

Effect of End Group Content on Photochromic Behavior of Spiropyran in Polycaprolactone–Poly(ethylene succinate) Blends

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ABSTRACT: The photochromic behavior of the spiropyran 1',3'-dihydro-8-methoxy-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole] has been investigated in thin films of polycaprolactone–poly(ethylene succinate) blends containing different weight ratios of poly(ethylene succinate) (PESu) and spiropyran. The effects of molecular weight and end group content (–COOH and –OH) of PESu into the coloration–decoloration rate of the fabricated photochromic films have also been examined. The films were exposed to UV radiation (365 nm) at ambient temperature and the absorbance spectra of each polymer blend film were recorded for different time periods. The increase of the amount of PESu in the polymer substrate from 20 to 40 wt % shifts the absorbance towards shorter wavelengths. The same trend was also observed with the increase of carboxyl and hydroxyl

groups of the macromolecular chain of the added PESu. Interactions between the polar polymer groups and the spiropyran species, which are formed under the UV excitation, seem to contribute to the color stabilization of the photochromic films. The photochromic response revealed unexceptional repeatability between the slightly colored spiropyran and the intense colored amphoteric species for all the examined polymer matrices. The decoloration rate of the spiropyran–polymer blends follow the kinetic of a first order reaction. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3623–3633, 2007

Key words: photochromic behavior; spiropyran; polycaprolactone; poly(ethylene succinate); polymer blends; UV-absorbance

INTRODUCTION

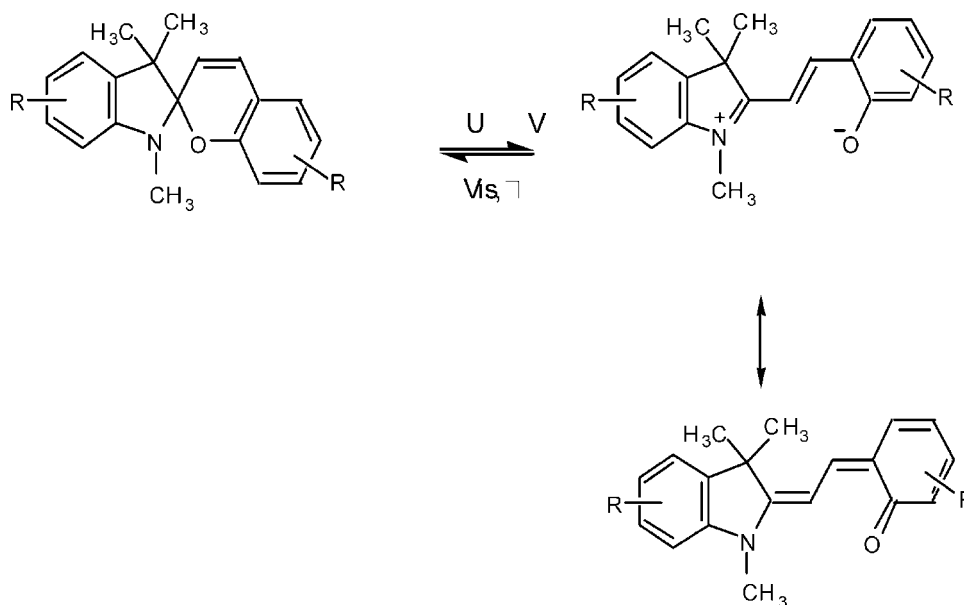
The photochromism of spiropyrans—first discovered by Fischer and Hirshberg¹ and independently by Chaude and Rumpf²—is defined as the ability of a chemical species to undergo a reversible change between two forms having different absorption spectra under the action of electromagnetic radiation.³ Since then, this class of photochromic compounds has attracted remarkable attention because of their wide application potential in many fields.^{4–8} The possibility of controlling the amount of UV radiation as in case of chemical dosimeters has been quoted.⁹ The use of applicable polymers that are effective in protecting spiropyrans and provide stability against degradation without reducing their photochromic activity is a crucial factor. The photochromic behavior of spiropyrans in polymer films is of increasing

interest^{10–16} despite the fact that their photocoloration rate decreases compared with that of liquid solutions, after the dispersion into the polymer matrix. Also, the number of cycles in which the photochromic systems undergo a reversible transformation is limited because of photodegradation processes.

Spiropyrans are photochromic organic compounds composed of two heterocyclic parts linked together by a tetrahedral sp³ spiro carbon atom. Irradiation of the spiropyrans with UV light induces heterolytic cleavage of the spiro carbon–oxygen bond, producing the ring opened form, the intensively colored merocyanine (MC). Merocyanine returns to the initial spiropyran form in the dark or by visible light irradiation^{17,18} and the time to resume the initial color depends on temperature and on the nature of the compound. It presents a characteristic absorption band in the visible spectral region between 570 and 610 nm depending on the polarity of the polymer substrate.

The equilibrium between the SP and the MC is depicted in Scheme 1. Because of the conjugated double bonds, merocyanine may exist in different geometrical isomers.

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Scheme 1 Equilibrium between the spiropyran and the merocyanine forms.

From our previous study concerning the effect of polymer matrix polarity on the coloration and decoloration rates of spiropyran it was found that both rates were higher in the case of polycaprolactone (PCL) than that of polystyrene (PS).¹⁹ Since PCL is a more polar polymer compared with PS, this acceleration was attributed to the interactions that take place between carboxyl and hydroxyl end groups of PCL and merocyanine. Furthermore, the addition of a UV absorber and an antioxidant compound, which are two of the most frequently used stabilizers in polymers, has also an accelerating effect. Coloration and decoloration became faster than those in the case of pure polymers because of the existence of $-\text{SO}_3\text{H}$ and $-\text{OH}$ polar groups in UV absorber—and secondary amine—as well as hydroxyl groups in antioxidant. Therefore, the reactive end groups were the main constituents contributing in the accelerating of degradation of spiropyran.

To make more clear with further evidence and strength the explanation of the above discussed finding, in the present study, poly(ethylene succinate) (PESu) polyesters containing different carboxyl and hydroxyl end groups were prepared. However, because of low molecular weights of these synthesized polyesters their films are very brittle and it is not possible to measure such effect. For this reason the photochromic spiropyran 1',3'-dihydro-8-methoxy-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole], has been incorporated into PCL–PESu blends containing 20 and 40 wt % PESu. Both polymers have received much attention, as they are biocompatible and biodegradable materials.^{20,21} Furthermore, the particular aliphatic polyesters present a wide diversity in their physical and chemical proper-

ties, which are directly comparable to many non-biodegradable polymers like low density polyethylene (LDPE) and polypropylene (PP). Both polyesters are characterized by their propensity to form miscible or compatible blends with a variety of polymers.^{22,23}

EXPERIMENTAL

Materials

The 1',3'-dihydro-8-methoxy-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole] (Sigma-Aldrich, Germany) was used as received. Chloroform (Fluka, Germany) was p.a. grade. Polycaprolactone with molecular weight 65,000 g/mol was purchased from Aldrich.

The synthesis and the characterization of the poly(ethylene succinate) (PESu) has been described previously.^{24,25} Briefly, the proper amount of succinic acid (SA) and ethylene glycol in a molar ratio 1/1.1 and the catalyst (3×10^{-4} mol TBT/mol SA) were charged into the reaction tube of the polyesterification apparatus. The apparatus with the reagents was evacuated several times and filled with argon in order that the whole oxygen amount to be removed. The reaction mixture was heated at 190°C under argon atmosphere and stirring at a constant speed (500 rpm). This first step (esterification) is considered to be completed after the collection of theoretical amount of H₂O, which was removed from the reaction mixture by distillation and collected in a graduated cylinder. In the second step of polycondensation, polyphosphoric acid (PPA) was added (5×10^{-4} mol PPA/mol SA) to prevent side reactions such as etherification and thermal decomposition. A vacuum (5.0 Pa) was applied slowly over a period

time of about 30 min to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. To prepare samples with different molecular weights, polycondensation was performed at different temperatures e.g., 170 and 230°C. The polycondensation time was stable, about 60 min, for all prepared polyesters while stirring speed was increased at 720 rpm. After the polycondensation reaction was completed, the polyesters were easily removed, milled, and washed with methanol.

PESu characterization

Intrinsic viscosity and molecular weight determination

Intrinsic viscosity $[\eta]$ measurements were performed, by using an Ubbelohde viscometer at 25°C in chloroform. All polyesters were dissolved at room temperature to prepare solutions of 1 wt % and filtered through a disposable membrane filter 0.2 μm (Teflon).

Molecular weights were determined by using Waters 150C gel permeation chromatography (GPC) equipped with differential refractometer as detector and three ultrastyrigel (103, 104, 105 Å) columns in series. CHCl_3 was used as the solvent (1 mL/min) and the measurements were performed at 35°C, and the calibration was performed using polystyrene standards with a narrow molecular weight distribution.

Carboxyl end group content determination

Carboxyl end group content of the resins was determined as follows: About 0.1 g of polyesters was dissolved in chloroform at room temperature and the solution was titrated by using a standard NaOH in methanol ($N/10$) and phenol red as indicator.

For hydroxyl groups determination 1 g of polyester was dissolved in 50 mL of chloroform. Acetic anhydride solution in pyridine was added and the mixture was refluxed for 1 h. After that, 2 mL of water was added and the mixture was heated continuously for 10 min. The solution was titrated and a blank titration was used for the calculations, while the content of carboxyl groups was also taken into account.

Photochromic film preparation

The films of the polymeric blends were fabricated according to the following procedure: for PCL–PESu 80–20 w/w polymer blend 1.6 g of polycaprolactone and 0.4 g of each different PESu sample having 0.15 and 0.57 dL/g IV were dissolved in chloroform. Into

the polymer solution, 0.1, 0.25, and 0.5 wt % of the photochromic spiropyran dissolved in 5 mL of chloroform was added and stirred well, to mix. Then, the solution remained at room temperature to remove the solvent. The resulting films were kept in the dark to prevent their degradation by direct sunlight prior to the spectroscopic measurements. The thickness of the photochromic films was approximately at 40 μm to have comparable results. PCL–PESu 60–40 w/w polymer blends were prepared in a similar way.

Film characterization

Scanning electron microscopy (SEM)

The morphology of the prepared PCL–PESu films was examined in a Scanning Electron Microscope (SEM) type Jeol (JMS–840) equipped with an Energy-Dispersive X-ray (EDX) Oxford ISIS 300 microanalytical system. The films were covered with a carbon coating to have good conductivity of the electron beam. As operating conditions were used accelerating voltage 20 kV, probe current 45 nA and counting time 60 s.

Thermal analysis

A Perkin–Elmer, Pyris 1 differential scanning calorimeter (DSC), calibrated with Indium and Zinc standards, was used for thermal measurements. A sample of about 10 mg was used for each test, placed in an aluminum seal and heated to 35°C above the melting point of PESu polyester at a heating rate 20°C/min. The sample remained at that temperature for 5 min to erase any thermal history. After that it was quenched into liquid nitrogen and scanned again using the same heating rate as before. The melting temperatures (T_m) and the heat of fusions (ΔH_m) were measured.

Photochromic measurements

A 20 W Hg lamp (Philips) with maximum absorbance at 365 nm was used as an excitation UV source for the isomerization between spiropyran and merocyanine. The spectroscopic measurements were performed with a UV-visible absorption spectrophotometer (Perkin–Elmer, Lambda 18).

The spectral region for all the examined photochromic films was between 200 and 800 nm. The polymer films were irradiated firstly, with the Hg lamp for various time periods between 2 and 10 s and the relation between absorbance and wavelength was recorded. Secondly, the absorbance spectra of the films were followed until the maximum absorbance decreased to that of the nonirradiated films.

TABLE I
Properties of PESu Samples with Different Molecular Weights

	T_{pol} (°C) ^a	IV (dL/g)	M_n	M_w	T_m (°C)	ΔH_m (J/g)	[–OH] (eq/10 ^{–6})	[–COOH] (eq/10 ^{–6})
1	170	0.15	3560	9820	101	67.7	213	178
2	230	0.57	17100	43780	105	59.1	33	16

^a T_{pol} : the polycondensation temperature.

Then, the variation of maximum absorbance was examined against time.

RESULTS AND DISCUSSION

Synthesis of PESu with different molecular weights

In the first stage of the polymerization process, SA reacts with ethylene glycol and water eliminated as by-products. The reaction takes place at elevated temperature (190°C), so the formed water can be easily removed from reactor and oligomers are prepared. To synthesize polyesters with different molecular weights, polycondensation of oligomers was performed at different temperatures in the range 170–230°C, keeping the reaction time constant as 1 h, and with the application of high vacuum. As the temperature is increased, the ability of polycondensation by the removal of by-products (ethylene glycol and water) also increases. Thus, samples with higher molecular weights are prepared only at elevated temperatures, as can be seen from Table I. The low molecular weight was achieved for polycondensation temperature 170°C (about 3560 g/mol) because of the low ability of by-products elimination, while the high molecular weight was achieved

at 230°C (about 17,100 g/mol).²⁶ Despite their completely different molecular weights their melting points have a very small difference; while heat of fusion is decreased with the increase of molecular weight, this being an indication of higher difficulty in crystallization. However, the most characteristic difference is in their end group content. As can be seen in Table I carboxyl as well as hydroxyl end groups are decreasing with the increase of molecular weight, which was also the target of the present study.

Preparation and characterization of PCL–PESu films containing spiropyran

PCL–PESu films have a milky color due to the crystallization of both polymers. This is an indication that the prepared blends may be immiscible in the entire composition area, which can be revealed from DSC thermograms, as the melting points of both polymers are recorded (Fig. 1). This is a strong indication of a two-phase existence. Melting point of PCL predominates because it is in higher amount. Furthermore, the addition of spiropyran has a negligible elasticising effect on polymers crystallization since the individual melting points of each one polymer are almost at the same temperatures as in the

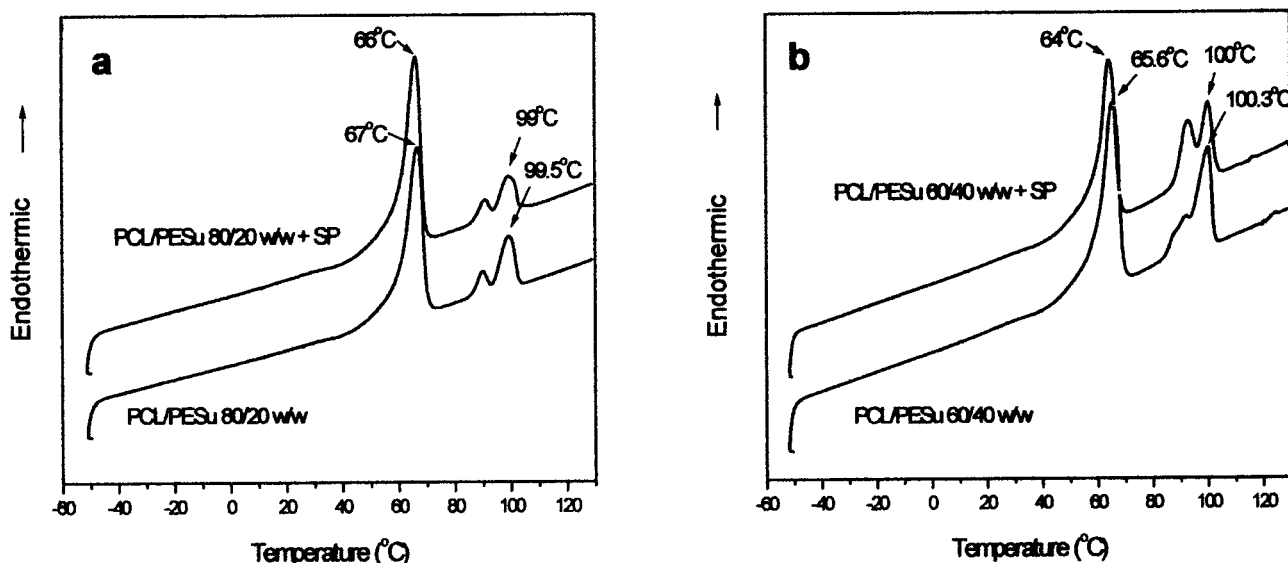


Figure 1 DSC thermograms of PCL–PESu blends containing (a) 20 wt % PESu and (b) 40 wt % PESu.

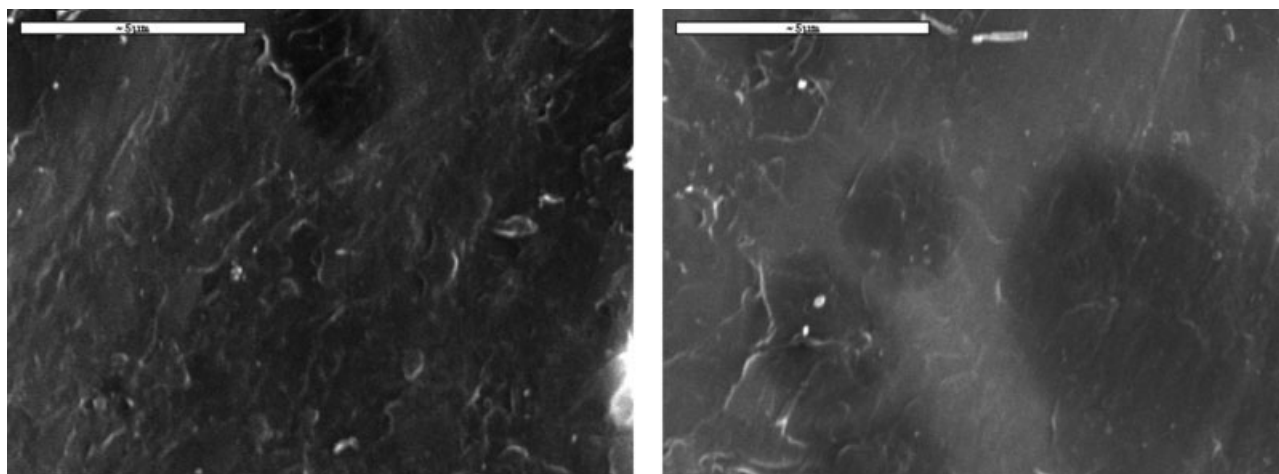


Figure 2 SEM microphotographs of PCL-PESu blends (a) 80–20 w/w without spiropyran and (b) 80–20 w/w containing 0.5 wt % spiropyran.

films without spiropyran. The difference in all blends after SP addition is only 1°C. Such elasticising effect was also observed in our previous study.¹⁹

The prepared films were additionally examined with SEM, to clarify whether the blends are miscible or compatible. As can be seen, SEM microphotographs (Fig. 2) taken from blends without and with spiropyran, are smooth-uniform, while PESu phase, which is the component with the minor participation, is hardly detected. The dispersed phase of PESu as is observed in both blends containing 20 or 40 wt % PESu, presents dispersion smaller than 1 μm. This may be due to cocrystallization that takes place between the two polyesters as was found from our previous study in similar polyesters²⁷ and PESu disperses in the nanoscale. Consequently, PESu is very finely dispersed into PCL matrix and is hardly distinguished by SEM, resulting to a compatible system. Furthermore, SEM micrographs of PCL-PESu containing spiropyran seem to have the same appearance, this being an evidence that the photochromic compound is also well dispersed into polymeric matrix and does not affect the blend homogeneity. Taking all these into account the PCL-PESu blends can be considered as one, uniform and well-homogenized system since the particular systems are compatible. Mechanical properties such as tensile strength and elongation at break verified this finding. Neat PCL has tensile strength at break about 25.2 MPa and elongation at break 860%, while neat PESu with intrinsic viscosity 0.15 dL/g has 7.5 MPa tensile strength and 45% elongation at break. These values are slightly higher for PESu with IV = 0.57 in the prepared blends mechanical properties ranged between these values, and the absence of a minimum verifies that the blends are compatible each other. Thus, for the blend containing PCL/PESu 80/

20 w/w tensile strength is 14.1 MPa and the elongation at break 470%, while for the blend containing 40 wt % PESu these values are 9.7 MPa and 180%, respectively.

Photochromic behavior of PCL-PESu films

Absorption spectra of spiropyran in PCL-PESu films before irradiation

In contrast with the pure PCL-SP films that were studied in our previous work¹⁸ the introduction of the SP into blends of polymers with PCL and PESu results in a faintly violet coloration of the unirradiated films. The coloration of the films indicates that into the PCL-PESu films a fraction of the SP is present in the opened merocyanine form which is stable under these conditions. Since this was not observed in pure PCL films, this coloration must be attributed to the addition of PESu. The intensity of the initial color and its absorbance magnitude were examined relative to three factors: the PESu content into the polymer matrix, the different PESu molecular weights and the SP concentration. The absorbance spectra of the unirradiated PCL-PESu 80–20 w/w films with different molecular weight of PESu into the polymer substrate and SP concentrations are shown in Figure 3.

In the spectra of Figure 3 are verified two well-defined absorption bands between 450 and 600 nm and a broad one between 200 and 400 nm in the UV region. These are attributed to the pure PCL-PESu blend and the colorless form of the spiropyran.¹⁹ The latter has an absorption band at around 350 nm and does not absorb in the visible region. The most intense and distinguishable peaks occur between 486 and 488 and 577–583 nm. These peaks are attributed to the interaction between merocyanine and PESu,

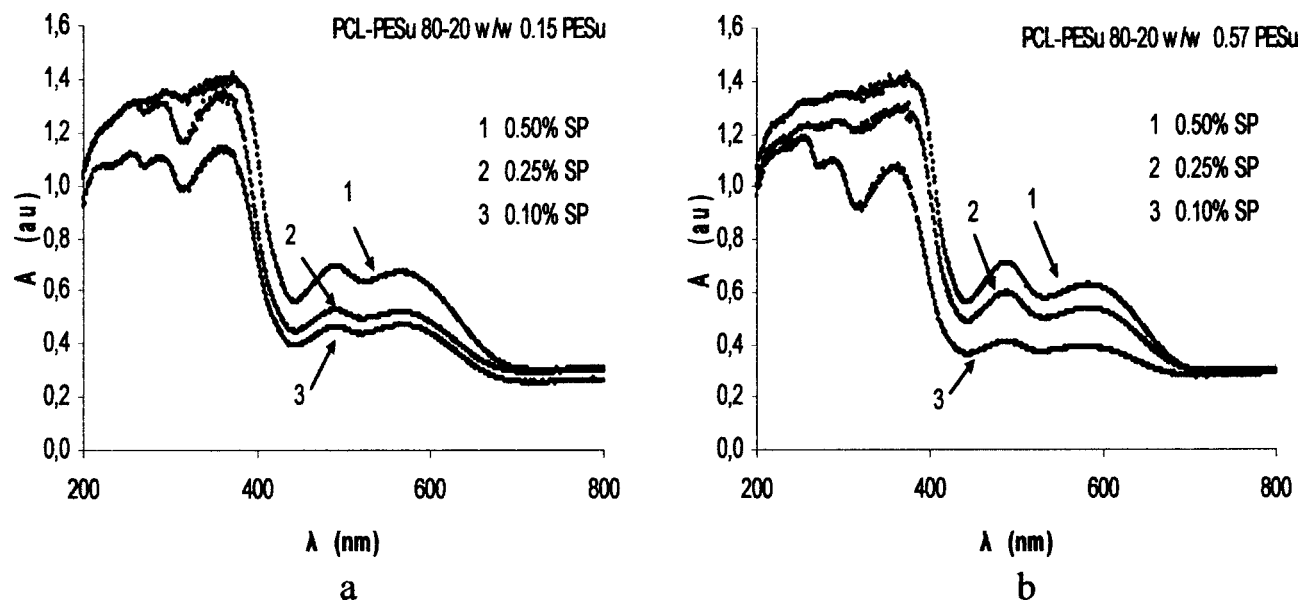


Figure 3 Absorbance spectra of the unirradiated PCL–PESu 80–20 w/w films (a) 0.15 PESu and (b) 0.57 PESu having different SP concentrations.

for the 486–488 nm band, and merocyanine–PCL for the 577–583 nm band respectively.¹⁹ So, it seems that each polymer has its own contribution to the coloration behavior of the films. Furthermore, as it is depicted, increment of the SP concentration in the polymer blend from 0.1 to 0.5% induces an increment at the absorbance intensity for both absorption bands between 450 and 600 nm. A similar behavior was observed when the PESu content into the polymer blend was increased from 20 to 40 wt %. Examining these spectra more carefully it can also be observed that the increase of SP amount beyond the increase in the intensity results in a shift of wavenumbers maximum to lower values. This is an indication that the evolved interactions are higher in magnitude.

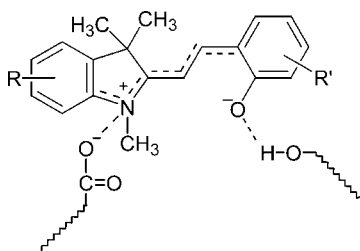
From the above spectra the effect of different molecular weights of PESu on the maximum wavelength intensity as well as on the wavelength position can be evaluated and are presented in Table II.

As can be seen the maximum absorbance intensity for the first absorption band stands between 486 and

492 nm, depending of the PESu molecular weight. As the molecular weight decreases the wavelength shifts to a slightly lower position. Such effect should not be attributed to the different molecular weights but to the different number of carboxyl and hydroxyl end groups of PESu that is decreasing with the decrease of the molecular weight of PESu (Table I). The excess of carboxyl and hydroxyl groups in the polymer chain of PESu, especially in the case of PESu with IV = 0.15 dL/g, could involve interactions with the merocyanine like form of the spiro-*pyran* (Scheme 2). Additionally, the presence of polar ester groups in the macromolecular chain of both polyesters (PCL and PESu) must be taken into account. In general, this behavior is explained by the partial stabilization of the colored merocyanine forms in the presence of polar groups. This is also stated in cases of spiro-*pyran* solutions in solvents of high polarity. The equilibrium between the spiro-*pyran* and the merocyanine is shifted toward the colored species with increasing the solvent polarity.^{28,29} Similar behavior has also been reported by using

TABLE II
The Maximum Absorption Wavelength and Absorbance of the PCL–PESu (80–20 w/w) and PCL–PESu (60–40 w/w) Films before Irradiation in Various PESu Molecular Weights and Spiropyran Concentrations (at 25°C)

PCL–PESu blends	IV PESu	SP					
		0.1 %		0.25%		0.50%	
		λ (nm), <i>A</i> (au)		λ (nm), <i>A</i> (au)		λ (nm), <i>A</i> (au)	
80–20 w/w	0.15	491(0.46)	578(0.47)	488(0.52)	576(0.51)	486(0.69)	577(0.66)
	0.57	492(0.59)	583(0.59)	490(0.59)	583(0.53)	488(0.70)	582(0.62)
60–40 w/w	0.15	486(0.47)	576(0.46)	484(0.59)	577(0.57)	482(0.68)	577(0.62)
	0.57	489(0.65)	486(0.63)	487(0.71)	577(0.65)	486(0.84)	582(0.76)



Scheme 2 Possible interactions between PCL end groups and merocyanine, which is open form of spiropyran.

poly(methylmethacrylate) (PMMA) in comparison with that of styrene–butadiene–styrene copolymer (SBS)¹¹ and polycaprolactone (PCL) instead of polystyrene (PS).¹⁹ The more polar substrate shifts the absorbance to the red wavelength region. Furthermore, Tork et al.³⁰ reported a possible explanation mechanism into poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVA) films considering that the spiropyran molecules cannot go ring closure and interact with the polymer substrate.

A similar behavior was also observed for the second peak that is attributed to PCL. The maximum wavenumber occurs between 576 and 582 nm and presents a similar but unexpected shift to lower wavenumbers. Since the molecular weight of PCL is stable in the blends, the wavelength of the second absorption band should be also stable and unaffected from the PESu variation. However, in our case the wavelength shifts also to a lower positions by reducing the PESu molecular weight. Pure PCL has an absorbance at 589 nm while in the blends containing PESu with $IV = 0.57$ this band shifts at 582–583 nm and in the blend prepared with $IV = 0.15$ the shift is even higher at 576–577 nm. This behavior could be explained only assuming that these blends are compatible each other, which was also verified from SEM micrographs. It is well known in the polymer blends that compatibility increases by decreasing the molecular weight of one polymer. In the blends where PESu was used with $IV = 0.15$ this compatibility is more intense resulting to a higher shift of maximum wavenumber to lower positions.

Coloration process of the merocyanine in PCL–PESu films

So far, the behavior of the PCL–PESu films regarding the PESu intrinsic viscosity and content into the polymer blend as well as the SP concentration was presented without any reference to UV irradiation. However, of significant interest is the photochromic behavior of the films after a UV excitation for various time periods. In Figures 4 and 5 are presented the absorbance spectra of the PCL–PESu films containing 20 and 40 wt % of PESu, respectively. The

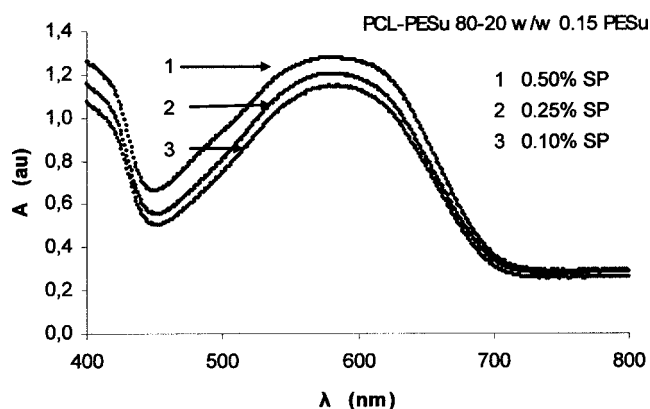


Figure 4 Absorbance spectra for different SP concentrations of the PCL–PESu 80–20 w/w films with 0.15 PESu for irradiation time of 2 s.

UV excitation was performed for 2 s using a 365 nm Hg lamp. It must be pointed that all the films turn from faint violet color that was before irradiation to deep blue, under UV-irradiation. This behavior is due to the cleavage of the spiro carbon–oxygen bond between the indolinic and the chromene moiety of the spiropyran and the formation of a metastable ion (Scheme 1). The explanation of the film coloring is ascribed to this ion with a merocyanine–quinoidal resonance form. In each figure the different molecular weight of PESu into the PCL substrate is indicated to have comparable results about the photochromic response of the polymer blend films.

As it is shown in all blends there is only one peak and the maximum absorbance peaks for the SP into the PCL–PESu films were observed between 598 and 606 nm with very small differences between the blends containing different molecular weights of PESu. However, such behavior was not detected in the films before irradiation where two separate peaks were recorded, corresponding to constituent poly-

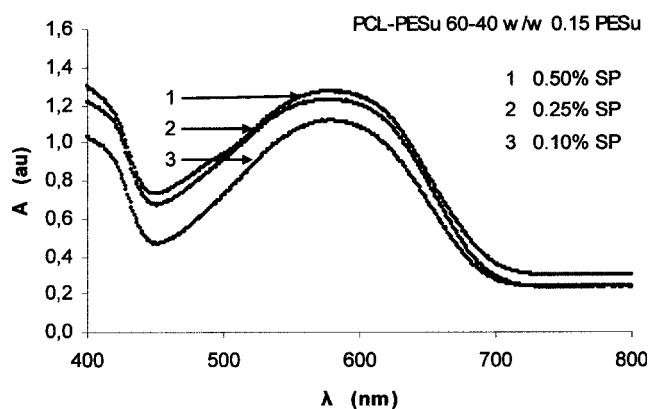


Figure 5 Absorbance spectra for different SP concentrations of the PCL–PESu 60–40 w/w films with 0.15 PESu for irradiation time of 2 s.

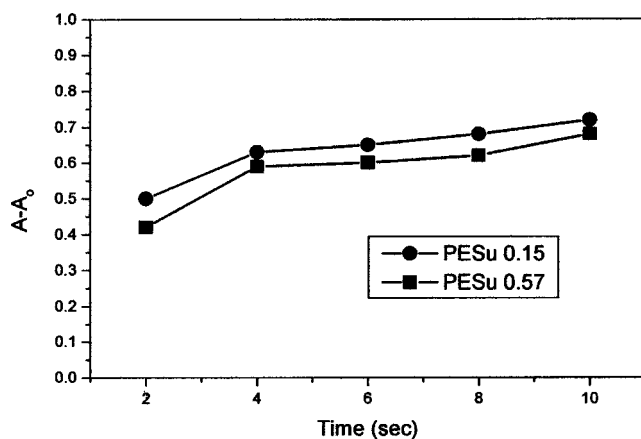


Figure 6 Dependence of absorbance at maximum on time for the PCL-PESu 80-20 w/w films (0.5% SP) with the two molecular weights.

mers. So, it seems that the two absorbance peaks recorded before UV irradiation merge forming one broad peak with high intensity. This must be attributed to the high absorption capability of the metastable ion formed after UV irradiation. Comparing the intensities of the films after irradiation with that before irradiation (Fig. 3) it can be seen that after UV irradiation the intensity was doubled. This observation proves that the extent of SP cleavage is very high after irradiation, as it was expected, and the whole amount of SP is probably in the open form. When the concentration of the SP into the polymer films increases from 0.10 to 0.50% the absorbance increases in the same way, which is in accordance with the trend in unirradiated samples. This behavior is observed in all PCL-PESu films for both PESu molecular weights. Similar results were obtained during coloration of PMMA with different concentration of spirooxazines.³¹

Apart from the SP concentration in the polymer blend, the molecular weight of PESu also has a small

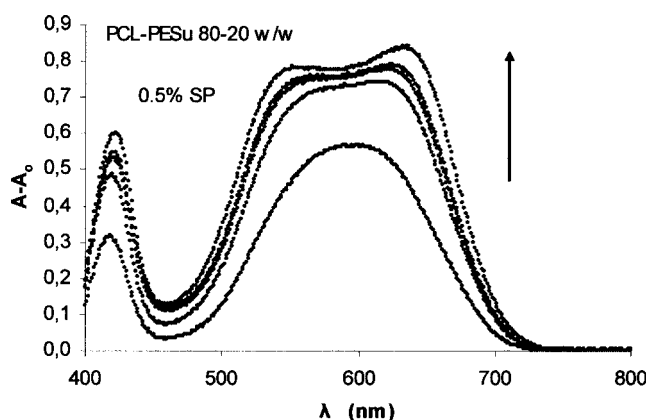


Figure 7 Dependence of absorbance with time for the PCL-PESu 80-20 w/w (0.57 PESu) films.

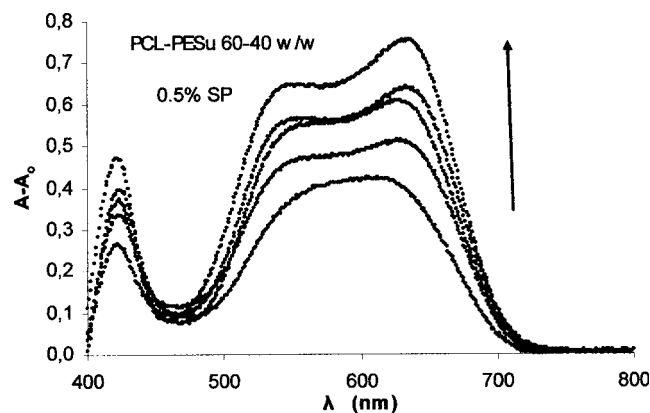


Figure 8 Dependence of absorbance with time for the PCL-PESu 60-40 w/w (0.57 PESu) films.

effect. The variation of the absorbance with irradiation time for the blend containing 20 wt % PESu with the two molecular weights is presented in Figure 6. The maximum absorbance is continuously higher in the blends with PESu IV = 0.15 dL/g in accordance with the behavior of unirradiated samples. A similar trend is also recorded for the samples containing 40 wt % PESu. Consequently, it seems that the end groups also play an important role during samples coloration as in the unirradiated samples.

The increase of the irradiation time up to 12 s results in completely different appearance of UV spectra. A broad absorption band, consisting of two maxima, is formed in both polymer blends presenting the shape of the unirradiated film absorbance spectra, for irradiation higher than 4 s. Figures 7 and 8 represent the coloration of the two polymer films ratios containing 0.57 PESu and 0.5% SP with increasing the excitation time from 4 to 12 s. The arrow in the spectra indicates the direction of the absorbance spectra with increasing time. The two maxima are distinguishable for irradiation time $t > 6$ s when the SP concentration is 0.25 or 0.50 wt %, while for the films with 0.1% SP only one maximum

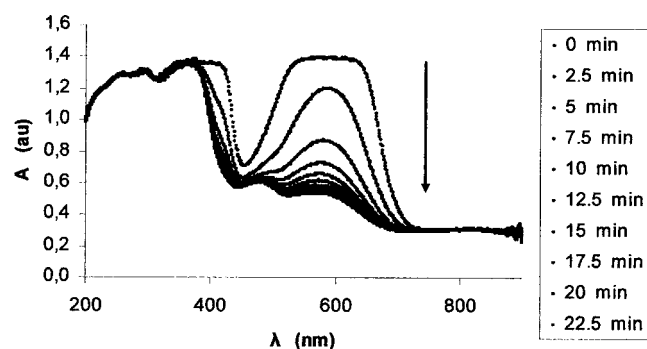


Figure 9 Decoloration spectra of spiropyran in PCL-PESu 80-20 w/w film prepared by using 0.57 PESu (0.5% SP).

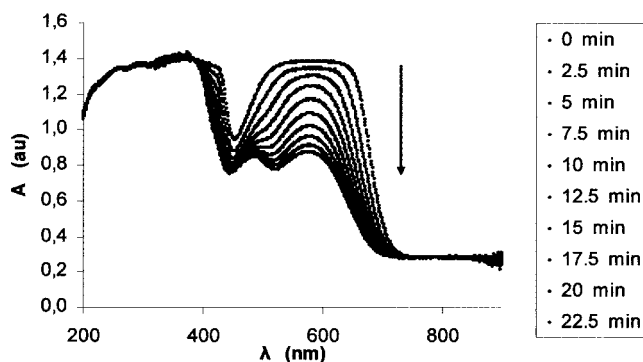


Figure 10 Decoloration spectra of spiropyran in PCL-PESu 60-40 w/w film prepared by using 0.57 PESu (0.5% SP).

is formed for the same irradiation time durations. At the low SP concentration the contribution of the two polymers in the effect cannot be distinguished as the amount of SP is not enough while for higher concentration (> 0.25 wt %) the trend is easily followed. This increase is accompanied by a remarkable shift of the wavelength corresponding to both polymers, but in different directions. PCL maxima wavelength is shifted to higher wavelengths, from 600 to 630 nm, approximately in all films. However, for the peak that corresponds to PESu, the shift is to a significantly lower wavelength, by increasing the time of irradiation. This is also the expected behavior during irradiation. By increasing the irradiation time the interactions between PESu and SP are in higher intense, the peaks are separated and are well distinguished while, the absorbance shifted to lower wavenumbers. However, for the absorbance corre-

sponding to the PCL peak, this shift to higher wavenumbers is presently unexplained. It seems that progressively the interactions between PCL and SP are being less intense.

With a further increase of the irradiation time of the two peaks tend to merge again to one peak, similar to that recorded for irradiation less than 4 s. When the UV excitation is performed for 2 min the detection of the maximum absorbance is an obscured procedure. The two contributions and their effects cannot be well discriminated and appear to be unified since a broad range band was recorded. The opposite will occur during decoloration after a UV irradiation for defined time period and will be discussed in detail in the following sections.

Decoloration process of merocyanine in PCL-PESu films

Figures 9 and 10 show the absorbance spectra of the SP in the PCL-PESu 80-20 w/w and PCL-PESu 60-40 w/w films respectively, prepared with $IV = 0.57$ dL/g PESu during decoloration, after initial irradiation with UV light for 2 min. Each spectrum was taken 30 s after the sweep ending to record the decoloration rate of the photochromic films. As it is shown, after 5-7.5 min the peaks are discriminated and two different peaks are observed in both PCL-PESu blends. As can be seen, the intensity progressively decreases since the interactions between the polymers and SP become weaker and thus the effect of each different polymer during decoloration can be easily followed.

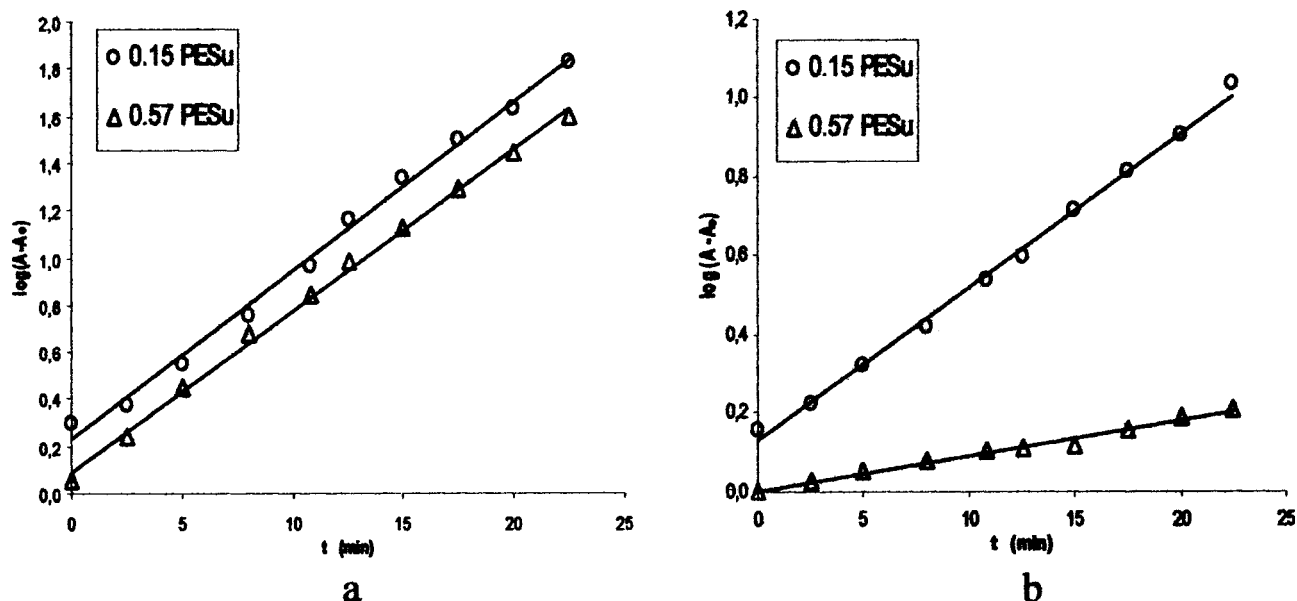


Figure 11 Log dependence of maximum absorbance during decoloration time after 2 min of initial irradiation at 365 nm for PCL-PESu (a) 80-20 w/w and (b) 60-40 w/w films.

TABLE III
Rate Constants for the Decoloration of the PCL–PESu (80–20 w/w) and PCL–PESu (60–40 w/w) Films at 25°C

Irradiation time (s)	$k_{\text{obs}} \cdot 10^{-3} \text{ (s}^{-1}\text{)}$			
	PCL–PESu 80–20 w/w		PCL–PESu 60–40 w/w	
	0.15	0.57	0.15	0.57
150	7.88	6.14	6.91	4.25
300	5.23	3.72	4.36	2.85
450	4.54	3.09	3.25	2.14
600	4.22	2.63	2.80	1.94
750	3.99	2.54	2.47	1.80
900	3.76	2.40	2.28	1.69
1050	3.58	2.29	2.18	1.61
1200	3.45	2.16	2.09	1.59
1350	3.35	2.10	2.04	1.60

Considering that the decoloration rate of the PCL–PESu films is a first order reaction, and by plotting the log of the maximum absorbance against time, a linear dependence must be observed. The dependence between the log of the maximum absorbance with time for the PCL–PESu films is shown in Figure 11. The dependence between the log of maximum absorbance and time is linear for both, 80–20 and 60–40 w/w, polymer blends. For PCL–PESu 80–20 w/w films the slopes of $\log(A-A_0)$ versus t are well resolved, especially after the 5th min. As it is shown, the decoloration rates for the PCL–PESu 80–20 or 60–40 w/w films are faster in the case that PESu was used with $IV = 0.15 \text{ dL/g}$, revealing the effect of the higher end groups content of PESu. For both PESu contents in the polymer blends the film with the higher number of carboxyl–hydroxyl groups in the macromolecular chain appear to have higher slope, leading to the conclusion that the more polar blend contributes to a faster decoloration rate. This was also obtained from our previous study between the polar PCL and the non polar PS.¹⁹ The rate in the PCL was found to be lower, under identical experimental conditions, than that of the PS film.

The first order rate constant k for the decoloration of the PCL–PESu films after the UV irradiation can be determined according to the following equation³²:

$$k = (2.303/t) \log(A_0/A_t - A_a)$$

where A_0 , A_t , and A_a are the absorbances at the beginning of the run, at time t and after complete return, respectively. The results are summarized in Table III for the PCL/PESu photochromic films. As is demonstrated the rate constant k decreases with increase of the decoloration time of the films.

The decoloration rates of the PCL–PESu photochromic films until the 10th min presented significant variation in the rate constant indicating that the

decoloration of the films proceeds at higher rates. It is also interesting to notice that until the 10th min the color recovery of the films is more than the 50% of the initial, without the UV excitation and coloration. As shown, the decoloration rate of the PCL–PESu 60–40 w/w films is slower in relation with that of the PCL–PESu 80–20 w/w films.

CONCLUSIONS

We have investigated the effect of different proportion and molecular weight of PESu biodegradable polyester on the photochromic behavior of a spiro-pyran incorporated into PCL–PESu thin films. Additionally, the role of different spiro-pyran concentrations was examined.

The wavelength region of absorbance peak at maximum of the PCL–PESu 80–20 w/w films is close to that of pure PCL photochromic films. On the contrary, for the PCL–PESu 60–40 w/w films, a red shift in the absorption spectra occurs with the decreasing of the molecular weight of the PESu in the PCL substrate. This is an indication that the interactions between carboxyl and hydroxyl end groups of PESu with the merocyanine form of the spiro-pyran are more intense.

The decoloration rate of the spiro-pyran in the PCL–PESu blends follow the kinetics of a first order reaction and the rate constants for all the films were obtained. It was also found that the decoloration rate of 60–40 w/w is slower in comparison with that of the 80–20 w/w films. Finally, a significant resistance to photocoloration fatigue with successive UV irradiation was observed for all the prepared blends of polymers in comparison with what was observed for pure PCL films.

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