. Environmental degradation of biodegradable polyesters. Polym Degrad Stab 2002;75(2):347–55.

[16] Ohtaki A, Sato N, Nakasaki K. Biodegradation of poly-epsilon-caprolactone under controlled composting conditions. Polym Degrad Stab 1998;61(3):499–505.

[17] Koleske SV. In: Paul OR, Neuman S, editors. Polymer blends. New York; 1978. p. 369–89.

[18] Lawrie NG, North AM. Internal-rotation in molecules dispersed in polymer matrices. Eur Polym J 1973;9(4):345–55.

[19] Mistry BB, Patel RG, Patel VS. Synthesis and characterization of photochromic homopolymer/copolymer. J Appl Polym Sci 1997;64(5):841–8.

[20] Meriwether LS, Breitner EC, Clothup NB. Kinetic and infrared study of photochromism of metal dithizonates. J Am Chem Soc 1965;87(20): 4448–54.

[21] Lutz JT. Thermoplastic polymer additives. New York: Marcel Dekker; 1989.

[22] Hummel D, Scholl F. Atlas of polymer and plastics analysis, vol. III. Munich; 1983.

[23] Karayannidis GP, Sideridou ID, Zamboulis DX, Stalidis GA, Bikiaris DN, Wilmes A. Effect of some current antioxidants on the thermooxidative stability of poly(ethylene-terephtalate). Polym Degrad Stab 1994;44(1):9–15.